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SMITHSONIAN CONTRIBUTIONS TO MUSEUM CONSERVATION • NUMBER 9

Aluminum: History, Technology, and Conservation

Proceedings from the 2014 International Conference

Edited by
Claudia Chemello, Malcolm Collum, Paul Mardikian,
Joe Sembrat, and Lisa Young

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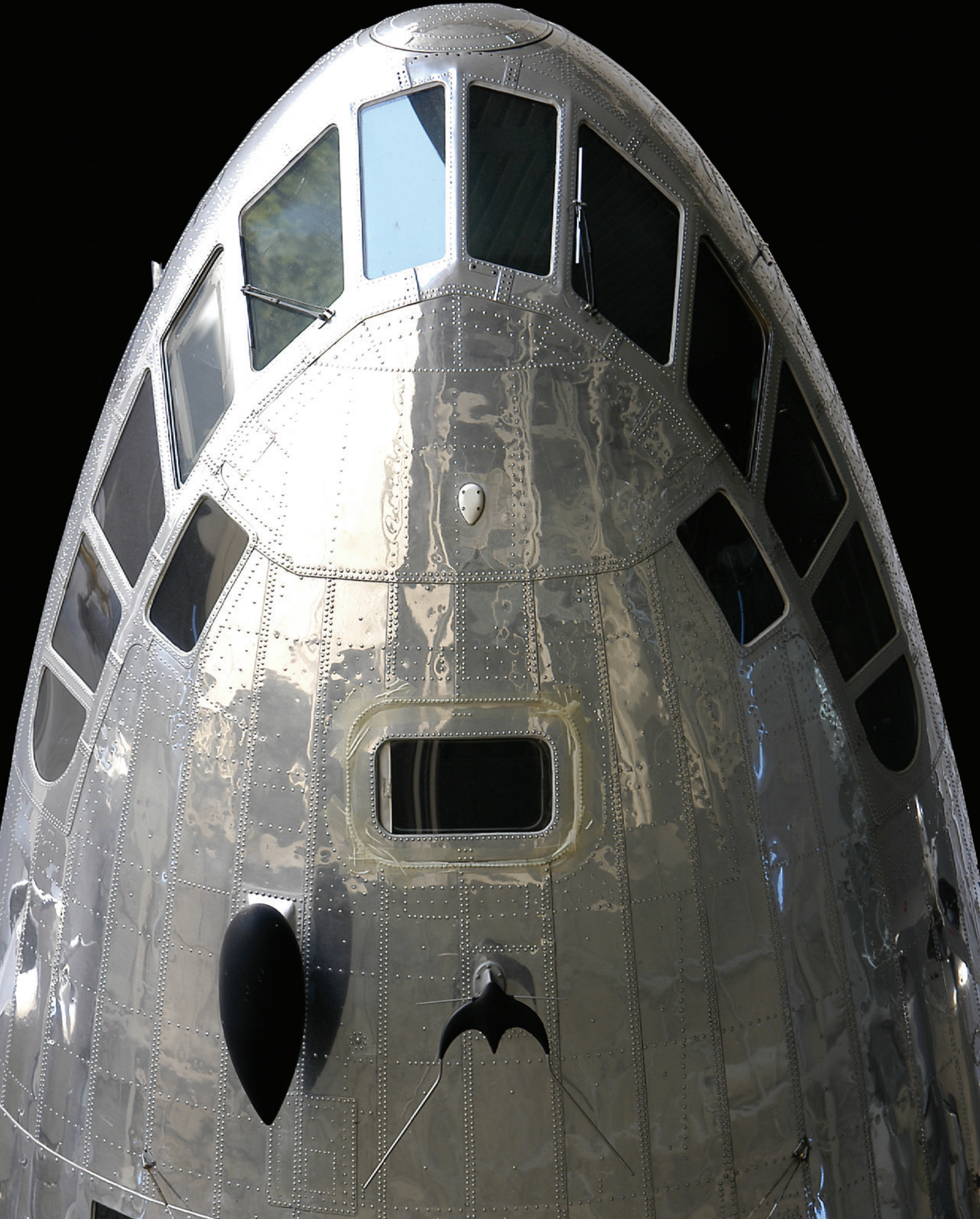

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ABSTRACT

Chemello, Claudia, Malcolm Collum, Paul Mardikian, Joe Sembrat, and Lisa Young. Aluminum: History, Technology, and Conservation. Proceedings from the 2014 International Conference. *Smithsonian Contributions to Museum Conservation*, number 9, xii + 220 pages, 190 figures, 18 tables, 2019. — The current volume brings together papers presented at the 2014 "Aluminum: History, Technology and Conservation" conference held at the Smithsonian Institution's American Art Museum; the conference was followed by a hands-on workshop held at the National Air and Space Museum's Steven F. Udvar-Hazy Center, which utilized the museum's collections to illustrate aluminum's use, conservation challenges, and repair techniques as well as to introduce participants to analytical techniques such as X-ray fluorescence for the identification of aluminum alloys and finishes. The three day international conference and two-day workshop were co-hosted with the Smithsonian Institution, the Foundation for the American Institute for Conservation and the International Council of Museums Committee for Conservation Metals Working Group. An unprecedented group of speakers, organizers, and sponsors made possible the first ever conservation conference solely dedicated to aluminum. The conference featured presentations by twenty-seven speakers from Europe, Asia, Australia, and North America who explored various aspects of degradation phenomena and conservation strategies for aluminum objects, from sculpture to aircraft, from nineteenth-century jewelry to underwater archaeological objects. The proceedings are divided into eight categories and represent the various themed sessions: the history and manufacturing of aluminum, corrosion and deterioration, characterization and identification, conservation of archaeological objects, conservation and use in contemporary art, conservation of architectural elements, surface treatments and inhibition, and preventative conservation.

Cover images: (Left) *Stainless Steel, Aluminum, Monochrome I, Built to Live Anywhere, at Home Here* (2011), Nancy Rubins. Albright-Knox Art Gallery, Buffalo, NY. George B. and Jenny R. Mathews Fund, by exchange. Photograph by Erich Koyama. (Center) Divers record corrosion parameters on the *Emily* flying boat wreck site in Chuuk Lagoon. Courtesy of Earthwatch, Bill Jeffery. (Right) *The Throne of the Third Heaven of the Nations' Millennium General Assembly*, James Hampton. Courtesy of Smithsonian American Art Museum, gift of anonymous donors.

Frontispiece: The Boeing 307 Stratoliner was first flown in 1938 and was the first airliner to have a pressurized fuselage. After restoration in 2003, the plane was delivered to the Smithsonian's National Air and Space Museum Steven F. Udvar-Hazy Center where it is currently on display to the public. Photo by Dane A. Penland, Smithsonian National Air and Space Museum (NASM2019-01858).

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Foreword

The preservation of the world's cultural and scientific heritage has been an important concern for centuries. Over time, conservation has evolved from the disguise of past damage by artists to a scientifically informed discipline of professionals trained in the processes of deterioration and the tenets of preventive care. Understanding the chemical composition of an object and the effects of the agents of deterioration on its physical structure and integrity has been the driving force of preventive care and conservation. With the continuing invention of new materials comes the ever-increasing challenge of determining the appropriate treatments and techniques for mitigating deterioration, damage, or potential loss – including the preservation of objects constructed in whole or in part from aluminum alloys.

As in many museums, aluminum is found in almost all of the collections at the Smithsonian, from airplanes to spacecraft, works of art to historical artifacts, architectural elements to archaeological material, and industrial objects to objects of everyday life; thus, the Smithsonian welcomed the opportunity to host the inaugural conference dedicated to this unique metal and its alloys in April 2014. The aim of the conference was to increase the technical knowledge and body of literature within the professional community regarding the conservation of these collections through professional dialogue, study, and publication regarding the history, technology, and conservation of aluminum alloys.

The conference and this proceedings volume reinforce the need for interdisciplinary collaboration in the proper care, conservation, and display of this specialized modern material. The best approach within an organization is collaboration of the required stakeholders as well as the professional community at large to address common needs and concerns through shared solutions – with the goal of collectively becoming better stewards of the collections we hold in trust for current and future generations to enjoy and study. Interdisciplinary collaboration and global dialogue among museum professionals is especially critical, with the understanding that all museums face similar challenges. Equally important is involving experts from industry in this dialogue and discussion. Museum professionals must recognize the value of and welcome the involvement of subject matter experts in the field who manufacture, fabricate, and study this specialized material. We must commit ourselves to furthering our understanding and knowledge of aluminum and improving communication and collaboration among the critical stakeholders in the museum and aluminum industry fields. Only through cross-pollination and communication will we improve our knowledge of this material, its history, the modes of deterioration, and how best to provide preventive care and conservation.

Preserving, managing, and making collections accessible is a collective responsibility shared by a variety of disciplines. This volume is a critical first step towards codifying best practices and standards in the preservation and conservation of objects containing aluminum. I want to thank the conference organizing committee – Claudia Chemello, Malcolm Collum, Paul Mardikian, Joe Sembrat and Lisa Young – for their leadership, vision, and hard work in convening the conference and this publication, and all of the speakers for sharing their knowledge and expertise and contributing to this important dialogue. I also wish to acknowledge the generous support of the Foundation of the American Institute for Conservation, the Lunder Conservation Center, the National Air and Space Museum, and the International Council of Museums Committee for Conservation Metals Working Group. I think this volume will serve as an invaluable resource to conservators, collections managers, and curators around the globe who are responsible for the care and management of specialized modern materials – including collections containing aluminum.

William G. Tompkins, Director, National
Collections Program, Smithsonian Institution

Introduction

This volume features the proceedings of Aluminum: History, Technology and Conservation, a joint meeting organized by the Foundation of the American Institute for Conservation of Historic and Artistic Works, the International Council of Museums International Committee for Conservation (ICOM-CC) Metals Working Group, the Lunder Conservation Center, and the Smithsonian National Air and Space Museum. The conference took place at the Smithsonian American Art Museum in Washington, DC, from April 7–9, 2014, followed by a hands-on workshop on the identification of aluminum alloys and finishes at the Emil Buehler Conservation Laboratory at the National Air and Space Museum, Steven F. Udvar-Hazy Center, in Chantilly, Virginia, on April 10 and 11.

We are very pleased to present this volume on a subject matter that is not well understood in the conservation community. This interdisciplinary conference brought together professionals and practitioners from the fields of conservation, scientific research, and industry to examine the current state of the field and facilitate an exchange of knowledge, experiences, and expertise in the deterioration and conservation of aluminum alloys. This was the first ever conference convened to address these fundamental issues and dedicated to the conservation of aluminum.

The conference featured twenty-six speakers from Europe, Asia, Australia, and North America who explored various aspects of caring for aluminum objects found in a range of contexts. Objects varied from sculpture to aircraft, from 19th century jewelry to marine archaeological aluminum and museum collections containing historic aluminum objects.

The conservation of contemporary materials is a now a focus of many government heritage agencies, nonprofit institutions, and professional organizations worldwide. A sub-genre within the broad field of modern materials is that of modern metals, with many collections containing objects made from metals like aluminum. Very little information is available within the conservation community on this vast subject and the material conservation problems that these objects face. Yet a wealth of information exists within industry, and it is critical to bring this information into our field of cultural heritage preservation.

Many of the characteristics of modern alloys are not widely known or understood in the heritage community. The widespread use of these materials with the rise of industrial methods of production presents a clear challenge to traditional conservation approaches and raises new issues for practitioners dealing with objects made from materials such as aluminum.

Creative thinking and innovative research, particularly for characterization and identification of modern metals and new methods of conserving modern metals are needed to tackle these issues and develop appropriate protocols for conservation treatment. A determined effort is needed to collect, analyze and disseminate existing information; identify areas where knowledge is lacking; and gather information to fill in those gaps.

This conference attempted to address some of these needs with respect to aluminum. It originated from a desire by the organizers to know more about this magical material and how to preserve the numerous objects made from aluminum in collections worldwide. Publication of the proceedings to disseminate the information to the heritage community was also a primary goal. We hope this volume has fulfilled these goals and trust you will find these proceedings thought provoking and educational.

Claudia Chemello, Coordinator, ICOM-CC Metals Working Group
David Hallam, Coordinator, ICOM-CC Metals Working Group (2008–2013)

Aluminum: A Modern Metal in Cultural Heritage

Lyndsie Selwyn

ABSTRACT. Aluminum is a modern metal because of its early nineteenth century discovery. It is now widely used and is finding its way into museum collections and aluminum alloys have become part of our cultural heritage. This review of aluminum covers its properties, early history, alloys, and corrosion, with consideration of issues that are relevant to conservation. The early history covers the period from 1808 until 1890 when industry began producing cheaper aluminum, thanks to the development of the Hall–Héroult process. The unique comprehensive designation system developed for aluminum alloys (wrought and cast) is described. Corrosion reactions which restrict the use of the alloys are discussed in terms of pitting corrosion and the role of chloride ions. Additionally galvanic and cathodic corrosion, several forms of structural corrosion, the role of the environment, and methods of surface protection are covered since these aspects affect the long-term stability of the aluminum alloys.

Keywords: aluminum alloys, early history, corrosion, chloride removal

INTRODUCTION

Aluminum is considered a modern metal because it was not characterized until the early nineteenth century (Table 1). But with its many useful properties—low density, high electrical and thermal conductivity, and high strength when alloyed with other metals—aluminum alloys are ubiquitous, from airplanes and electrical cables to kitchen utensils and modern sculpture. The early history of aluminum starts around 1808, when Davy named the metal he was trying to isolate (Davy, 1808) and ends in 1886, when Hall and Héroult developed a commercially viable process for producing it (Vargel, 2004). During this period, aluminum was so expensive and difficult to isolate that it was considered a precious metal. But by 1890, industry began producing greater amounts of aluminum with the Hall–Héroult process. Today there is such an array of aluminum alloys that industry needs a systematic convention of alloy numbers to describe the various series of wrought and cast alloys. These numbers provide not only alloy compositions but also the hardness and strength (achieved by mechanical working or heat treatment, or both). The alloy number is a valuable piece of information for conservators with an aluminum object needing conservation treatment. Knowing the alloy number allows access to the material and corrosion data published by industry and can save on expensive analysis.

Despite being a highly reactive metal, aluminum resists corrosion because a thin, adherent and passivating oxide film rapidly forms on its surface. When the film fails, various forms of corrosion occur. Several aspects of corrosion are discussed: pitting corrosion, galvanic corrosion, cathodic protection and cathodic corrosion, the forms of structural corrosion, and filiform corrosion under coatings. Also discussed are the role

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of the environment—indoor, outdoor, freshwater, seawater and soil—and methods of surface protection—anodizing, chemical conversion coatings, and organic coatings. The information on different aspects of aluminum corrosion should be useful to conservators who are developing a conservation treatment for damaged or corroded aluminum objects. For example, pitting corrosion is often caused by chloride ions, so chloride removal is particularly important from museum objects. Additionally, aluminum alloys in contact with or containing copper are particularly susceptible to galvanic corrosion or various types of structural corrosion, and problems can be expected if aluminum alloys are used in outdoor objects.

TABLE 1. Approximate date of first widespread use of common metals (Killick, 2001; Amundsen et al., 2012).

Metal	Approximate date of first widespread use
Copper	~7000 B.C. (Near East) for native copper ~5000 B.C. (Near East) for smelted copper
Lead	6000–5000 B.C. (Near East/Balkans)
Gold	5000–4000 B.C. (Balkans)
Tin	4000–3000 B.C. (Near East)
Silver	4000–3000 B.C. (Balkans/Near East)
Nickel	2000–1000 B.C. (Near East) for copper/nickel alloys
Iron	1000–0 B.C. (Near East)
Zinc	100–200 A.D. (Rome) for copper/zinc alloys 900–1000 A.D. (India) for zinc metal
Aluminum	1800–1900 A.D. (Europe/United States)
Magnesium	1800–1900 A.D. (Europe/United States)

This paper is written for conservators and other professionals working with aluminum in a cultural heritage context. It gives an overview of aluminum, its properties, early history, alloys, and corrosion, emphasizing aspects that are relevant to conservation.

Properties

Aluminum is silvery-white to dull gray in color, depending on the surface roughness. It is non-magnetic, and although very reactive, it does not easily ignite and is non-sparking (Greenwood and Earnshaw, 1997). Aluminum is corrosion resistant because a tough oxide film forms on its surface in air. Aluminum has many useful properties, including low density, relatively low melting point, high electrical and thermal conductivity, and high strength when alloyed with other metals. In addition, the low transmission of water vapor through a thin aluminum film has resulted in its use in laminated vapor barrier films, such as Marvelseal 360 (Burke, 1992). Several properties of selected metals, including aluminum, are listed in Table 2.

Low Density

One of the most useful properties of aluminum is its low density, a value much lower than other common metals. Another important property is that pure aluminum can be strengthened by alloying with small amounts of copper, magnesium and silicon. The birth of the aerospace industry in the early 1900s started with the invention of the airplane by the Wright brothers. Their plane, first flown in 1903, carried a cast aluminum engine block (Goodway and Leyes, 1993; Gayle and Goodway, 1994). The aerospace industry has taken advantage of the lightness of

TABLE 2. Properties of pure metals (Lide, 1998). The ↑ arrow shows the maximum value in the column and the ↓ arrow shows the minimum value in the column.

Metal	Principal oxidation number(s)	Atomic weight (g mol^{-1})	Density at 25°C (g cm^{-3})	Melting point (°C)	Linear expansivity at 25°C (°C^{-1})	Electrical conductivity at 25°C (S m^{-1})	Thermal conductivity at 25°C (W cm^{-1} °C^{-1})
Aluminum	Al^{3+}	26.98	2.70	660	23.1×10^{-6}	3.69×10^{7}	2.37
Copper	Cu^{1+}, Cu^{2+}	63.55	8.96	1085	16.5×10^{-6}	5.85×10^{7}	4.01
Gold	Au^{1+}, Au^{3+}	196.97	19.3↑	1064	14.2×10^{-6}	4.42×10^{7}	3.17
Iron	Fe^{2+}, Fe^{3+}	55.85	7.87	1538↑	11.8×10^{-6}↓	1.01×10^{7}	0.80
Lead	Pb^{2+}, Pb^{4+}	207.20↑	11.3	327	28.9×10^{-6}	0.47×10^{7}↓	0.35↓
Magnesium	Mg^{2+}	24.30↓	1.74↓	650	24.8×10^{-6}	2.23×10^{7}	1.56
Nickel	Ni^{2+}	58.69	8.90	1455	13.4×10^{-6}	1.40×10^{7}	0.91
Silver	Ag^{1+}	107.87	10.5	962	18.9×10^{-6}	6.17×10^{7}↑	4.29↑
Tin	Sn^{2+}, Sn^{4+}	118.71	7.26	232↓	22.0×10^{-6}	0.87×10^{7}	0.67
Zinc	Zn^{2+}	65.39	7.14	420	30.2×10^{-6}↑	1.66×10^{7}	1.16

aluminum and aluminum alloys, and developed structurally reliable, strong, and fracture-resistant parts for airframes, missile bodies, and satellite components (Davis, 1999).

Low Melting Point

The pure metal melts at a relatively low temperature (660°C) and is easily cast. Examples of early cast aluminum include the pyramidal cap on top of the Washington Monument in Washington, DC (set in place 1884). The cap, which was cast in 1884 (at great expense), is the first American architectural use of aluminum (Kelley, 1995). It weighs 100 ounces (2.8 kg) and is 8.9 inches high (22.6 cm) (Binczewski, 1995). At that time aluminum was still considered a precious metal. The other notable early architectural use of aluminum was the statue of *Eros*, cast c. 1890 in London (unveiled 1893) in nominally pure aluminum, as pure as could be refined at the time (West, 1984). It stands 8 feet (2.4 m) tall.

With its low melting point, aluminum is easily recycled. Remelting aluminum for recycling requires only about 5% of the energy needed to extract aluminum from aluminum oxide (Davis, 1999; Emsley, 2001).

Formability

Wrought aluminum alloys are easily machined and extruded into complex shapes. They are formable by many metal-working processes and accept a wide variety of finishes (Frank et al., 2012). Wrought alloys have a wide range of uses in architecture (Kelley, 1995; Nichols, 2000) and have even been used to build prototypes of houses. Buckminster Fuller's Dymaxion House of the late 1920s (Ashby, 2000; Trentelman et al., 2002) and the experimental Aluminaire House exhibited in 1932 (Jandl, 1991) are examples of this early use of wrought alloys for structural domestic architecture.

Ductility and Softness

Pure aluminum is ductile and malleable (only gold is more malleable) and can be pulled into a thin wire or rolled into a thin foil (Greenwood and Earnshaw, 1997). Aluminum foil (typically 0.02 mm thick) and imitation silver leaf (made from aluminum) are two examples. A less common example, developed in the 1950s, is aluminum yarn (e.g., Lurex, Reymet, Metlon) that can be woven into a lamé fabric (Moncrieff, 1970; Járó et al., 2000; Nichols, 2000). Pure aluminum is soft and easily scratched by harder materials, and should be handled with care.

Reflectivity

Aluminum can take a high polish and is highly reflective; its reflectivity, as high as 95%, is almost as high as that of silver for visible light (Strong, 1934; Greenwood and Earnshaw, 1997; Davis, 1999). It is used in mirrors, including those in large telescopes, and reflectors. The paint industry uses aluminum flakes as pigments in paint (Davis, 1999).

Electrical Conductivity

Because of its high electrical conductivity, aluminum is used extensively for electrical transmission lines. It is also used in house wiring but, prior to the mid-1970s, there were contact problems. Contacts with other metals, such as copper, could loosen with time and overheat because of differences in expansion between aluminum and the other metals (Newbury and Greenwald, 1980). Special contact techniques have been developed since that time.

Health and Safety

Aluminum is nontoxic and is routinely used in containers for food and beverages (Davis, 1999). Aluminum sulfate is used in water purification to remove organic matter and clarify the water (Helmboldt et al., 2007). Many foods contain aluminum compounds and it is estimated that people consume about 10 mg of aluminum per day instigating the claim that aluminum could contribute to Alzheimer's disease, but there is no evidence to support this (Vargel, 2004). The main concern when dealing with aluminum and its compounds is the fine dust, which can irritate the lower respiratory tract (ACGIH, 2011).

EARLY HISTORY

Natural Occurrence

Aluminum is the third most abundant element (8.3% by weight) in the Earth's crust after oxygen and silicon (Greenwood and Earnshaw, 1997; Emsley, 2001). Because aluminum metal is so reactive, aluminum (Al) is found in nature as aluminum ions (Al^{3+}) combined with other elements, mainly as stable oxide and silicate minerals such as feldspars, micas, and clays (Greenwood and Earnshaw, 1997). Large amounts of energy and high temperatures are required to reduce these compounds to metal (Frank et al., 2012).

Discovery and Naming

In the late 1700s and early 1800s, scientists tried to isolate what they were convinced was an undiscovered metal that formed the base of alumina, a common clay (Emsley, 2001; Frank et al., 2012). In 1808, the British chemist Sir Humphry Davy proposed the name "alumium" for the metal he was trying to isolate from alumina (Davy, 1808) and later agreed to change it to "aluminum". This conformed to the "um" spellings for elements (e.g., platinum, molybdenum, tantalum). Shortly thereafter, the name "aluminium" was adopted to conform with the "ium" ending of other newly discovered elements of the time (e.g., potassium, sodium, magnesium) (Lide, 1998). Two variants of the metal's name are now in current use, aluminium and aluminum. The spelling aluminum predominates in the United States and Canada whereas the spelling aluminium is preferred in most other countries.

First Isolation 1827

The German chemist Fredrich Wöhler is generally credited with having isolated aluminum in 1827 (Lide, 1998). He passed dry aluminum chloride ($AlCl_3$) vapor over molten potassium metal (K) to produce globules of aluminum and potassium chloride (KCl) (Frank et al., 2012). In the reaction, the aluminum is electrochemically reduced from its chloride salt by the more reactive potassium metal (Equation 1).

$$AlCl_3\ (g) + 3\ K\ (l) \rightarrow Al\ (s) + 3\ KCl\ (s) \qquad (1)$$

The process was expensive because of the difficulty in producing aluminum chloride and potassium metal at that time. The newly isolated aluminum was pure enough for Wöhler to determine some properties, including its low density (Vargel, 2004).

Production by Chemical Displacement

The first commercially successful process to produce aluminum was devised in France in 1854 by Henri Deville (Greenwood and Earnshaw, 1997). He modified the Wöhler process and used the less volatile sodium aluminum chloride ($NaAlCl_4$) salt instead of aluminum chloride and sodium metal (Na) instead of potassium to produce aluminum and sodium chloride (NaCl) (Vargel, 2004; Bourgarit and Plateau, 2007; Frank et al., 2012) (Equation 2).

$$NaAlCl_4\ (l) + 3\ Na\ (l) \rightarrow Al\ (s) + 4\ NaCl\ (s) \qquad (2)$$

Deville displayed a few early pieces made from aluminum at the Paris Exposition in 1855 (Nichols, 2000) when aluminum was as valuable as gold (Bourgarit and Plateau, 2007), including an aluminum balance arm (from a scientific balance) that dates from 1855 and is one of the earliest surviving examples of aluminum (Nichols, 2000). Deville set up a plant in Paris in 1856 to produce aluminum and moved it to Nanterre in 1857. By 1859, production had reached 500 kg (Vargel, 2004).

Production by Electrolytic Reduction (Hall–Héroult Process)

The aluminum industry grew through the second half of the 1800s using chemical displacement processes (Frank et al., 2012). However, because potassium and sodium metals were expensive, aluminum remained a laboratory chemical and a curiosity until about 1890 when production of aluminum using the electrolytic reduction process became economically feasible.

Several factors were in place by 1886 for the development of a commercially viable process for making cheap aluminum metal. First was the knowledge that aluminum could be recovered from molten aluminum salts by electrolytic reduction. As early as 1854, scientists in France (Deville) and Germany (Bunsen) had figured out how to make small quantities of aluminum by the electrolytic reduction of molten sodium aluminum chloride using batteries, although that process was not commercially viable (Greenwood and Earnshaw, 1997; Frank et al., 2012). Other factors were the increasing availability of cheap electricity for major industrial uses after 1867 when a practical design of the dynamo was patented (Greenwood and Earnshaw, 1997); the development of the Bayer process (patented 1888) for the extraction and purification of alumina (aluminum oxide, α-Al_2O_3) from bauxite, the most important aluminum ore (Hudson et al., 2005); and Deville's discovery that aluminum oxide dissolved in molten cryolite (Na_3AlF_6) (Frank et al., 2012). In 1886, Charles Hall (USA) and Paul Héroult (France), both 22 years old at the time, independently discovered and patented a workable electrolytic process in which carbon electrodes are used to produce aluminum by reducing aluminum oxide dissolved in molten cryolite (Vargel, 2004; Shakhashiri, 2008; Frank et al., 2012; Sanders, 2012).

Introduction of the Hall–Héroult process greatly lowered the cost of production and started to replace Deville's chemical displacement process (Frank et al., 2012). By 1890, aluminum metal was being commercially produced by the Hall–Héroult process and the "Age of Aluminum" had begun (Nichols, 2000). The Hall–Héroult process is now the only method by which aluminum metal is produced commercially (Shakhashiri, 2008).

ALUMINUM ALLOYS

Today there is such an array of commercially available aluminum alloys that industry developed a systematic naming convention to describe the various series of wrought and cast alloys, their thermal history and their surface finish (see Appendix 1). One of the first steps for a conservator in dealing with an aluminum object should be to try to find this alloy number. This number opens up a wealth of information available from the aluminum industry. Just from the series that an alloy belongs to, one can tell a great deal about its chemical composition and characteristics (Kaufman, 2000). All of this information can be invaluable in developing a conservation treatment for damaged or corroded aluminum. This section summarizes the different designation categories.

The Aluminum Association (AA) introduced its designation system for wrought aluminum alloys in 1954 (Kissell and Ferry, 2002) and for cast aluminum alloys around 1980 (Kaufman, 2000). These designation systems are still managed by the AA and there is a carefully controlled registration process for alloys. (Web addresses for various aluminum associations and institutes are given in Appendix 1.) The alloys are divided into two categories, wrought or cast, according to how they will be formed, and each registered alloy is given a four-digit number.

Wrought Aluminum Alloys

Wrought aluminum alloys are designed to be formed by a wide variety of processes such as rolling into sheet or foil, or extrusion into bars or wire. For the wrought alloy system, there is a near-worldwide accord on alloy designations (Kaufman, 2002). The naming is based on the four-digit convention established by the AA. The designation and chemical composition is contained in the registration record, also known as "Teal Sheets", available on-line (AA, 2009). This convention allows for easy identification of the composition of most internationally available wrought aluminum alloys. Details are given in Appendix 1.

Cast Aluminum Alloys

Cast aluminum alloys are specially formulated to flow. For the cast alloy system, there are no internationally accepted alloy designations (Kaufman and Rooy, 2004). In North America, the Aluminum Association's naming convention is used for cast alloys, and it is based on a four-digit number. This convention and others used in the Unified Numbering System (UNS) and in Europe are discussed in Appendix 1.

Temper

The temper of an aluminum alloy indicates its hardness and strength. An alloy is somewhat strengthened through the addition of the alloying elements (an effect known as solution hardening), but in general, aluminum alloys are strengthened further by processes called tempering. They are mainly strengthened by heat treatment involving precipitation hardening, but also by strain hardening (cold working) (Kissell and Ferry, 2002; Sanders, 2012). The AA has established a temper designation system for aluminum alloys, both wrought and cast (Davis, 1999; Kaufman, 2000; Kissell and Ferry, 2002). More information about temper is provided in Appendix 1.

Surface Finishes

Industry can produce a variety of finishes on aluminum alloys. These finishes can be classified according to a designation system developed by the Aluminum Association. The three major categories are mechanical, chemical, and coatings (Zahner, 1995; AA, 2003). Mechanical finishes are designated by the letter M followed by a two-digit number, such as M22 for specular (a reflective smooth finish) or M44 for coarse matte. Finishes produced by chemical treatments are designated similarly, but with the letter C; for example, C23 denotes coarse matte and C43 denotes alkaline chromate. The final category, coatings, is subdivided into five classes, designated by A for anodic, R for resinous, V for vitreous, E for electroplated and L for laminated. To date, only anodic coatings have a numbering system (such as A21 for clear anodizing) while the remaining four classes remain tentative. (Further information on anodic coatings and anodizing is discussed below.)

Alclad Products

The term alclad refers to wrought aluminum products (e.g., plates, sheets, tubes, wires) with a layered or sandwich structure. Alclad material consists of an aluminum alloy core which has a thin outer layer (cladding) of a more corrosion-resistant material (either pure aluminum or another aluminum alloy) on one or both sides (Zahner, 1995). Examples of common alclad material are described in Appendix 1.

Plating

Aluminum alloys can be plated with chromium, nickel, cadmium, copper, tin, zinc, gold or silver (Davis, 1993; Sheasby and Pinner, 2001), but are more difficult to electroplate than the more common metals because of aluminum's high affinity for oxygen. Prior to electroplating, the aluminum is briefly immersed in a solution containing zinc or tin salts where a thin layer of metallic zinc or tin is plated over the aluminum as the aluminum corrodes. (There are many terms for this reaction, including electrochemical replacement, cementation, or displacement.)

Iron or steel can be coated with aluminum using a hot-dipping process that was developed in the 1940s (Zahner, 1995). As the iron passes through the molten aluminum bath, the aluminum becomes metallurgically bonded to the underlying iron by the formation of intermetallic aluminum-iron compounds, generally identified as Al_5Fe_2 (Davis, 1993). This "aluminized steel" is available in two forms: the type 1 coating is a thin, aluminum-silicon alloy (5 to 11% Si) used in automobile exhausts, and the type 2 coating is a thicker, unalloyed aluminum used for outdoor applications such as roofing (Zahner, 1995; Davis, 2000). During the 1970s, steel hot-dipped with aluminum-zinc alloys were developed and proved to be more corrosion resistant than traditional galvanized (zinc-coated) steel (Zahner, 1995; Davis, 2000). One popular aluminum-zinc coating contains 45% zinc and 55% aluminum (trade names Galvalume, Zincalume, Aluzink). Steel coated with this alloy coating generally lasts two to four times longer than steel coated with an equal thickness of zinc (Davis, 2000). Aluminum can also be electroplated onto steel (Davis, 1993), but this process is difficult because it requires a water-free electrolyte and elevated temperatures.

CORROSION

Reactivity

Aluminum metal has a standard equilibrium reduction potential of −1.662 V versus a standard hydrogen electrode (SHE) (Lide, 1998) for the reaction (Equation 3)

$$Al^{3+} + 3e^{-} \rightleftarrows Al\,(s) \tag{3}$$

where e^- represents an electron. The highly negative potential means that aluminum is a very reactive metal and one of the easiest metals to oxidize. It is also why so much energy is required to recover aluminum metal from its oxide ore and why it is not possible to make aluminum metal in an aqueous environment.

The reactivity of aluminum metal is taken advantage of when aluminum powders are used in fireworks and rocket fuel (Reboul and Baroux, 2011), or in the thermite process, where powdered aluminum metal reacts with powdered iron oxide (Fe_2O_3) to form iron (Fe) metal and aluminum oxide (Greenwood and Earnshaw, 1997) as shown below (Equation 4):

$$2\ \mathrm{Al}\ (s) + \mathrm{Fe_2O_3}\ (s) \rightarrow 2\ \mathrm{Fe}\ (s) + \mathrm{Al_2O_3}\ (s) + \text{heat} \qquad (4)$$

The thermite process, which can produce temperatures of 3000°C, is used in thermite bombs and in welding large pieces of steel in place.

Natural Oxide Film

Given the high reactivity, why is aluminum so stable and corrosion resistant? The stability results from a protective film composed of aluminum oxide, oxyhydroxide, or hydroxide. (For simplicity the film will be called an "oxide film" in the following, unless the details of the composition are being discussed.) Whenever aluminum metal is exposed to air or an oxidizing media such as water, it spontaneously reacts with oxygen and becomes covered with a thin, continuous, adherent and protective aluminum oxide film (Vargel, 2004). If the oxide is removed by abrasion, cutting, or machining, a new oxide reforms on the metal within a few milliseconds in both air and water (Vargel, 2004; Reboul and Baroux, 2011). This natural oxide film is a tough, colorless coating that strongly bonds to the aluminum, and prevents further exposure to oxygen and corrosion (unless a substance or condition is present that destroys the film) (Davis, 1999).

The oxide film consists of layers with a total thickness of 4 to 10 nm, as sketched in Figure 1 (Dunlop and Benmalek, 1997; Vargel, 2004). The inner layer next to the metal surface is a compact amorphous (non-crystalline) aluminum oxide (Al_2O_3), often simply called alumina, with an initial thickness of 2 to 4 nm (Vargel, 2004; Reboul and Baroux, 2011). It is referred to as a barrier layer because it is an almost perfect electrical insulator (Reboul and Baroux, 2011). The outer part is converted to a hydrous form by reaction with water vapor in the air. This layer consists of bayerite (aluminum hydroxide, $Al(OH)_3$) and a small amount of hydrated boehmite (pseudo-boehmite, written as $AlO(OH){\cdot}H_2O$) (Holyroyd, 2001; Reboul and Baroux, 2011). It is porous and less compact than the underlying barrier layer, and so can become contaminated with oils or lubricants during

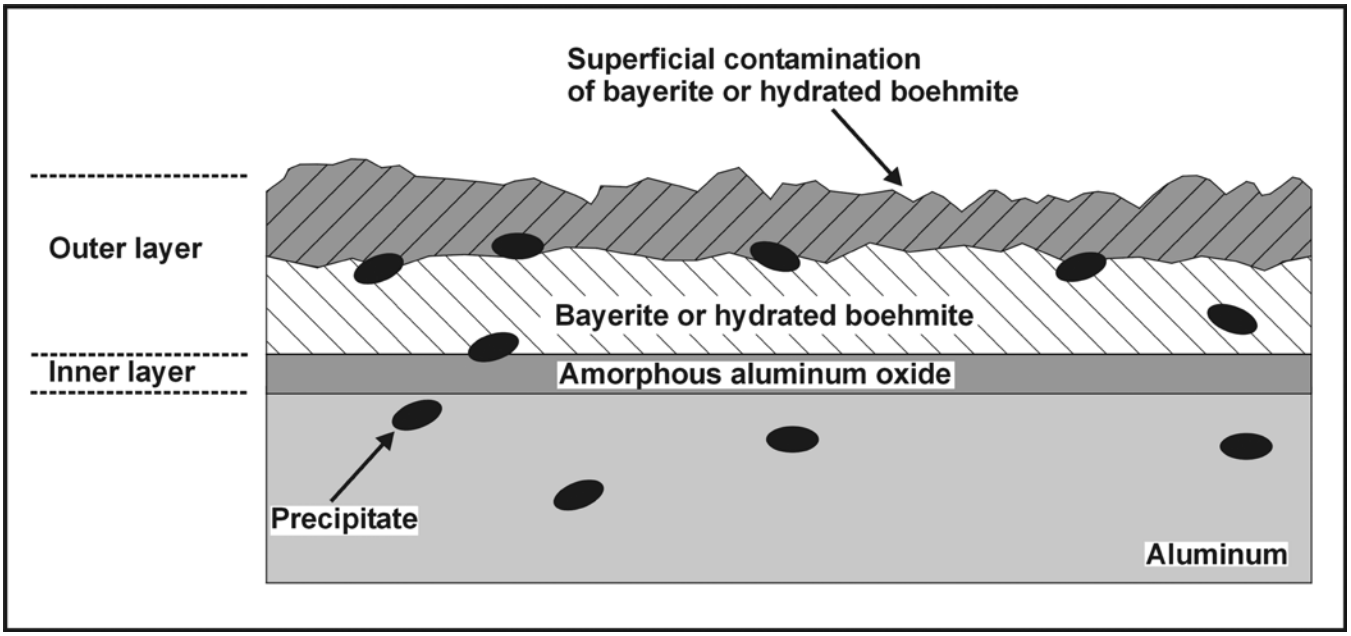

FIGURE 1. Schematic diagram of oxide film on an aluminum alloy. The inner layer is compact, amorphous aluminum oxide and the outer layer is porous bayerite or hydrated boehmite. The exterior surface can become contaminated with oil residues or dirt. Intermetallic precipitates are shown in both the aluminum and the oxide. Based on Dunlop and Benmalek (1997) and Vargel (2004). © Government of Canada, Canadian Conservation Institute.

rolling or extrusion operations, or pick up soot and other particles in dirty environments. Industry often regenerates the surface of processed aluminum by pickling (dissolving the protective film in acid), especially if other surface treatments are to be applied (Vargel, 2004).

Aluminum Oxides and Hydroxides

Alumina, bayerite, and boehmite are just three of the compounds of aluminum with oxygen or hydroxide. Table 3 lists other aluminum oxide compounds. Gibbsite, boehmite and diaspore are abundant in nature (Hudson et al., 2005). Alpha alumina occurs in nature as the mineral corundum and, because of its inertness, high melting point (2045°C) and hardness, it is used as an abrasive (Greenwood and Earnshaw, 1997). Nordstrandite and doyleite are minerals and have not been reported as corrosion products.

When aluminum hydroxides or hydroxide oxides are heated in air, they undergo a series of compositional and structural changes before ultimately being converted to corundum (Greenwood and Earnshaw, 1997; Hudson et al., 2005). Bayerite and gibbsite convert to boehmite at about 100°C (Holroyd, 2001). Diaspore converts to corundum around 600°C while other aluminum hydroxide oxides convert above about 1100°C. Gamma alumina, a less compact form of aluminum oxide, is made by industry by heating gibbsite or boehmite at temperatures less than 450°C to remove water. Heating gamma alumina above 1000°C converts it to alpha alumina.

When pure, the compounds in Table 3 are white or colorless, depending on particle size, whereas when found in nature, or detected as corrosion products, they may be colored by impurities. Corundum, for example, is pure aluminum oxide and it is colorless (Greenwood and Earnshaw, 1997). The gemstones ruby and sapphire are aluminum oxide with trace impurities—the red in rubies is caused by trace amounts of chromium and the blue in sapphires is from small amounts of both iron and titanium (Nassau, 2001). Aluminum corrosion products are generally white but can be stained green if copper is present.

ELECTROCHEMICAL REACTIONS

When aluminum is covered with enough water to form an electrolyte, the corrosion process is electrochemical. (Some of the terminology of electrochemistry is summarized in Appendix 2.) The half-reaction for aluminum oxidation (Equation 5) is:

$$\mathrm{Al\ (s)} \rightarrow \mathrm{Al^{3+}} + 3\mathrm{e^-} \tag{5}$$

This is called an anodic reaction, and the areas where it occurs are called anodic sites. In the reaction, aluminum forms the trivalent ion (Al^{3+}) in solution. This reaction is balanced by a simultaneous reduction reaction (called a cathodic reaction) in solution at cathodic sites. In aqueous solutions, the reduction reaction usually involves either the reduction of dissolved oxygen (O_2) gas or the reduction of hydrogen (H^+) ions to form hydroxide (OH^-) ions or hydrogen (H_2) gas (Vargel, 2004). Each of these reduction reactions can be written in two ways (Equations 6 and 7) (Schweitzer and Pesterfield, 2010):

$$\mathrm{O_2\ (g)} + 4\ \mathrm{H^+} + 4\mathrm{e^-} \rightarrow 2\ \mathrm{H_2O} \ \text{ or } \ \mathrm{O_2\ (g)} + 2\ \mathrm{H_2O} + 4\mathrm{e^-} \rightarrow 4\ \mathrm{OH^-} \tag{6}$$

$$2\ \mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{H_2\ (g)} \ \text{ or } \ 2\ \mathrm{H_2O} + 2\mathrm{e^-} \rightarrow \mathrm{H_2\ (g)} + 2\ \mathrm{OH^-} \tag{7}$$

If the Al^{3+} ions combine with OH^- to form solid $Al(OH)_3$, the net reactions (Equations 8 and 9) are:

$$4\ \mathrm{Al\ (s)} + 3\ \mathrm{O_2\ (g)} + 2\ \mathrm{H_2O} \rightarrow 4\ \mathrm{Al(OH)_3\ (s)} \tag{8}$$

$$2\ \mathrm{Al\ (s)} + 6\ \mathrm{H_2O} \rightarrow 2\ \mathrm{Al(OH)_3\ (s)} + 3\ \mathrm{H_2\ (g)} \tag{9}$$

TABLE 3. Aluminum and its compounds with oxygen and hydroxide (Greenwood and Earnshaw, 1997; Frank et al., 2009).

Chemical name	Formula	Mineral name	Mohs hardness
Aluminum	Al	-	2.75
Aluminum oxide (alpha alumina)	α-Al_2O_3	corundum	9
Aluminum oxide (gamma alumina)	γ-Al_2O_3	-	8
Aluminum hydroxide oxide, alpha form	α-AlO(OH)	diaspore	6.5 to 7
Aluminum hydroxide oxide, gamma form	γ-AlO(OH)	boehmite (böhmite)	3.5 to 4
Aluminum hydroxide oxide hydrate	γ-$AlO(OH)\cdot H_2O$	pseudo boehmite[a]	-
Aluminum trihydroxide, alpha form	α-$Al(OH)_3$	bayerite	-
Aluminum trihydroxide, beta form	β-$Al(OH)_3$	nordstrandite	-
Aluminum trihydroxide, gamma form	γ-$Al(OH)_3$	gibbsite (hydrargillite)	2.5 to 3.5
Aluminum trihydroxide	$Al(OH)_3$	doyleite	-

[a] also called hydrated boehmite

In Equation 8, oxygen promotes aluminum corrosion by acting as an oxidizing agent at cathodic sites. But oxygen also contributes to the repair of the natural oxide layer that protects the aluminum from corrosion (Vargel, 2004).

Potential–pH (Pourbaix) Diagram

The conditions under which the protective oxide film is stable in water can be seen in the potential–pH (or Pourbaix) diagram in Figure 2 (Pourbaix, 1974). The diagram is divided into regions by the solid lines, according to the aluminum-bearing species that is the most thermodynamically stable—aluminum metal, solid $Al(OH)_3$, or the aqueous ions Al^{3+} in acidic conditions or aluminate ($Al(OH)_4^-$) in strongly alkaline conditions. (The aluminate ion is sometimes written in its dehydrated form AlO_2^- (Schweitzer and Pesterfield, 2010).) The broken lines refer to water, which is stable between the broken lines (a) and (b); above line (b) water is oxidized to oxygen gas, and below line (a) it is reduced to hydrogen gas. Aluminum should be passive (i.e., protected by its oxide film) in the pH range where solid $Al(OH)_3$ is the stable species, pH between about 4 and 8.5 in Figure 2. The calculated limits of the passive range depend on certain assumptions. For example, in Figure 2 an aluminum ion concentration of 10^{-6} M is used to determine the boundaries; it is assumed that if the ion concentration is below this limit the aluminum is not corroding (passive or immune regions), and if it is above this limit the aluminum is corroding (active region). The limits of the passive range vary with temperature and with the form of oxide film (Davis, 1999).

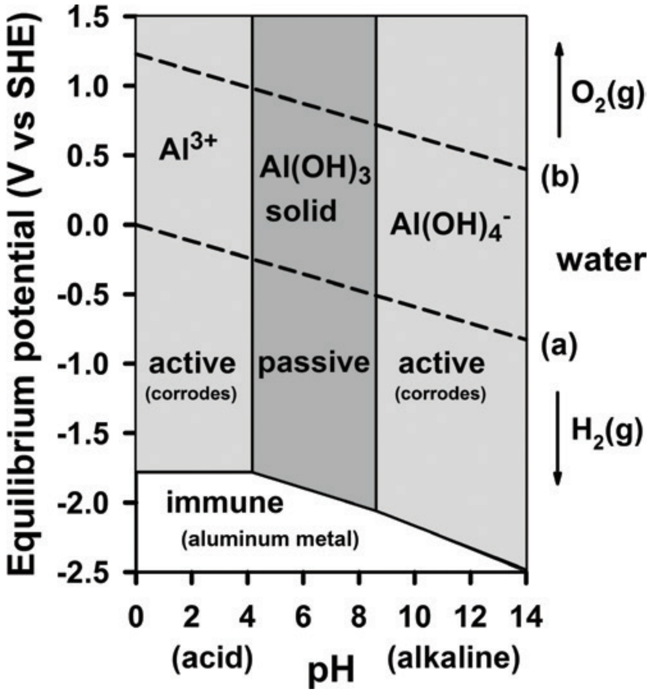

FIGURE 2. A potential-pH (or Pourbaix) diagram for an aluminum-water system at 25°C and 1 atmosphere pressure. The Al^{3+} concentration is 10^{-6} M. In the passive region, the aluminum is assumed to be protected by a film of gibbsite. SHE stands for a standard hydrogen electrode. © Government of Canada, Canadian Conservation Institute.

The form of the protective film in the passive region depends on time. Initially, amorphous aluminum hydroxide ($Al(OH)_3$) forms. It is insoluble in water and precipitates as a white gel (Vargel, 2004). Because it is amorphous rather than crystalline, it is difficult to identify by X-ray diffraction (Rocca et al., 2010). As the gel ages, it changes to crystalline bayerite (α-$Al(OH)_3$). Gibbsite (γ-$Al(OH)_3$) may also form, especially if alkali metals ions, such as magnesium or calcium, are present (Davis, 1999; Ghali, 2000). Crystalline bayerite forms rapidly at higher temperatures (e.g., 60 to 90°C) and boehmite (γ-$AlO(OH)$) forms above 90°C (Vargel, 2004). The solubility of freshly precipitated aluminum hydroxide is about 10^{-6} M at neutral pH but drops to about 10^{-9} M as the oxide ages (Berzins et al., 1977a).

The protective film is amphoteric; that is, it dissolves both in strong acids and in strong alkalis (Greenwood and Earnshaw, 1997), forming Al^{3+} ions in acids and the aluminate ion in alkaline solutions. In the active ranges, where the protective film dissolves, the aluminum corrodes uniformly at a steady corrosion rate (Davis, 1999). Thus aluminum corrodes not only in acidic solutions but also in contact with alkaline material such as sodium hydroxide or trisodium phosphate (Ghali, 2010). Construction materials such as concrete, plaster, mortar, stucco, or cement are alkaline and can cause superficial surface attack on aluminum, at least initially while still wet (Davis, 1999).

Corrosion Potential

The lines in a Pourbaix diagram are drawn for equilibrium potentials calculated for one reaction at a time. But on a metal in an electrolyte, the reactions are not in equilibrium, and both anodic and cathodic half-reactions are occurring on the metal surface at the same time. The potential of the metal is determined by both half reactions; it is a so-called mixed potential, as opposed to an equilibrium potential, and its value is somewhere between the equilibrium potentials for the half-reactions involved. This mixed potential is usually called the corrosion potential. The corrosion potential of aluminum in most aqueous media is in the order of −0.50 V versus a standard hydrogen electrode (SHE) (Vargel, 2004), a value that lies roughly midway between the line (b) in the Pourbaix diagram (the equilibrium potential for the reduction of oxygen) and the potential of the line above the immune region of aluminum metal. MacLeod (2006) measured corrosion potentials from −0.37 V/SHE to −0.52 V/SHE on aircraft in seawater.

The corrosion potential of aluminum typically lies below line (a), the reaction to produce hydrogen gas (Equation 7), but this reaction is not significant when oxygen is present. If oxygen is removed, the corrosion potential drops. Gimenez et al. (1981) gives an example of the range of corrosion potentials of alloy 5086 measured in 3% sodium chloride solutions (pH 5.5 to 9) with oxygen (−0.50 V/SHE) and without oxygen (−0.65 to −0.88 V/SHE).

In aluminum alloys, the corrosion potential depends on the composition of the alloy (Davis, 1999), but it also depends on the composition of the solution that the alloy is immersed in (Lowson, 1978), and it can change with time. To compare corrosion potentials of alloys one needs a standard solution and a standard procedure to ensure reliable and reproducible results. For example, the ASTM G69 standard (ASTM, 2006b) uses an oxidizing chloride solution containing 58.5 g sodium chloride (NaCl, 1 M) and 9 mL of 30% hydrogen peroxide (H_2O_2) per liter of solution. Table 4 lists the corrosion potentials for several selected aluminum alloys along with some metals measured in that solution.

The position of a metal or alloy in Table 4 indicates its relative reactivity. The more noble the metal, the less likely it is to corrode. The ones higher on the list are said to be more noble or cathodic, and the ones lower on the list are more active or anodic. Aluminum alloys containing copper (2xxx series) and manganese (3xxx series) tend to be more noble than pure aluminum, with higher (less negative) corrosion potentials, while those containing zinc (7xxx series) or magnesium (5xxx series) tend to be more active than pure aluminum, with lower (more negative) corrosion potentials. The potential of heat-treatable aluminum alloys depends on the rate of quenching (ASTM, 2006b). In alclad products (Table 10 in Appendix 1), the outer cladding layer is chosen to be more negative, by about 100 mV, than the core alloy.

TABLE 4. Corrosion potentials of selected metals and alloys in an oxidizing chloride solution (Burleigh et al., 1993).

	Corrosion potential in oxidizing chloride solution		
Metal	versus SCE[a] (V)	versus SHE[b] (V)	Relative activity
Nickel (Ni, 270)	+0.12	+0.36	Noble (cathodic)
Copper (Cu)	+0.08 to −0.11	+0.32 to +0.13	
Bronze (94% Cu, 6% Sn)	−0.02 to −0.08	+0.22 to +0.16	
Brass (63% Cu, 37% Zn)	−0.08 to −0.30	+0.16 to −0.06	
Tin (Sn)	−0.19 to −0.40	+0.05 to −0.16	
Manganese (Mn)	−0.40 to −0.80	−0.16 to −0.56	
Stainless steel (321)	−0.25 to −0.31	−0.01 to −0.07	
Iron (Fe)	−0.49 to −0.60	−0.25 to −0.36	
2024-T3[c] (Al + Cu)	−0.59 to −0.62	−0.35 to −0.38	
8090-T3 (Al + Li + Cu)	−0.70	−0.46	
Lead (Pb)	−0.45 to −0.71	−0.21 to −0.47	
2024-T8[c] (Al + Cu)	−0.71 to −0.73	−0.47 to −0.49	
6013-T6 (Al + Mg + Si)	−0.73 to −0.74	−0.49 to −0.50	
3003[c] (Al + Mn)	−0.74	−0.50	
Aluminum (99.999%)	−0.73 to −0.76	−0.49 to −0.52	
Alclad 2024[c] (outer cladding 1230 is 99.3% Al)	−0.76	−0.52	
5042 (Al + Mg)	−0.77	−0.53	
Alclad 3003[c] (outer cladding 7072 is Al + Zn)	−0.87	−0.63	
7003 (Al + Zn)	−0.94	−0.70	
Zinc (Zn)	−0.98 to −1.01	−0.74 to −0.77	
Magnesium[c] (Mg)	−1.64	−1.40	Active (anodic)

[a] Saturated calomel electrode

[b] Standard hydrogen electrode

[c] Measured against a 0.1 N calomel electrode in a solution of 53 g sodium chloride and 3 g hydrogen peroxide per liter of solution; converted to the SCE scale by adding 0.92 mV.

Pitting Corrosion

In the active regions of the Pourbaix diagram, aluminum corrodes uniformly. In the passive region, the oxide film protects against uniform corrosion, but it may not prevent a localized form of corrosion called pitting corrosion. Pitting corrosion starts at localized breaks in the film, and produces irregularly shaped holes (Vargel, 2004; Ghali, 2010). Most pitting corrosion is thought to occur if there are: (1) sufficient chloride ions (Cl^-) and (2) sufficient dissolved oxygen (or a sufficiently oxidizing environment) (Szklarska-Smialowska, 1999; Reboul and Baroux, 2011). Other ions may also contribute to pitting corrosion (Leygraf and Graedel, 2000; Vargel, 2004).

Pitting corrosion begins with pit initiation, which involves the following steps (McCafferty, 2003): adsorption of chloride ions, penetration of chloride ions through the oxide film, and localized dissolution of aluminum at the metal/oxide interface. Adsorption of chloride ions occurs at surface defects in the hydrated aluminum oxide (Vargel, 2004; Reboul and Baroux, 2011), as shown schematically in Figure 3a. Adsorption is determined by the surface charge, which is controlled by pH. At a pH in the range 8–10, aluminum hydroxides and hydroxide oxides are neutral (at their isoelectric point) because there are an equal concentration of surface $–OH^-$ and $–H^+$ species (Monticelli et al., 1991; McCafferty, 2003; Blücher et al., 2006). At pH values less than about 9, the hydrated oxide surface is positive and attracts negative chloride ions, with the amount of adsorbed chloride increasing as the pH decreases (McCafferty, 2003). Some of the chloride ions penetrate into the film (McCafferty, 2003), and can be difficult to remove.

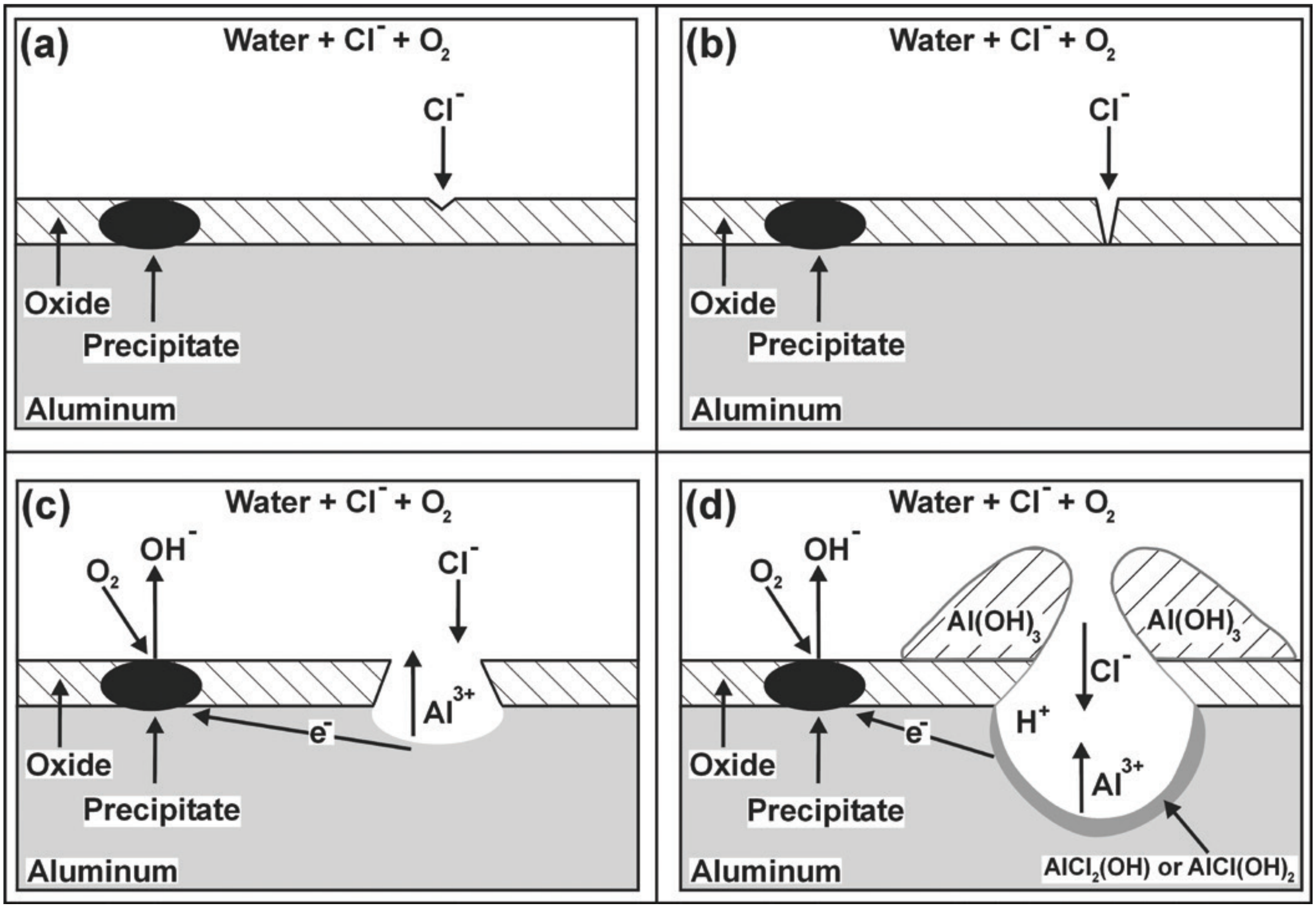

FIGURE 3. Schematic diagram of pitting corrosion caused by chloride ions. (a) Chloride ions adsorb at defects. (b) Aluminum oxide film breaks down. (c) Aluminum begins to corrode and a pit develops. (d) Aluminum, chloride and hydrogen ions concentrate inside the pit and aluminum hydroxide precipitates outside the pit. Other species, such as $Al(OH)^{2+}$ and $Al(OH)_2^+$ are also present in the pit but are not shown. Adapted from Reboul and Baroux (2011). © Government of Canada, Canadian Conservation Institute.

Although chloride ions are thought to cause the aluminum oxide film to break down (Davis, 1999), as shown in Figure 3b, the details of how they do this is not well understood (Szklarska-Smialowska, 1999). Chloride ions are small and mobile, and may replace oxygen atoms in the film (Vargel, 2004), since the radius of the chloride ion is only slightly larger than that of an oxide ion (1.81 vs 1.40 Å) (McCafferty, 2003). This replacement may cause the film to break down, or it may impede oxygen from repairing damage to the film (Lowson, 1978). Berzins et al. (1977a) observed that chloride ions slowed down the development of a protective film, and attributed their observations to the competition between oxygen and chloride in repair and attack of the oxide film.

Once the oxide film has broken down, the aluminum begins to corrode and a pit develops (Reboul et al., 1996; Reboul and Baroux, 2011), as shown in Figure 3c. The aluminum lining the pit is the anodic site; as the aluminum corrodes, Al^{3+} ions are released into the pit (Equation 5). Except at low pH, the Al^{3+} ions react with water (hydrolyze) to form aluminum hydroxide ions, such as $Al(OH)^{2+}$ and $Al(OH)_2^+$, or aluminum hydroxide $Al(OH)_3$ (Equations 10, 11, and 12) (Stumm and Morgan, 1996; Schweitzer and Pesterfield, 2010):

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \tag{10}$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \tag{11}$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+ \tag{12}$$

These reactions release H^+, so the solution in the pit becomes acidic. Because the influx of positively charged ions upsets the charge balance in the pit, negatively charged counter ions, such as chloride ions, are pulled in and concentrated in the pit.

The aluminum corrosion half-reaction (Equation 5) is an anodic reaction, and must be counterbalanced by a cathodic half-reaction, in this case oxygen reduction (Equation 6). Oxygen is usually reduced on intermetallic phases that are more noble than the surrounding aluminum matrix. These phases can act as cathodes when the aluminum corrodes, in effect producing a galvanic cell between the cathodic intermetallics and the anodic aluminum matrix. Examples of cathodic intermetallics include the copper-containing intermetallic compound Al_2Cu and the iron-containing ones Al_3Fe or Al_6Fe (Szklarska-Smialowska, 1999). Since the oxygen reduction reaction releases OH^-, as shown in Figure 3c, the pH increases around the cathodic intermetallics. In alloys that contain copper-rich intermetallic precipitates (such as the 2xxx series), the pits form at copper-depleted areas adjacent to the precipitates (Balbo et al., 2013). Resistance to pitting depends on the alloy series; in decreasing order, relative pitting resistance is: 1xxx (most resistant), 5xxx, 3xxx, 6xxx, 7xxx, 2xxx (least resistant) (Davis, 1999). The 2xxx and 7xxx series alloys with higher copper contents are the most susceptible to pitting corrosion (Davis, 1999).

As the pit grows, the concentration of aluminum, chloride and hydrogen ions increases in the pit. Well-developed pits have high chloride ion concentrations and low pH (Ghali, 2010). Lowson (1978) determined that a critical concentration of 1.6 M chloride ion in the bulk solution is needed to maintain pit growth. The pH inside active pits is usually between 3 and 4 (Wong and Alkire, 1990; Reboul et al., 1996) although lower pHs (as low as 1) have been noted (Szklarska-Smialowska, 1999; MacLeod and Kelly, 2001; McCafferty, 2003). A solid forms on the bottom of the pits (Figure 3d) and this solid is thought to be a necessary condition for pit growth (Szklarska-Smialowska, 1999; Reboul and Baroux, 2011). The solid is presumably an aluminum chloride hydroxide, such as $AlCl(OH)_2$ and $AlCl_2(OH)$, as proposed by Wong and Alkire (1990).

As aluminum ions diffuse out of the pit, they meet a less acidic medium and form an unsightly white, voluminous and gelatinous precipitate of $Al(OH)_3$ that is much bigger than the underlying cavity (Vargel, 2004). This cone-shaped cap forms a physical barrier over the pit, restricting diffusion between the pit and the bulk liquid (Ghali, 2010; Reboul and Baroux, 2011). If the solution in the pit is acidic enough, hydrogen ions can be reduced within the pit through the cathodic half-reaction in Equation 7, generating bubbles of hydrogen gas (Reboul and Baroux, 2011). These bubbles help to push up the aluminum hydroxide cap and form a more volcano-like dome (Vargel, 2004).

Pit growth will stop if the corrosion of aluminum is slowed enough to allow the solid chloride-containing material at the bottom of the pit to dissolve and be replaced by the passive oxide film; this is sometimes called repassivation and pit death. Once corrosion slows, the aggressive solution inside the pit will be diluted by the bulk solution (Reboul and Baroux, 2011). Repassivation may occur if the pit cover is disrupted, allowing bulk solution more access to the pit (Ghali, 2010). Pitting can be prevented by removing dissolved oxygen, the reducible species required for a cathodic reaction (Ghali, 2010). In the absence of dissolved oxygen, most pits stop growing and repassivate after a few days (Vargel, 2004; Lyle et al., 2005; Ghali, 2010).

Crevice Corrosion

Crevices are large pits, and crevice corrosion is just a more severe form of pitting (Davis, 1999). Crevices form where the aluminum surface is shielded by another material and water is restricted, such as under gaskets, biofouling, external deposits, or between joints. The crevice limits access to dissolved oxygen when the oxygen has been consumed. Once the oxygen concentration inside the crevice is lower than outside, the outside becomes cathodic and the inside anodic, and the inside begins to corrode. As aluminum ions dissolve, the anodic area inside the crevice becomes acidic (Davis, 1999). In a chloride-containing environment, chloride ions build up inside the crevice just as in pitting corrosion, creating an aggressive environment that breaks down the passive layer on aluminum. Many aluminum alloys, with the exception of copper-containing ones, are resistant to crevice corrosion (Reboul and Baroux, 2011).

GALVANIC CORROSION

When two different metals are placed in electrical contact in the same electrolyte, the more active metal becomes the anode (where oxidation occurs) and the less active metal becomes the cathode (where reduction occurs) (Davis, 1999). The more active metal begins to corrode more rapidly, and the less active metal corrodes more slowly. The enhanced corrosion of the more active metal is called galvanic corrosion. Galvanic corrosion often attacks the more active metal in areas adjacent to the less active metal (Vargel, 2004). Severe damage, for example, can occur on aluminum roofs that become perforated around bolts or screws. To minimize corrosion of aluminum in contact with a more cathodic (less active) metal, the ratio of the exposed area of aluminum to the area of the other metal should be kept as high as possible (Davis, 1999).

Aluminum is anodic to (more active than) most metals (except for magnesium, zinc, and galvanized steel), so it is generally the aluminum that corrodes when aluminum is galvanically coupled to another metal (Davis, 1999; Vargel, 2004). The rate of galvanic corrosion depends on how far apart the corrosion potentials of the two metals are (see Table 4)—the farther apart, the faster the aluminum corrodes. Thus corrosion is more severe when aluminum is in contact with copper or copper-based alloys (brass, bronze, copper-nickel alloys) than when it is in contact with most other metals.

Galvanic corrosion can occur between different aluminum alloys if the alloys have different corrosion potentials. For example, aluminum alloy rivets in contact with more noble aluminum alloy panels in aircraft have suffered severe galvanic corrosion after immersion in fresh water or exposure to marine atmospheres (MacLeod, 1983). Galvanic corrosion of aluminum also occurs when the aluminum is in contact with semiconductors such as graphite or magnetite (Davis, 1999; Vargel, 2004). For this reason, graphitic greases should not be used on aluminum.

Galvanic attack is more serious when dissimilar metals are immersed than when they are used outdoors (Davis, 1999). Outdoors, galvanic corrosion is more pronounced in marine atmospheres (or where deicing salts are used) than in rural or industrial locations (Davis, 1999; Vargel, 2004; Ghali, 2010). In practice, contact can be made between aluminum and certain construction metals (such as stainless steels, zinc, or chromium-plated steels) without serious problems as long as moisture is not trapped at the contact points (Davis, 1999; Vargel, 2004).

Metal Ions

When aluminum is covered with a solution containing metal ions more noble than aluminum (e.g., copper, lead, mercury), the aluminum oxidizes and corrodes, and the metal ions are reduced and deposit onto the surface of the aluminum (Ghali, 2010). This is known as an electrochemical replacement or cementation reaction. To avoid this reaction, paints with such metal ions should never be used on aluminum. These paints include red lead primers, and copper- or mercury-containing antifouling paints (Davis, 1999; Vargel, 2004).

Of all the metal salts, mercury can cause the most damage to aluminum and any concentration of more than 0.01 parts per billion can be detrimental (Ghali, 2010). Moreover, no amount of metallic mercury should be allowed to come into contact with aluminum. Metallic mercury amalgamates with aluminum, which can destroy the existing oxide film, prevent the formation of a new film, and cause rapid pitting (Bessone, 2006). In the presence of moisture, voluminous columnar corrosion products (of mainly aluminum oxide) will form because aluminum, being slightly soluble in mercury, can diffuse through the mercury to the surface and oxidize.

An important reaction is between aluminum metal and copper ions (Equation 13) (Vargel, 2004):

$$3\ \mathrm{Cu}^{2+} + 2\ \mathrm{Al}\ (s) \rightarrow 2\ \mathrm{Al}^{3+} + 3\ \mathrm{Cu}\ (s) \qquad (13)$$

If rain runs over a copper alloy surface, such as a large copper roof, and then runs over an aluminum surface, dissolved copper ions plate out as copper metal on the aluminum. The plated copper disrupts the formation of the aluminum oxide film and provides efficient cathodic sites for oxygen reduction leading to pitting (MacLeod and Kelly, 2001; Reboul and Baroux, 2011). Electrons are then readily transferred between copper and the underlying aluminum. Even a copper-ion concentration of 0.02 parts per million in neutral or acidic solutions is considered dangerous (Ghali, 2010). The source of copper ions in solution can even come from the corrosion of $\mathrm{Al_2Cu}$ intermetallic particles in copper-containing aluminum alloys (Szklarska-Smialowska, 1999). Copper ions in recirculated water, such as in a fountain, can be removed by passing the water through a tower packed with aluminum chips (Ghali, 2010).

Cathodic Protection

Galvanic corrosion becomes an advantage when a more active metal is intentionally connected to a less active metal. Since the more active metal acts as the anode and corrodes preferentially, the less active metal corrodes more slowly and so is protected. The active metal is called a sacrificial anode, and the process is known as cathodic protection. Cathodic protection can also be achieved by using an impressed potential (Davis, 1999). In seawater, aluminum alloys can be protected by attaching sacrificial zinc or aluminum-zinc anodes (Davis, 1999; Vargel, 2004), and, in turn, sacrificial aluminum anodes are used to protect iron and steel (Davis, 1999; Ghali, 2010). Whether the protection is from an anode or from an impressed potential, the current should not be high enough to make the solutions too alkaline (Davis, 1999). Magnesium anodes should not be used to protect aluminum because the potential is lowered too much and this causes a severe form of corrosion called cathodic corrosion.

Cathodic Corrosion

When the local environment becomes too alkaline, aluminum can corrode because the protective oxide film dissolves at high pH. If the alkalinity is created by cathodic polarization, the corrosion is known as cathodic corrosion. The mechanism of cathodic corrosion is shown in Figure 4. The cathodic half-reactions, which usually take place at intermetallic compounds in the aluminum alloy surface, generate OH^- (or consume H^+), thus increasing the local pH. If the local pH becomes too high, the nearby protective aluminum oxide film dissolves as soluble aluminate ($Al(OH)_4^-$) species form (Equation 14) (Blücher et al., 2006):

$$Al(OH)_3\ (s) + OH^- \rightarrow Al(OH)_4^- \qquad (14)$$

Once the passive film has dissolved, the aluminum corrodes in the presence of excess OH^- ions (Equation 15) (Vargel, 2004):

$$Al\ (s) + OH^- + 3\ H_2O \rightarrow Al(OH)_4^- + 3\ H_2\ (g) \qquad (15)$$

In this way, somewhat counterintuitively, a cathodic polarization can produce an anodic reaction (the corrosion of aluminum). The process eventually leads to pits as the aluminum matrix surrounding the precipitates is consumed; this eliminates the

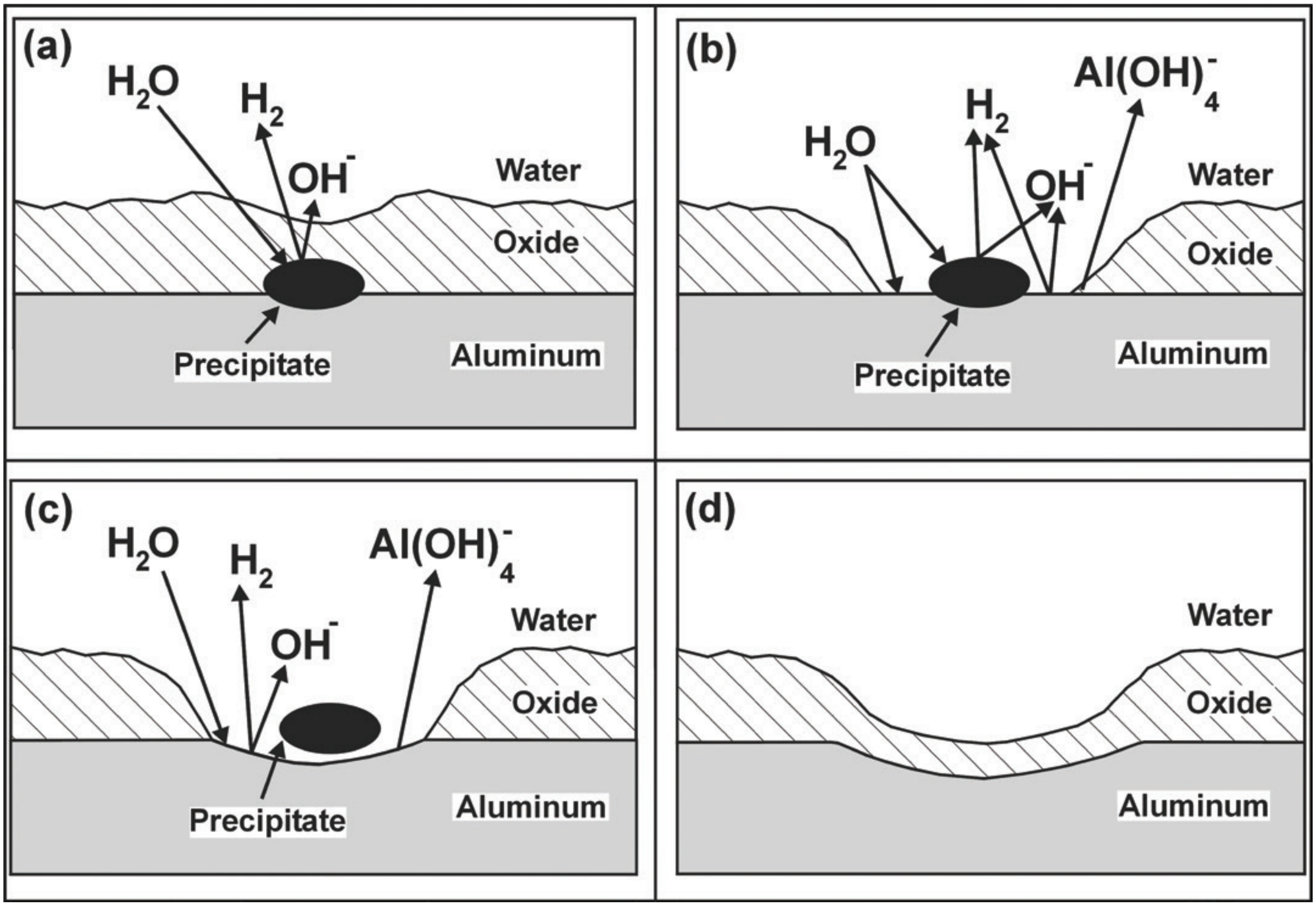

FIGURE 4. Schematic diagram of cathodic corrosion that can happen during cathodic polarization. (a) Water is reduced at precipitates (cathodic sites), generating hydrogen gas and increasing local pH. (b) Alkaline pH dissolves the oxide film around the precipitate and exposes aluminum metal. (c) Aluminum metal starts to corrode and the precipitate is released. (d) Oxide layer reforms, leaving a pit behind. Adapted from Degrigny (1993). © Government of Canada, Canadian Conservation Institute.

precipitates, and the oxide film reforms (Moon and Pyun, 1997). According to Vargel (2004), aluminum is safe from cathodic corrosion in seawater if the potential falls in the range −0.60 V to −0.90 V/SHE. According to Davis (1999), aluminum buried in soil should not be polarized to a potential of less than −0.90 V/SHE to avoid cathodic corrosion.

Alclad Products

In alclad products and aluminum-coated iron, the outer aluminum layer is anodic to the underlying metal. In alclads, the outer cladding layer is more negative by about 100 mV, as shown in Table 4 (Davis, 1999; Vargel, 2004). The outer layer acts as a sacrificial surface and protects the underlying layer against corrosion when the underlying layer is exposed to moisture at cut edges, rivet holes, or scratches (Zahner, 1995; Ghali, 2000). The process is similar to the way zinc galvanizing protects steel (Zahner, 1995; Kaufman, 2000; Kissell and Ferry, 2002; Vargel, 2004). As corrosion attacks the surface (slowly for relatively pure aluminum alloys), it progresses only to the cladding/core interface and then spreads laterally along the clad layer, rather than perforating the sheet (Hollingsworth et al., 1989; Zahner, 1995). Alclad products are used extensively where perforation cannot be tolerated (Hollingsworth et al., 1989). The exterior of aircraft, often exposed to saltwater environments, is usually fabricated from clad alloys (Davis, 1999). For example, Alclad 7075 combines the strength advantages of 7075 with the corrosion-resisting properties of relatively pure aluminum-clad surface (7072, see Table 10 in Appendix 1) (Davis, 1999). The life of the clad coating depends on the severity of exposure, the environment, and the thickness of the alclad surface material. When used outdoors in rural and light industrial areas, the luster of reflective alclad products can last more than 12 years; in coastal and heavy industrial areas, the luster will dull in about 4 to 6 years (Zahner, 1995).

STRUCTURAL CORROSION

Structural corrosion is the term used to define the aspects of corrosion when the overall physical integrity of the alloy has been weakened. It is often intergranular in nature and is associated with a heterogeneous distribution of alloying elements or intermetallic particles. The heterogeneous distribution can lead to galvanic cells on a microscopic scale if the aluminum matrix and the intermetallic particles have different corrosion potentials (Davis, 1999; Vargel, 2004). The galvanic cells can result in intergranular corrosion, exfoliation corrosion, or stress-corrosion cracking (Vargel, 2004). Structural corrosion affects high strength alloys in the 2xxx, 6xxx, 7xxx, 8xxx series, and the 5xxx series with Mg > 3.5% (Reboul and Baroux, 2011, Eswara Prasad et al., 2013). Industry applies special annealing heat treatments to sensitive alloys to reduce or eliminate the susceptibility to this type of corrosion (Vargel, 2004; Reboul and Baroux, 2011).

Intergranular Corrosion

A piece of metal is composed of metallic grains touching at grain boundaries. Intermetallic compounds can precipitate along the grain boundaries. For example, in 2xxx (Al-Cu) alloys, precipitates of Al_2Cu form along grain boundaries if the alloy is not quenched fast enough (Reboul and Baroux, 2011).The presence of precipitates can make the region near the grain boundaries more reactive than the bulk of the grains, causing this region to corrode preferentially. This is classified as intergranular or intercrystalline corrosion. It can result in the disintegration of an alloy as the grains fall out, even though there is no appreciable corrosion of the grains themselves (Davis, 1999).

Exfoliation Corrosion

Exfoliation, also called layer or lamellar corrosion, is an extreme form of structural corrosion that occurs mainly in copper-containing wrought aluminum alloys. It forms in alloys susceptible to intergranular corrosion (5xxx, 2xxx, 7xxx) and occurs predominantly in thin pieces with highly cold-worked, elongated grain structures such as thin rolled sheets or thin extruded pieces (Davis, 1999). These pieces have a highly directional microstructure and corrosion propagates along grain boundaries in planes parallel to the direction of rolling or extrusion (Vargel, 2004). The corrosion results in alternating layers of thin, relatively uncorroded metal and thicker corrosion layers (Davis, 1999). The expanding corrosion products cause the layers to delaminate and the metal to swell (Reboul and Baroux, 2011). In an extreme case, exfoliation corrosion caused a 1.3 mm thick sheet to swell to 25 mm (Davis, 1999). Severe exfoliation was found in extruded aluminum in the Dymaxion House, especially near points of attachment where the aluminum had been pierced (Trentelman et al., 2002). In mild cases, exfoliation corrosion takes the form of blisters that resemble volcanoes, with corrosion products in the center (Davis, 1999). The intensity of exfoliation increases in slightly acidic environments and develops most rapidly in marine exposures.

Stress-Corrosion Cracking

Stress-corrosion cracking refers to cracks that form in certain alloys when they are exposed simultaneously to mechanical stress and corrosive environments. The corrosion is intergranular, with corrosion propagating selectively along grain boundaries (Davis, 1999; Vargel, 2004). Cracks initiate in a direction perpendicular to the applied stress and propagate until failure (Reboul and Baroux, 2011). Stress corrosion cracking is sometimes considered as a special case of intergranular corrosion in which mechanical stress accelerates crack propagation along grain boundaries (Vargel, 2004). Alloys of high mechanical strength in the 2xxx and 7xxx series as well as 5xxx alloys with ≥7% Mg are susceptible to stress corrosion cracking (Vargel, 2004). It only occurs when the stress and corrosion are combined; either factor acting alone would not lead to cracking. The stress can be caused by machining, cold-working, welding, or non-uniform cooling after casting or residual stresses in high strength heat-treatable alloys (Davis, 1993). As an example, stress corrosion cracking caused an outdoor cast aluminum sculpture to break and fall after 65 years of being exposed to a marine industrial atmosphere (Martini et al., 2012). Stress-corrosion cracking is also an important consideration for aerospace aluminum alloys (Wanhill et al., 2011).

CORROSION ENVIRONMENTS

Indoors

The surface film on aluminum protects it in clean air as long as the relative humidity (RH) remains below about 70% (Graedel, 1989; Leygraf and Graedel, 2000). Above 70%, the surface film absorbs sufficient moisture to stimulate corrosion, and it gradually thickens. Indoor pollutants and dust particles contaminated with salts (chlorides or sulfates) all contribute to aluminum corrosion, causing the aluminum finish to dull (Graedel, 1989; Green and Thickett, 1993). Aluminum objects can be attacked by acidic organic gases (e.g., methanoic acid [formic acid]) that build up in an enclosed showcase or storage area (Green and Thickett, 1993). White, gray, or black stains can develop on aluminum if drops of water are left on it (Zahner, 1995; Vargel, 2004). Water staining can also occur when aluminum sheets are stacked and water condenses between layers, such as during storage or shipping.

Changes are most noticeable on highly reflective surfaces, which become less reflective as they corrode. For example, the surface of the 200-inch (5 m) mirror in the Hale telescope at the Palomar Observatory in California has a thin layer (100 nm thick) of aluminum applied to a polished Pyrex glass base by an evaporation technique (Strong, 1934; Destefani, 2008). The mirror surface degrades over time so every 18 to 24 months the aluminum is removed and reapplied.

Outdoors

In outdoor environments, aluminum usually corrodes more slowly than other common metals (see Table 5). This resistance to weathering, especially for alloys of the 1xxx, 3xxx, 5xxx and 6xxx series without copper, is attributed to the natural oxide film and the ability of certain elements, such as magnesium, to strengthen the protectiveness of the film (Vargel, 2004). Copper, on the other hand, weakens the protectiveness of the film.

As aluminum weathers outdoors, a gray patina develops as the natural oxide thickens and atmospheric pollution becomes incorporated into the porous film. The surface dulls, becomes rough, and slowly turns various shades of gray (Zahner, 1995; Vargel, 2004). If the atmosphere contains soot, this will be incorporated into the corrosion products and the patina will be darker (Mattsson, 1982). Exterior aluminum on buildings that are exposed to rain usually age uniformly and develop an even patina, but any sections that are sheltered generally develop an uneven color (Hollingsworth et al., 1989). This unevenness can be prevented by regularly washing these sections with clean water. The change in surface appearance is faster in more polluted conditions, or in sheltered areas where rain is unable to clean the surface and dirt accumulates (Vargel, 2004). The oldest known example of aluminum weathering outdoors is the dome of the San Gioacchino church in Rome, erected in 1898 and now covered with a yellowish gray patina (Vargel, 2004).

Atmospheric corrosion occurs when the aluminum surface is covered with a relatively thin film of well-aerated water (from high humidity, condensation, or rain) containing atmospheric pollutants (Vargel, 2004). Condensation is favored on a rough surface compared to a smooth, polished one. The natural oxide film reacts with moisture and first forms a thin layer of boehmite, which is subsequently covered with aluminum hydroxides (e.g., bayerite or gibbsite) (Graedel, 1989). MacLeod (1983) detected gibbsite on an aluminum float in a marine atmosphere, and Martini et al. (2012) found it on an aluminum sculpture. The corrosion rate of aluminum is increased in the presence of

TABLE 5. Corrosion rates for common metals outdoors (Cook and Smith, 1982; Mattsson, 1982; Mattsson and Holm, 1982).

Metal	**Rural (μm yr^{-1})**	**Urban (μm yr^{-1})**	**Industrial (μm yr^{-1})**	**Marine (μm yr^{-1})**
Aluminum[a]	0 – 0.1	~1	-	0.4 – 0.6
Copper	~0.5	1 – 2	2.5	~1
Iron[b]	4 – 65	23 – 71	26 – 175	26 – 104
Lead	0.1 – 1.4	1 – 2	0.4 – 2	0.5 – 2
Zinc	0.2 – 3	2 – 16	2 – 16	0.5 – 8

[a] alloy AlMn 1.2 (similar to alloy 3003)

[b] unalloyed carbon steel

pollutants such as sulfur dioxide (SO_2) and soluble salts, such as those containing chloride ions (e.g., marine locations) and sulfate ions (e.g., urban locations) (Graedel, 1989; Blücher et al., 2005). Salts contribute to the formation of an electrolyte on the surface, especially if they are hygroscopic. For example, aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, chloraluminite) deliquesces in the range of 30 to 40% RH; sodium chloride (NaCl, halite) deliquesces at 75% RH; and sodium sulfate (Na_2SO_4, thenardite) picks up waters of hydration at 81% RH to form sodium sulfate hydrate ($Na_2SO_4 \cdot 10H_2O$, mirabilite), which deliquesces at 93% RH (Richardson and Malthus, 1955; Waller, 1992; Blücher et al., 2006). These soluble salts, especially the highly soluble ones containing aluminum and chloride ions, are readily removed by rain (Graedel, 1989; Leygraf and Graedel, 2000).

Chloride and sulfate anions become incorporated into the corrosion layer (Mattsson, 1982). For example, amorphous aluminum sulfate hydrate ($Al_x(SO_4)_y \cdot (H_2O)_z$) is the most abundant corrosion product on aluminum exposed to marine and industrial atmospheres (Graedel, 1989; Leygraf and Graedel, 2000). Crystalline salts are sometimes identified, such as aluminite (an aluminum hydroxide sulfate, $Al_2(OH)_4SO_4 \cdot 7H_2O$) or cadwaladerite (an aluminum chloride hydroxide, $AlCl(OH)_2 \cdot 4H_2O$) (Graedel, 1989). Other corrosion products identified under controlled laboratory conditions (where the corrosion products were not removed by rinsing) include an hydrated aluminum chloride hydroxide ($Al_2Cl(OH)_5 \cdot 2H_2O$), a sodium aluminum carbonate hydroxide ($NaAl(OH)_2CO_3$, dawsonite) and a sodium aluminum sulfate ($NaAl(SO_4)_2 \cdot 11H_2O$, mendozite) (Blücher et al., 2006).

Atmospheric corrosion generally develops in polluted humid environments with a pH close to neutral, leading to pitting corrosion (Vargel, 2004). For many aluminum alloys, only small, shallow pits develop. These are barely visible and covered with crusts of aluminum corrosion products (Mattsson, 1982). Pits grow fastest during the first few years of exposure; their growth eventually slows and the pit depth approaches a nearly constant value (Mattsson, 1982; Vargel, 2004). Reboul and Baroux (2011) note a relatively fast pit penetration of 150 to 200 μm for the first year of exposure (alloys 1050, 3003, 5052) in a marine environment followed by slower pit penetration of 350 μm after 5 years and 600 μm after 20 years. Mattsson (1982) reports the following maximum pit depths after twenty years of exposure for the aluminum alloy AlMn 1.2 (similar to the alloy 3003): 10 to 55 μm (rural), 100 to 190 μm (urban), and 85 to 260 μm (marine).

Freshwater

The corrosion resistance of aluminum in freshwater depends on the stability of its protective film. The existing natural film reacts with water for a few days until an equilibrium thickness of the protective film is reached (Davis, 1999). After that, the amount of metal dissolved by the water becomes negligible. Berzins et al. (1977a; 1977b) detected a thin layer of boehmite on top of the air-formed film after about 10 hours immersion in water; at longer times, bayerite formed the top layer. In general, the aluminum hydroxides bayerite and gibbsite are favored at room temperature. These may be amorphous or crystalline.

Most freshwaters have a pH range close to neutral, where aluminum is sensitive to pitting corrosion in the presence of chloride ions. The density and depth of pitting tends to increase with increasing chloride ion concentration (Vargel, 2004). In addition, aluminum is more likely to undergo pitting in stagnant water than in moving (or frequently replaced) water. Water movement helps to remove corrosion products and dilutes local excesses of H^+ and OH^- ions; furthermore, moving water tends to be aerated, and the oxygen repairs the protective layer. Pits formed in stagnant water can have large diameters (1–5 mm). They can become covered with voluminous white pustules, and sometimes with a deposit of hard, light yellow scale made up of carbonates (Vargel, 2004). When the deposit is removed, the pit depth may exceed 1 or 2 mm. This type of corrosion is often found in aluminum water tanks whose water is only rarely changed.

Seawater

Severe corrosion was encountered on the early aluminum marine vessels, such as on the Alfred Nobel's yacht *Mignon*, purchased in 1902 (Vargel, 2004). Since the 1950s, however, aluminum alloys have been developed for marine applications, and many modern aluminum alloys are fairly resistant to corrosion in seawater. Seawater is slightly alkaline (at pH 8.2), giving aluminum its usual protective film (MacLeod and Kelly, 2001), but the high concentration (0.57 M) of chloride ions produces pitting corrosion (MacLeod, 1983). As in freshwater, pitting tends to slow down over time and is deeper in stagnant seawater than in flowing seawater (Vargel, 2004). The maximum pitting depth rarely exceeds 1.5 mm after 10 years of immersion in seawater for series alloys 1xxx, 3xxx, 5xxx, and 6xxx. The 5xxx series alloys gives the best compromise between mechanical strength and corrosion resistance in this aggressive environment (Reboul and Baroux, 2011) and is the most widely used (Davis, 1999; Vargel, 2004). Alloys of the 2xxx and 7xxx series (which contain copper) are much less resistant to corrosion in seawater and are either used as alclad products or given a protective coating (Davis, 1999).

Because aluminum salts and oxides are not toxic to marine organisms, these compounds offer no antifouling protection (Davis, 1999). Biological growth quickly covers aluminum immersed in seawater, if local conditions allow their growth. When a barnacle attaches, local acidity develops beneath it and the aluminum surface can be superficially etched (Vargel, 2004).

Soil

The corrosion resistance of aluminum in soil is difficult to characterize because of the wide variation of properties such as water content and pH, soil structure and resistivity, and concentration of various species (e.g., dissolved oxygen, inorganic salts, organic acids) (Davis, 1999; Vargel, 2004). In general, aluminum buried in soil can exhibit pitting corrosion due to aggressive anions and lower availability of passivating oxygen. Industry protects buried aluminum with various measures, such as paint or bituminous coatings, polymer sheathing, or cathodic protection (Davis, 1999; Vargel, 2004).

SURFACE PROTECTION

Aluminum alloys are often used without protection other than their naturally formed oxide. When additional protection is needed, protective coatings are used (Davis, 1993; Sheasby and Pinner, 2001; Vargel, 2004). These may involve the intentional formation of a thicker oxide film, either by anodizing or by chemical conversion. The chemical conversion coatings may be followed by a coat of paint to protect the aluminum further.

Anodizing

Although aluminum oxide is hard, the natural oxide layer on aluminum and its alloys is too thin (about 5 nm or 0.005 µm) to protect the underlying aluminum from scratching. This layer can be thickened by the electrochemical process of anodizing, making the surface more resistant to abrasion and corrosion. During anodizing, the aluminum is made the anode in an electrochemical cell, so that the metal is forced to corrode, and an amorphous Al_2O_3 layer grows (Takahashi, 2003). The overall reaction is given below (Equation 16) (Alwitt, 2002):

$$2\ \mathrm{Al}\ (s) + 3\ \mathrm{H_2O} \rightarrow \mathrm{Al_2O_3}\ (s) + 3\ \mathrm{H_2}\ (g) \qquad (16)$$

Hydrogen gas is produced at the cathode and an adherent aluminum oxide film grows on the surface of the aluminum alloy being anodized.

There are many different procedures and electrolytes for anodizing (Sheasby and Pinner, 2001; Takahashi, 2003; Vargel, 2004), several of which are listed in Table 6. In neutral electrolytes, the oxide layer forms a thin, compact, barrier-type film. In acidic electrolytes, the oxide coating is thicker and contains a high density of microscopic pores, giving rise to a porous-type film suitable for coloring; the procedure for producing these films is sometimes referred to as soft anodizing (Ghali, 2010). An extremely hard and durable porous film can be grown in sulfuric acid at low temperatures, a process called hard anodizing (Ghali, 2010). Surface preparation is important because surface imperfections (scratches, streaks) are not removed but instead accentuated by the anodizing process (Zahner, 1995). In addition, if the acidic anodizing solution is not completely rinsed out of aluminum assemblies after anodizing, streaking may develop later.

Porous films grow in acidic conditions because of a competition between oxide dissolution and oxide growth. Most anodizing conditions produce porous films that are disordered, with a distribution of cell size and pore diameter in the pore structure. The cell diameter is in the range 50 to 300 nm and the pore diameter is typically ⅓ to ½ of the cell diameter (Alwitt, 2002). In hard anodizing, the aluminum oxide structure contains small diameter pores (Alwitt, 2002). High-purity aluminum (e.g., alloy 1100) and alloys containing up to 2% magnesium produce the highest luster and most transparent (clear) anodized films (Frank et al., 2012).

Under certain carefully controlled conditions, a highly ordered oxide layer can be formed. An idealized structure is shown in Figure 5. This ordered layer has a honeycomb structure, with columns of parallel hexagonal cells. Each cell contains a central cylindrical pore resulting in an array of straight channels perpendicular to the metal surface (Asoh et al., 2001). The pores in these structures have diameters of 25 to 250 nm (Crouse et al., 2000). The ratio of the film thickness to pore diameter (the aspect ratio) can be greater than 500 (Asoh et al., 2001). The bottom of a porous layer is a barrier layer (about 0.2 µm or 200 nm thick) that separates the pores from the underlying aluminum (Alwitt, 2002; Takahashi, 2003).

After the film is grown, the film surface can be sealed by immersion in boiling water for about 30 minutes (Ghali, 2010). Sealing closes the pores of the oxide film. In boiling water, the oxide on the surface and within the pores reacts to fill and cover the pores with either boehmite or pseudo-boehmite (Holroyd, 2001; Takahashi, 2003).

TABLE 6. Some types of anodizing (Takahashi, 2003; Vargel, 2004).

Film type	Electrolyte	Thickness	Uses
Barrier	neutral solutions	1.3 – 1.6 µm	high electrical resistance products (e.g., printed circuit boards)
Porous	sulfuric acid	2 – 4 µm	highly polished finishes (e.g., reflective surfaces)
Porous	sulfuric acid	5 – 8 µm	consumer products (e.g., Apple iPods)
Porous	sulfuric acid	15 – 25 µm	architectural elements (e.g., 6063 extrusions)
Porous	chromic acid	5 µm	corrosion resistant aeronautical alloys (e.g., 2xxx, 7xxx)
Porous	sulfuric acid (cold)	50 – 100 µm	wear resistance objects (e.g., screws, gears)

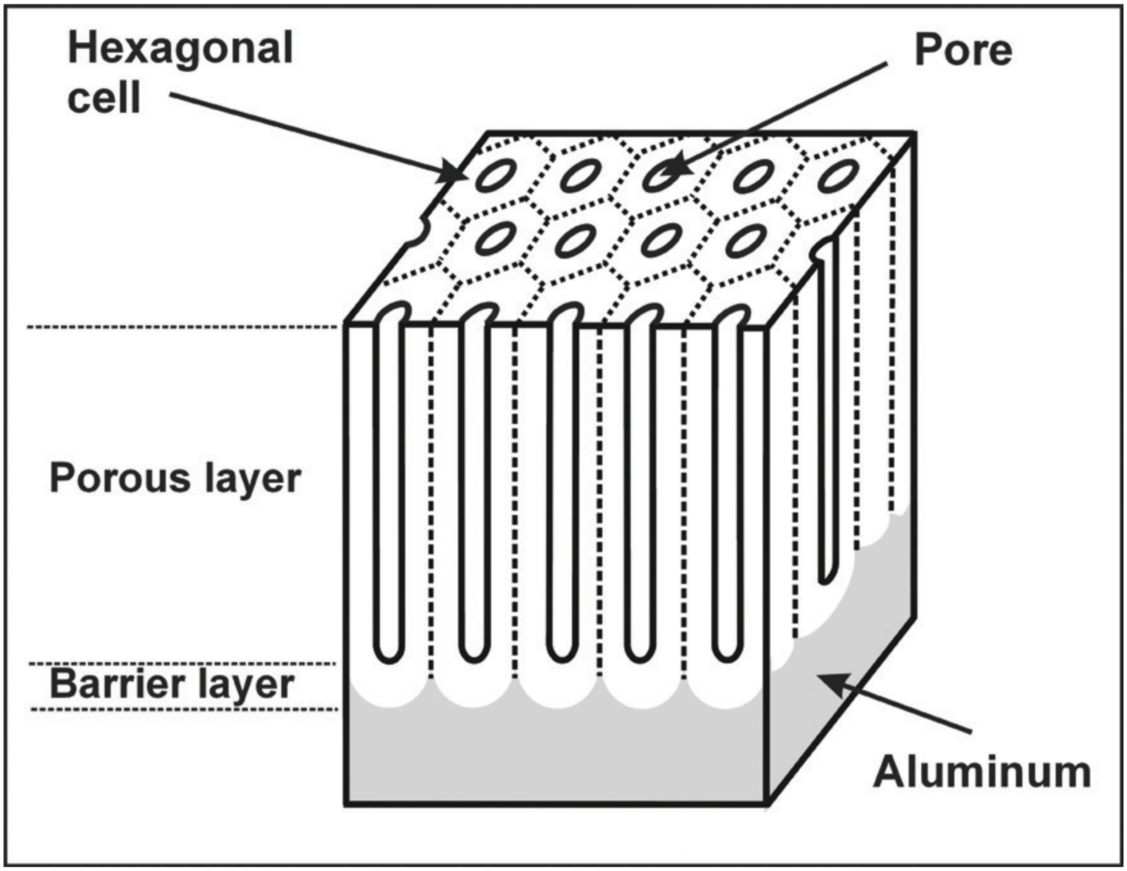

FIGURE 5. Idealized structure of an ordered aluminum oxide (alumina, Al_2O_3) film on anodized aluminum. Adapted from Asoh et al. (2001). © Government of Canada, Canadian Conservation Institute.

Dyes and other colored compounds can be incorporated into the open, porous structure of freshly formed aluminum oxide and then trapped inside the pores by the sealing process. There are three processes for coloring films: integral coloring, dyeing, and electrolytic coloring (Zahner, 1995; Takahashi, 2003; Ghali, 2010). In integral coloring, an older method for coloring, the color (grays, bronze, black) is achieved by chemical reactions between the electrolyte and the alloying constituents in the aluminum. Dyes or pigments can be used to color anodized films with flashy colors (e.g., gold, yellow, blue, green) because the dyes are absorbed on the pore walls. The inorganic pigments tend to be more lightfast than the dyes. Electrolytic coloring (e.g., blue, bronze, black), where metal (e.g., cobalt, copper, nickel, tin) is deposited at the bottom of pores, has good light fastness and is often used for outdoor architectural applications (Takahashi, 2003; Vargel, 2004). Thin, porous anodic films also provide an excellent base for paint coatings (Sanders, 2012).

Anodizing was first patented in 1911 (Vargel, 2004) and then used commercially to produce industrial finishes in the 1920s (Kelley, 1995; Zahner, 1995). Since then, manufacturers have produced colored anodized aluminum objects in a rainbow of colors with a distinct metallic glow or luster. Examples include Heller Hostess-ware Colorama tumblers, Fanta Colored Aluminum Ware whistling kettles, and Everlast Metal Products ice buckets (Nichols, 2000). Today, artists are experimenting with dyes to create anodized aluminum paintings. In industry, anodizing processes have become standardized to the point that process designations are being assigned (AA, 2003; AAC, 2016).

Anodizing can reduce or prevent pitting corrosion on aluminum if the thickness is sufficient for a given environment (Vargel, 2004). Anodizing also helps retain the shiny appearance of aluminum when used outdoors. An oxide thickness of 20 μm will generally preserve the original aluminum appearance outdoors for decades (Mattsson, 1982); this is the minimum thickness recommended for aluminum exposed to industrial and marine atmospheres (Vargel, 2004). Alloys in the 5xxx and 6xxx series form anodic coatings that resist atmospheric corrosion best while alloys in the 2xxx series perform the worst (Vargel, 2004).

The surface appearance of anodized aluminum can change over time. After a short time outdoors (months to a few years), outdoor architectural pieces can develop iridescence, chalking and powdering (possibly from poor sealing) and after longer times (many years), pitting corrosion may develop and colors may fade (especially colors from dyes) (Vargel, 2004). Anodized surfaces exposed to weathering and dust must be cleaned periodically using appropriate neutral detergents to preserve their appearance and to avoid pitting corrosion, especially surfaces that are insufficiently cleaned by rain (Zahner, 1995; Vargel, 2004). The frequency of cleaning depends on local conditions, with more frequent cleaning required in urban and coastal environments. Zahner (1995) recommends starting at the top and working down, and washing with water and a mild detergent to remove most surface dirt, and using a sponge or soft brush to remove stubborn particles. He also recommends removing excess water before allowing the surface to air dry. Oil or adhesives can be removed with a suitable organic solvent or use of an appropriate detergent in the washing mixture.

Chemical Conversion Coatings

Chemical conversion coatings are adherent layers of low-solubility compounds produced by reacting chemicals with aluminum (Davis, 1993). These coatings provide improved adhesion for paints, lacquers and adhesives (Vargel, 2004). The first chemical conversion coating for aluminum was an alkaline type developed by Bauer and Vogel in 1915; later alkaline coatings include modified Bauer Vogel, Erftwek, Alrok, and Pylumin (Adams and Hallam, 1993; Davis, 1993; Sheasby and Pinner, 2001; Vargel, 2004). The color varies from light to dark gray, sometimes a greenish-gray (Davis, 1993). Acid-based processes were not developed until the 1940s. Some modern commercially available conversion coatings include Alocrom, Alodine, Bonderite, and Iridite (Adams and Hallam, 1993; Davis, 1993; Sheasby and Pinner, 2001). Solutions used in these processes contain a mixture of phosphates and chromates and the color varies from light bluish-green to olive green, to yellow and even dark brown, depending on the thickness of the layer (Davis, 1993; Vargel, 2004). In the late 1980s, replacement conversion coatings began to be considered because of the toxicity of hexavalent chromium. Solutions based on various other compounds (e.g., cerium or lithium salts, permanganate, titanium or zirconium oxides, molybdates) are currently being evaluated as replacements for chromates (Davis, 1999; Vargel, 2004). Conservators have to face the question of whether it is ethically sound to replace a chromate conversion coating with a new system of the same composition.

Organic Coatings

Aluminum is painted for both decoration and protection. For example, an outdoor painted aluminum sculpture by Lichtenstein was coated with an epoxy primer and topcoated with a polyurethane (Considine et al., 2010:148–156). To get an organic coating to adhere to aluminum, special surface treatments are needed to overcome the non-stick nature of the oxide coating (Vargel, 2004). Preparation usually involves several steps: degreasing, eliminating existing oxides, forming a base layer (such as by anodizing or applying a chemical conversion coating), and applying a primer (Davis, 1993; Sheasby and Pinner, 2001). Most organic coatings, such as paints, lacquers, and varnishes, can be applied on aluminum and its alloys using either traditional brushing or spray painting techniques or electrostatic powder methods (Vargel, 2004).

When aluminum has been covered with a thin organic coating (typically 0.1 mm thick), a special type of crevice corrosion, called filiform corrosion, can occur (Ghali, 2010). This form of corrosion was first detected on architectural aluminum in the early 1980s (Steele, 1994). The corrosion starts at coating defects (called holidays), such as scratches and weak points, and proceeds underneath the film. It grows in relatively straight lines that have a thread-like or filamentary appearance. The filaments are fine tunnels or channels containing white, gelatinous corrosion products that cause the surface coating to bulge and crack (Ghali, 2010). The underlying metal only suffers superficial attack (Delplancke et al., 2001). Defects in the organic film permits air and water to penetrate through the coating and reach the underlying aluminum. Aluminum corrosion and filament growth occurs at the tip of the filament in a small area called the active head, which contains a solution with low pH (about pH 2.5) (Steele, 1994; Delplancke et al., 2001). As the head moves forward, the region behind it becomes filled with dry corrosion products (aluminum oxide and amorphous aluminum hydroxide) in a channel called the inert tail (Delplancke et al., 2001). Filiform corrosion can develop under all types of paints and does not depend on the method of application (Steele, 1994). It is worse on rougher surfaces and tends to develop on aluminum that has received little or no surface preparation, or on a metal whose surface has been contaminated before coating (Vargel, 2004). Aluminum is more susceptible to filiform corrosion at high relative humidity (70–95%) (Delplancke et al., 2001). Filiform attack is particularly severe in warm coastal and tropical regions or in heavily polluted industrial areas (Ghali, 2010).

IMPLICATIONS FOR CONSERVATION

Cleaning

To keep a good appearance on aluminum, maintenance is necessary. The goal of cleaning is to eliminate inorganic and organic contamination without damaging the metal surface. Indoors, this might be as simple as periodic dusting or vacuuming. Outdoors, it might involve regular washing with aqueous solutions containing suitable surfactants to remove grease and grime. Cleaning may require more invasive techniques (such as steam cleaning, laser cleaning, waterjetting, dry-ice blasting or sponge blasting) to remove built-up dirt, graffiti, or old degraded finishes. Care must be taken when cleaning aluminum with these techniques because of its special properties such as the amphoteric nature of the oxide film, or the metal's softness.

With aqueous cleaning, the pH of the solution is important. It should be kept close to neutral to stay within the passive region in the Pourbaix diagram ($4 < pH < 8.5$). Acid cleaners (hydrochloric acid), and alkaline cleaners (sodium hydroxide, potassium hydroxide, sodium carbonate) should be avoided. Any cleaning solutions that contain chloride ions (because of the danger of pitting) should also be avoided. With steam cleaning, the high temperature may convert surface oxides from bayerite and gibbsite to boehmite, as happens when sealing the pores in boiling water as the final step of anodizing. If a porous aluminum oxide surface has accumulated dirt, then steam cleaning may seal in the dirt. Waterjetting has been used to remove old coatings, corrosion and soluble salts (Sembrat et al., 2005). Careful control of the pressure is required to avoid distorting the aluminum.

Organic solvents should be safe on aluminum (except possibly for chlorinated solvents) and are often used to remove residual lubricants, oil, grease, and other petroleum products (Davis, 1999). Aluminum manufacturers clean off visible lubricants but incomplete cleaning may leave a thin film (Nagy, 2004). During processing, fatty acid additives in lubricants can react to form aluminum soaps which, if not removed, will interfere with paint adhesion (Dunlop and Benmalek, 1997). Dry ice blasting is effective at removing spray paint from polished aluminum (van der Molen et al., 2010). Laser cleaning has been used to clean the 1929 cast aluminum Liverpool replica of *Eros* (Cooper, 1998:74). Although this technique worked well, care was needed to control the conditions to avoid melting the aluminum.

Aqueous Treatment to Remove Chloride Ions

When aluminum is removed from seawater and allowed to dry with no rinsing or only a quick rinse, it will continue to corrode even at low RH values (Adams and Hallam, 1993). The surface is covered with a complex salt mixture and the pits are filled with an acidic, chloride-rich solution. Chloride ions are “held” inside corroding pits to maintain charge balance and a simple rinse will not remove them. If the pit dries out, the salt in the pit is hygroscopic and will deliquesce when the humidity rises again and corrosion will continue. MacLeod and Kelly (2001) observed fresh outbreaks of frothy corrosion products on top of pits after the relative humidity increased on an aluminum alloy that had been contaminated with seawater. They found that washing the surface (scrubbing, not immersion) with deionized water did not stabilize it. Hallam and Bailey (1991) tested chloride-contaminated aluminum laboratory samples at high humidity and all corroded and gained weight during the two weeks of the experiment.

Immersion of marine aluminum in distilled water only slowly removes chloride ions. For example, when chloride ions are adsorbed on a corroding aluminum surface from sodium chloride solutions (pH 6.3–7.5), only about one third of the chlorides are removed after the aluminum is soaked for three days in distilled water (Berzins et al., 1977b). Although it is known that pits stop growing in the absence of dissolved oxygen (Vargel, 2004; Lyle et al., 2005; Ghali, 2010), there appear to be no systematic studies of chloride ion removal of archaeological marine aluminum using deaerated water.

MacLeod (1983) developed a treatment to remove chloride ions and plated metallic copper from a large 3.75 meter aluminum sea-plane float. The treatment was based on soaking the object in a 3100 liter tank for over a year in an aerated, pH 9.6 buffer solution of ammonia (0.25 M NH_3) and ammonium sulfate (0.125 M $(NH_4)_2SO_4$). Ammonia forms soluble complexes with copper ions (Smith and Martell, 2004). In addition to dissolving copper-based species, the treatment at pH 9.6 helped to neutralize acidity in pits and to allow chloride ions to diffuse out. During treatment, oxygen was thought to be important, allowing copper to corrode and form copper ions in solution.

Corrosion Inhibition during Treatment

Some corrosion inhibitors added to chloride-containing solutions can reduce or stop pitting corrosion of aluminum. The anionic surfactant sodium dodecyl sulfate (sodium lauryl sulfate) can adsorb onto an aluminum oxide surface, displace adsorbed chloride ions, and act as a corrosion inhibitor (Monticelli et al., 1991; Balbo et al., 2013). Mardikian et al. (2015) used Flash-Corr, an anionic surfactant and multi-metal corrosion inhibitor, in the treatment of an aluminum-containing rocket engine recovered from the ocean. Sodium silicate inhibitors, such as sodium metasilicate (Na_2SiO_3), can prevent solutions with alkaline pH from attacking aluminum alloys (Hallam et al., 1997; Vargel, 2004; Ghali, 2010). MacLeod and Kelly (2001) used a pH 9.0 sodium metasilicate solution to extract chloride ions from the interior of a contaminated aluminum yacht. Degrigny (1995) and Mardikian et al. (2015) used sodium metasilicate solutions to protect aluminum during the cathodic reduction treatments of iron-aluminum composites. Care must be taken when using corrosion inhibitors because their effectiveness can depend on the environment and the alloy composition (Ghali, 2010).

Cathodic Polarization to Remove Chlorides

Cathodic polarization has been recommended for removing chloride ions from marine aluminum (Degrigny, 1993). In this treatment, the aluminum is attached to a power supply so that it becomes the cathode in the electrochemical circuit. Its potential is shifted to values more negative than the corrosion potentials; this shift is called cathodic polarization. The polarization shifts the balance of reactions on the corroding surface, reducing the rate of anodic reactions (the corrosion of aluminum) and increasing the rate of cathodic reactions (the reduction of dissolved oxygen, Equation 6, or the reduction of hydrogen ions, Equation 7). If the corrosion can be slowed enough, chloride ions will no longer be held within the pits, and so can diffuse out of the pits and away from the surface (Vargel, 2004). In addition, the polarization makes the surface film more negatively charged, promoting desorption of chloride ions.

The polarization potential is a critical parameter—if it is too high, the treatment will not be effective, but if it is too low, cathodic corrosion can occur (Degrigny, 1995), and this must be avoided. In the reported treatments, the aluminum in aluminum-iron composites is polarized in the range of −0.60 to −0.85 V/SHE in a buffered sodium citrate solution (0.05 M citrate, pH 5.4) (Adams, 1992; Degrigny, 1995). When Bailey (2004) treated an aluminum aircraft piece using cathodic reduction in a similar citrate solution, all ferrous corrosion and white and blue-green stained aluminum corrosion products had disappeared after one month.

Other aspects of the citrate treatment can also help to avoid cathodic corrosion. The buffered sodium citrate solution helps to maintain a constant pH by reacting with hydroxide ions produced by the cathodic reduction of water (Equation 7). Stirring avoids zones of high alkalinity and removes hydrogen bubbles, which can interfere with the mixing of the solution and allow the pH to increase locally underneath the bubbles. Despite these precautions, cathodic corrosion may still occur through another mechanism—the negative potential can draw hydrogen ions into the protective film, weakening or thinning the film so that the aluminum underneath can corrode (Nişancioğlu and Holtan, 1979).

To improve outward diffusion of chloride ions from the pits, surface corrosion products should be removed to open the pits by treating corroded aluminum objects in a buffered citrate solution at pH 5.4 prior to polarization (Degrigny, 1993; Degrigny, 1995; Adams, 1992). Citrate anions form soluble complexes with metal ions (e.g., aluminum, copper, iron, magnesium, calcium) (Smith and Martell, 2004), and this helps to dissolve the surface corrosion products. In particular, this also removes dangerous copper(II) ions, which could plate out of solution onto the aluminum during the polarization step. In principle, the citrate could also dissolve the protective aluminum oxide film, but no problems were reported by Degrigny (1993, 1995) or Adams (1992) in their treatments, suggesting a kinetic stability of the oxide film.

CONCLUSIONS

If the composition of the aluminum alloy objects is known to the conservator, the extensive designation system for wrought and cast aluminum alloys provides material and corrosion data that is needed to assist in the development of a treatment program. The alloy number also provides details of the thermal history. Knowing the alloy number can save on expensive analysis, and give an idea of properties such as corrosion resistance, strength, or hardness.

Aluminum is a reactive metal, yet it resists corrosion because of its strongly protective oxide, and so the properties of the oxide are crucial to conservation. The amphoteric nature of the protective oxide means that both strong acids and strong bases must be avoided in cleaning. The oxide can be attacked even at neutral pH by chloride ions, leading to pitting corrosion. It is important to remove chloride ions, and some approaches have been developed based on ammonia or cathodic polarization, but more research is needed.

If the surface of the oxide is hydrated it can become porous and trap dirt, so that the color of the dark patina on aluminum may be mostly just dirt. Thick oxide can be grown deliberately on aluminum by anodizing—compact oxides for protection, or thicker porous oxides in which the pores can be filled with dyes or other colored compounds and then sealed. A wide variety of colors and finishes are possible, but scratches in the anodizing are difficult to repair. Other coatings are also used to protect the aluminum surface, and can lead to other problems such as filiform corrosion.

Indoors most problems with aluminum are associated with dirt or high relative humidity. Outdoors there are further problems from pollution, salt, and pooling water. In freshwater, aluminum is reasonably protected by its oxide, provided chlorides do not accumulate and cause pitting. Even in seawater, many modern aluminum alloys are reasonably resistant to corrosion, but the chlorides in seawater can lead to pitting, especially in stagnant water or under deposits. Since marine life is not poisoned by aluminum, it can easily become covered with biological growth. Buried aluminum suffers from pitting corrosion due to the presence of aggressive anions and a lack of oxygen to repassivate defects in the oxide film.

Although in widespread use today, aluminum has only been available as a metal for about 200 years, and so it is less commonly found in museums and other cultural heritage applications than other metals. For most of the nineteenth century it was rare and considered a precious metal, but once it could be mass produced it rapidly became an industrial commodity. Aside from a few artifacts from the early years, most aluminum objects a conservator will encounter will be industrial artifacts, household objects, or sculpture. Conservators will be treating aluminum more and more in the coming years. More research would be welcomed in cleaning aluminum, removing chlorides, and protecting aluminum objects with reversible finishes.

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APPENDIX 1: ALUMINUM ALLOY DESIGNATIONS

The aluminum industry engineers the properties of aluminum alloys through the alloy composition and fabrication process (Davis, 1999). It then assigns the alloy designation (and frequently a temper designation) to each alloy. This appendix summarizes these designations, and gives references that can be consulted for associated properties. Many properties depend on the metallurgical structure, which is controlled both by composition and processing (Lyle et al., 2005; Sanders, 2012). Most commercial aluminum alloys contain two or more alloying elements (elements in addition to aluminum), chosen to produce greater strength and fatigue and fracture resistance, improved casting characteristics, and increased corrosion resistance (Sanders, 2012; Eswara Prasad et al., 2014). For example, copper, magnesium, manganese, silicon, and zinc increase strength (Lyle et al., 2005), and magnesium and silicon also increase corrosion resistance (Kaufman, 2002). Alloying usually results in a lower melting point. Further information on the mechanical properties, key characteristics, and major applications of aluminum alloys can be found in Kaufman (2000), Kaufman (2002), Kissell and Ferry (2002), Lyle et al. (2005), Sanders (2012), and Eswara Prasad et al. (2014) as well as online at the web sites for aluminum associations and institutes (Table 7).

Wrought Aluminum Alloys

Table 8 lists the nine series for wrought aluminum alloys in the Aluminum Association's designation system and the main alloying elements (Kaufman, 2002). The series in Table 8 are sometimes referred to as groups, families or classes, such as the 1xxx class of alloys. (At this time the 9xxx series is unassigned which allows for future metallurgical developments.) The first digit of the 4-digit designation is assigned according to the major alloying elements and ranges from one to nine. The remaining digits are indicated by the x's in Table 8 and range from zero to nine. The second digit defines variations in the original alloy (zero for original composition, one for first variations, etc). In the 1xxx series, the last two digits specify the minimum aluminum percentage above 99.00% (e.g., alloy 1060 contains ≥ 99.60% Al) (Lyle et al., 2005). In the 2xxx through 9xxx series, the last two digits are assigned to alloys as a label but otherwise have no composition significance.

The 1xxx, 3xxx, and 6xxx series alloys are sometimes referred to as "soft", while the 2xxx, 5xxx, and 7xxx series alloys are called "hard" (Kissell and Ferry, 2002). This description refers to the ease of extruding the alloys: hard alloys are more difficult to extrude, requiring higher-capacity presses, and are therefore more expensive. The more corrosion resistant series are 1xxx, 3xxx, 5xxx, and 6xxx (Kaufman, 2002) and the latest third generation aluminum-lithium (Al-Li) alloys (Eswara Prasad et al., 2014). Alloy extrusions from the 5xxx series are generally only used in marine applications where their corrosion resistance justifies their cost (Kissell and Ferry, 2002). The 2xxx and 7xxx alloys are generally strong, but they have serious drawbacks, such as reduced corrosion resistance (except the latest Al-Li alloys) and poor conventional weldability. A few examples of uses of aluminum alloys (with the alloy number in brackets) are aluminum foil (1175), electrical wire (1350), aircraft and truck bodies (2024), cooking utensils and sheet metal work (3003), roofing and siding (3105), beverage cans (3004 for the body, 5182 for the ends), automotive body (5754), curtain walls (6063) and high-strength aircraft parts (numerous 2xxx and 7xxx alloys) (Kaufman, 2002; Eswara Prasad et al., 2014). Zahner (1995) provides information about common wrought aluminum alloys used in architectural applications.

Around the world, different prefixes are used before the 4-digit number designation, depending on the country and association. The prefix AA refers to Aluminum Association. The European Aluminium Association now uses the prefix "EN AW" for wrought aluminum alloys: EN refers to the Euronorm designation (i.e., European standard), A to aluminum, and W to wrought. In North America, the Unified Numbering System (UNS) uses the prefix A9. For example, alloy 7075 has the designations AA 7075, UNS A97075, and EN AW-7075. The UNS publication (SAE–ASTM, 2012) lists the composition of registered wrought aluminum alloys as well as the composition of inactive alloys. This publication also has extensive lists of cross-referenced specifications to other designation systems such as the American Society for Testing and Materials (ASTM). Old wrought alloy designations used by the AA before 1954 are available (Kaufman, 2000; Kissell and Ferry, 2002). Older designations used by other countries (for wrought and cast) have been compiled by Lyle et al. (2005) and by Cayless (1990), and more extensive lists can be found in Kehler (1980).

TABLE 7. Aluminum associations and institutes and their web sites.

Institute or Association	Web site [accessed 20 Sept 2016]
International Aluminium Institute	www.world-aluminium.org
The Aluminum Association	www.aluminum.org
European Aluminium Association	www.european-aluminium.eu
Aluminium Association of Canada	www.aluminium.ca
Institute for the History of Aluminium	www.histalu.org/english
Aluminum Anodizers Council	www.anodizing.org

TABLE 8. Main alloying elements in the wrought aluminum alloy designation system developed by the Aluminum Association (Kaufman, 2002; Eswara Prasad et al., 2014).

Wrought alloy series	Main alloying elements	Subseries	Main intermetallic compound	Only strain hardenable	Heat treatable
1xxx	Unalloyed aluminum (Al) with impurities, commonly iron (Fe) and silicon (Si)	Al	Al-Fe-Si	yes	
2xxx	Aluminum + copper (Cu)	Al-Cu Al-Cu-Mg Al-Cu-Si-Mg Al-Cu-Li-Mg-Ag*-Zr	Al_2Cu Al_2CuMg Al_3Li		yes
3xxx	Aluminum + manganese (Mn)	Al-Mn Al-Mn-Cu	Al_6Mn	yes	
4xxx	Aluminum + silicon	Al-Si	-	most	
5xxx	Aluminum + magnesium (Mg)	Al-Mg Al-Mg-Mn	Al_3Mg_2	yes	
6xxx	Aluminum + magnesium and silicon	Al-Mg-Si Al-Mg-Si-Mn	Mg_2Si		yes
7xxx	Aluminum + zinc (Zn), magnesium and copper	Al-Zn-Mg Al-Zn-Mg-Cu	$MgZn_2$ $Mg(ZnAlCu_2)$		yes
8xxx	Aluminum + other elements such as lithium (Li) and zirconium (Zr)	-	-		yes
9xxx	Unassigned	-	-	-	-

* silver (Ag)

Cast Aluminum Alloys

Table 9 lists the naming convention for cast aluminum alloys used by the Aluminum Association. The first digit (from 1 to 9, with 6 unassigned) indicates the assigned alloy category. The second and third digits (from 0 to 9) are indicated by the x's in Table 9. In the 1xx.x series, the second and third digits indicate the minimum aluminum percentage above 99.00% (Lyle et al., 2005). Alloy 170.0, for example, contains a minimum of 99.70% aluminum (Kaufman and Rooy, 2004). In the 2xx.x through 9xx.x series, the second and third digits are labels to identify different alloys within the group. A decimal point is used

TABLE 9. Main alloying elements in the cast aluminum alloy designation system (Kaufman, 2002).

Cast alloy series	Main alloying elements	Heat treatable
1xx.x	Pure aluminum, 99.00% or greater	
2xx.x	Aluminum + copper	yes
3xx.x	Aluminum + silicon with added copper and/or magnesium	yes
4xx.x	Aluminum + silicon	yes
5xx.x	Aluminum + magnesium	
6xx.x	Unused series	
7xx.x	Aluminum + zinc	yes
8xx.x	Aluminum + tin	yes
9xx.x	Aluminum + other elements	

between the third and fourth digit to distinguish cast designations from wrought designations. The fourth digit indicates the product form (e.g., 0 for castings, 1 and 2 for ingots). Often, the last digit is dropped (e.g., 356 instead of 356.0) (Kissell and Ferry, 2002). Sometimes a letter, assigned in alphabetical order, is placed before the number to indicate a modification of the original alloy (Kaufman, 2002).

The high-silicon 3xx.x series is the most widely used because of the ease of casting (Kaufman, 2002). The 2xx.x alloys provide the highest strengths but are more difficult to cast. The 5xx.x series has excellent resistance to corrosion and is used for components exposed to marine environments (Kaufman, 2002). Zahner (1995) provides information about common cast aluminum alloys used in architectural applications.

The Unified Numbering System (UNS) also classifies cast aluminum alloys (SAE–ASTM, 2012). The AA number is used, with an added prefix and without the decimal point. The most common prefix is A0 but sometimes A1 through A7 are used to indicate modifications to an original alloy (SAE–ASTM, 2012). For example, alloy 356.0 in the AA system becomes A03560, and A356.0 becomes A13560 (Kaufman, 2000). The UNS publication lists the composition of registered cast aluminum alloys, the composition of inactive alloys, and extensive lists of cross-referenced specifications to other designation systems (SAE–ASTM, 2012).

In Europe, the standards EN 1780 (BSI 2002) and EN 1706 (BSI 2010) have been developed as a cast aluminum designation system, and many European countries have adopted these standards. These standards use four series (instead of the 8 used by AA), grouped according to major alloying element and identified by a 5-digit number: 2xxxx (copper), 4xxxx (silicon), 5xxxx (magnesium), and 7xxxx (zinc). The system uses the prefix EN to identify the European standard and the letters A for aluminum and C for cast. An example is EN AC-42000. The number is usually followed by a letter that characterizes the casting process (e.g., D for die casting, S for sand casting). Some, but not all, of the registered casting alloys can be cross referenced between the systems; for example, AA 308.0 corresponds to UNS A03080 and EN AC-45000 (Kaufman and Rooy, 2004).

Older designations, some with cross references between designation systems, are available (Kehler, 1980; Cayless, 1990; Kaufman, 2000; Kaufman and Rooy, 2004; Lyle et al., 2005).

Temper

The first character in the temper designation established by the Aluminum Association is a capital letter indicating the general class of treatment: the temper letters are F (as fabricated), O (annealed), H (strain-hardened), W (solution heat-treated), and T (thermally treated) (Kaufman, 2000). The temper letter is followed by one or more digits, dividing temper letters into subdivisions, such as H1 to H4 and T1 to T10. Each combination of temper letter and associated number refers to some specific additional processing.

The temper designation system specifies how the product has been fabricated. It is based on the sequences of mechanical working or heat treatments, or both, used to produce the various tempers (Cayless, 1990; Davis, 1999; Kaufman, 2000). The temper designation is always listed immediately following the alloy number, separated by a hyphen (e.g., 2014-T6). An example is the tempering used in the production of 6061-T6 sheet (Kissell and Ferry, 2002). Alloy 6061 is readily available and widely used for structural extrusions because it provides the best combination of strength, economy, and corrosion resistance of aluminum alloys (Kissell and Ferry, 2002). From its initial condition, the 6061-O annealed material is heat treated to 530°C as rapidly as possible, then cooled as rapidly as possible, giving the temper T4. The material is then heated to 160°C and held for 18 hours; upon cooling to room temperature, the temper is T6. The T6 temper generally designates material aged to produce the highest practical alloy strength (Sanders, 2012).

Alloys are divided into two groups (non-heat-treatable and heat-treatable) based on whether or not their strengths can be increased by heat treating (Kissell and Ferry, 2002). Non-heat-treatable aluminum alloys are those whose mechanical properties can only be strengthened by strain hardening through mechanical deformation at room temperature (cold working), but not by heat treatment (Kissell and Ferry, 2002). For example, rolling reduces the thickness of sheet aluminum, and as the metal is worked, its strength increases and it becomes resistant to further deformation. Table 8 indicates which wrought aluminum alloy series are strain hardenable but generally not heat treatable (Kaufman, 2000; Kaufman, 2002; Kissell and Ferry, 2002).

Heat-treatable alloys are those whose mechanical properties can be altered by thermal treatments in addition to strain hardening. Tables 8 and 9 list wrought and cast aluminum alloy series that are heat-treatable (Kaufman, 2000; Kaufman, 2002). In general, the 2xxx, 6xxx, 7xxx, and 8xxx wrought series are heat treatable (Kissell and Ferry, 2002). The alloy series 4xxx and 9xx.x are generally not heat treatable, except for certain members of the series (Kaufman, 2000; Kaufman, 2002).

Heat-treatable aluminum alloys depend on precipitation from a supersaturated solid solution to develop high strength (Lyle et al., 2005). In these alloys, the alloying elements (e.g., copper, lithium, zinc, magnesium with silicon) have a high solid solubility in aluminum at elevated temperatures, and low solubility at room and moderate temperatures. The alloys can be heat-treated to encourage the formation of precipitates that strain the lattice, increase the alloy strength, and harden the alloy by age hardening (precipitation hardening). These precipitates are intermetallic compounds and they consist of two or more metals (or a metal and a non-metal) with an ordered, crystalline structure and usually a definite composition, such as Al_2Cu. Some of the main intermetallic compounds in the wrought alloy series are listed in Table 8 (Vargel, 2004; Reboul and Baroux, 2011).

Among the first of these heat-treatable aluminum alloys was Duralumin, developed by Wilm in Germany in the early 1900s (Doyle, 1985; Young, 1985; Ghali, 2010). (The modern alloy 2017 is similar to Duralumin.) Wilm discovered that the addition of a small amount of copper to aluminum increased its hardness. The copper-aluminum alloy containing 4 wt% copper is often used as a classic example of precipitation hardening. Figure 6 shows the partial phase diagram for aluminum and copper.

The treatment of Duralumin provides an example of the three steps generally used in heat treatment. First, the solid alloy is heated above about 500°C to dissolve the copper in the aluminum. The maximum solid solubility of copper in aluminum is 5.65 wt% at 548°C (Lyle et al., 2005). Next the alloy is cooled rapidly (quenched) to room temperature; here the solubility of copper in aluminum is less than 0.2 wt% (Lyle et al., 2005). Finally the alloy is aged at a temperature below 200°C, which causes the precipitation of the intermetallic compound Al_2Cu (which corresponds to the θ phase in the phase diagram). This hardening happens naturally over a period of a few days if the alloy is left at room temperature, but controlled heating below 200°C produces the optimum size and distribution of Al_2Cu.

Alclad Products

Table 10 contains selected examples of common alclad material. Sometimes a different cladding alloy is used instead of the common one, and then the name is altered. For example, when alloy 7075 is clad with 7008, it is called 7008 Alclad 7075 (ASTM, 2006a).

The core alloy is chosen for its mechanical properties, usually strength, and it makes up about 90% of the total thickness (Hollingsworth et al., 1989; Ghali, 2000). The cladding layer is usually a relatively pure aluminum alloy (e.g., 1230, 6003, 7072) that is corrosion resistant (Kissell and Ferry, 2002), and is usually only 4% or 5% of the total thickness (per side), although sometimes it is only 2.5% or 1.5% (Davis, 1993). The cladding layer is applied (often by hot rolling) so that it is metallurgically bonded to the core (Kaufman, 2000; Kissell and Ferry, 2002; Vargel, 2004). The cladding layer tends to be soft and easily scratched, such as by stacking or handling (Zahner, 1995). The development of alclad products made it possible to use high strength alloys such as 2024 in environments where previously they could not be used.

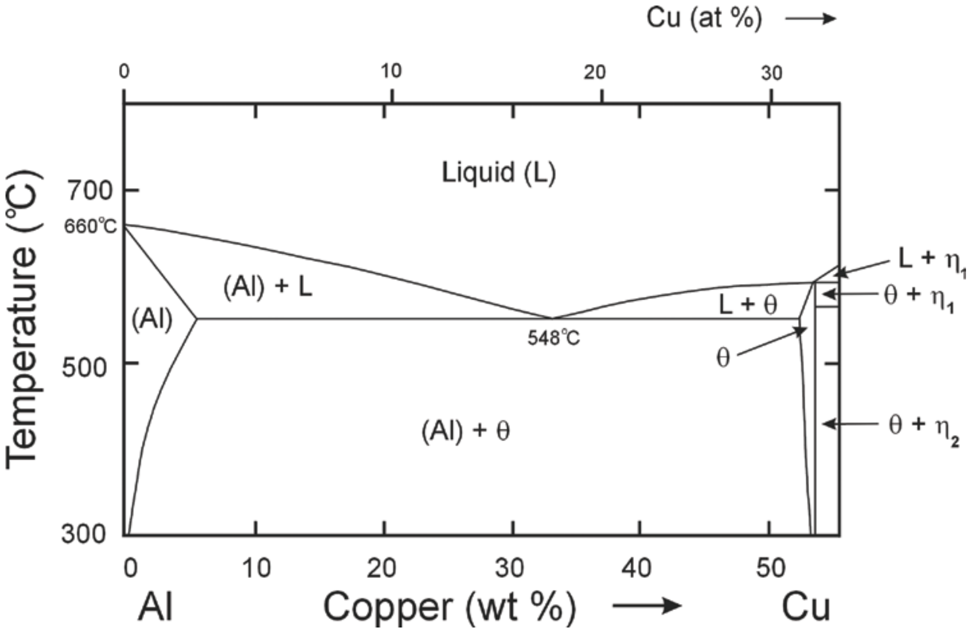

FIGURE 6. Partial equilibrium phase diagram for aluminum and copper. The bottom scale is weight percent and the top scale is atomic percent. The phase labeled theta (θ) is the intermetallic phase with composition of Al_2Cu. The phases labeled eta one (η_1) and eta two (η_2) have a composition of AlCu. Adapted from Baker (1992). © Government of Canada, Canadian Conservation Institute.

TABLE 10. Selected alclad materials, with the alloy names and numbers from either the Aluminum Association (AA), or the Unified Numbering System (UNS) (Kaufman, 2000; ASTM, 2006a; SAE–ASTM, 2012).

			Main alloying elements in core (percent)						
AA name	UNS number	Core alloy	Cu	Zn	Mg	Mn	Si	Cladding alloy	Main alloying elements in cladding (percent)
Alclad 2014	A82014	2014	4.4		0.5	0.8	0.8	6003	1.2 Mg, 0.7 Si
Alclad 2024	A82024	2024	4.4		1.5	0.6		1230	-[a]
Alclad 2219	A82219	2219	6.3			0.3		7072	1.0 Zn
Alclad 3003	A83003	3003	0.12			1.2		7072	1.0 Zn
Alclad 6061	A86061	6061	0.28		1.0		0.6	7072	1.0 Zn
Alclad 7075	A87075	7075	1.6	5.6	2.5			7072	1.0 Zn
Alclad 7178	A87178	7178	2.0	6.8	2.8			7072	1.0 Zn

[a] Contains >99.3% aluminum

APPENDIX 2: TERMINOLOGY OF ELECTROCHEMISTRY

The terminology of electrochemistry can be confusing and difficult to remember. Here is a brief review.

An anodic reaction is one that ejects electrons. The reaction causes one of the species involved to be oxidized (such as aluminum (Al) in Equation A1 or water (H_2O) in Equation A2).

$$\mathrm{Al\ (s)} \rightarrow \mathrm{Al}^{3+} + 3\mathrm{e}^{-} \qquad \text{(A1)}$$

$$2\ \mathrm{H_2O} \rightarrow \mathrm{O_2} + 4\ \mathrm{H}^{+} + 4\mathrm{e}^{-} \qquad \text{(A2)}$$

Anodic reactions may cause the solution to become more acidic. (This is obvious in the second reaction, which produces H^+, but the first reaction also acidifies the solution as Al^{3+} undergoes hydrolysis; see Equations 10 to 12.)

A cathodic reaction is one that consumes electrons. The reaction causes one of the species involved to be reduced (such as oxygen (O_2) in Equation A3 or water (H_2O) in Equation A4).

$$\mathrm{O_2} + 2\ \mathrm{H_2O} + 4\mathrm{e}^{-} \rightarrow 4\ \mathrm{OH}^{-} \qquad \text{(A3)}$$

$$2\ \mathrm{H_2O} + 2\mathrm{e}^{-} \rightarrow \mathrm{H_2} + 2\ \mathrm{OH}^{-} \qquad \text{(A4)}$$

Cathodic reactions may cause the solution to become more basic (both reactions here produce OH^-).

To help remember these concepts, note the words associated with anodic reactions start with vowels, and those with cathodic reactions start with consonants: *anodic, oxidation*, electrons *ejected*, solution more *acid*; *cathodic, reduction*, electrons *consumed*, solution more *basic*.

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Aluminum Alloy and Aircraft Construction: The Making of the Modern Airplane, 1903–1945

F. Robert van der Linden

ABSTRACT. There was time in the early twentieth century when aluminum's dominance in aircraft construction was not assured. The first generation of aircraft were built of wood and covered in fabric. This was a known and trusted technology. Designers were reluctant to embrace any new material until it was proven better than its predecessor. The debate between wood and aluminum advocates dominated the conversation until new methods to prevent corrosion corresponded with improvements in aerodynamics and powerplants made aluminum alloys the preferred choice of aircraft designers.

Keywords: Aluminum, Duraluminum, Dural, Wood, Alclad

"A Temple to Aluminum." That's how the Smithsonian's National Air and Space Museum was described by an executive of the Aluminum Corporation of America – Alcoa. To a large degree, his comment rings true. Were it not for aluminum – more specifically high strength aluminum alloys – the modern airplane as we know it would not exist. It is a testament to the enduring strength of this material that aircraft have used aluminum alloys for almost a century. Only now has its dominance been challenged with the advent of lightweight composites. Even with this new material making steady advances in aircraft design, aluminum alloys will remain a prominent part of the aviation community as their properties are well known, their users well trained in its application, and their costs low in relation to its presumed replacement.

These same arguments were made at the end of the First World War when metal aircraft were introduced. Almost all of the combat aircraft built during that titanic struggle were constructed from wood, particularly spruce, which is well known for its excellent strength and lightness. The properties of wood were well-understood from centuries of use in countless building projects. Most aircraft designers were well versed and comfortable in its use. If wood was so widely accepted, then why was it so quickly replaced? Historian Eric Schatzberg argues that this happened because of what he terms the "progressive ideology of metal."[1] This theory holds that, for engineers and designers, wood and fabric construction represented traditional construction techniques, that of centuries of use. Metal, instead, represented progress and modernism. It holds, therefore, that all aircraft designers became enamored with metal because it symbolized the future and not the past since metal was the new construction material of the industrial age.[2] This theory, while perhaps true to an extent, reduces the designer and engineer to an irrational, easily influenced puppet to ever-changing social and cultural norms.

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While some designers may have adopted an almost theological attraction to metal, most were, instead, extraordinarily practical individuals who were constantly searching for any better materials with which to build their flying machines. To an aircraft builder, the challenge is to create a machine that can fly as long as possible, as fast as possible, and with the greatest load possible, depending on the requirements for the aircraft. The enemy of aircraft performance is weight and also aerodynamic drag – the force that acts upon the structure as a whole which must be overcome by thrust provided by the engine. Most designers search for the lightest and the strongest materials possible to decrease the weight and lower drag. From the first successful aircraft – the 1903 Wright Flyer – until late World War I, that material was wood. It was strong and light but was unpredictable as it was a naturally growing material which varied considerably in terms of density and strength even within individual species of trees. Furthermore, wood readily absorbs moisture and is prone to rot, which weakened aircraft structure to the point of failure.[3] Wooden aircraft were usually covered in cotton or linen fabric that was made taut and protected from water by the addition of either cellulose nitrate, butyrate, or acetate dopes. The fabric contributed virtually nothing to the structural strength of the aircraft. Designers were well aware of wood's limitations and, as early as 1910, sought new and better construction materials to replace, what historian and aeronautics engineer John Anderson describes as "the vegetable airplane."[4]

In efforts to streamline aircraft designs and to reduce the drag resulting from the external wire bracing of the wings of traditional wood and fabric aircraft, the Germans, particularly Dr. Hugo Junkers, pioneered the internally supported, cantilevered monoplane. Aircraft produced by Junkers and other farsighted designers who followed his lead, were very successful because of the relative efficiency of their clean and strong wings. A thick cantilevered plywood biplane set of wings was the hallmark of the famous Fokker D.VII, generally considered the finest fighter of the First World War – so feared was it for its ability to "hang on its prop" because of the great lift provided by its wings and attack Allied aircraft from below – that the type was specifically banned by the terms of the Armistice Agreement in November 1918. The wing came from Junkers.[5]

Of great significance was Hugo Junkers' concurrent work in developing a practical all-metal aircraft. Experienced in working with many metals from his time as an engineer and professor of thermodynamics and engines at the University of Aachen, Junkers first experimented with iron in his Junkers J.1 attack plane. Although innovative, the aircraft, which was covered in very thin iron sheets, proved overweight and underpowered.[6] Clearly, while iron was strong, it was impractical because it was simply too heavy for the entire structure. Steel tubing was light enough for aircraft fuselages when covered in fabric, but too heavy when employed to cover the entire aircraft. Aluminum was light, durable, and easily worked, but it was too soft and, therefore, impractical. What to do?

The solution came from the German chemical and metallurgical industry. In 1901, German metallurgist Alfred Wilm, who also trained as a chemist, became interested in the properties of aluminum while working at the Goldschmidt Chemical Factories. By late 1903, at the same time that the Wright brothers were completing their first powered aircraft, Wilm had patented a method to strengthen aluminum-copper alloys by heating and cooling methods. That year, the German War Munitions Factory assumed control of his work in order to find an aluminum alloy as strong as brass. Wilm had developed a strong alloy by adding copper and manganese to aluminum. Unfortunately, it lacked hardness. Wilm added a small amount of magnesium to the mix and rolled a thin sheet of the new metal, after annealing it in a salt bath. Wilm and his assistant tested the strength of the new alloy and were mildly disappointed in the results. Leaving the material over the weekend, Wilm retested the material a week later and was astounded to discover that it was considerably harder while its strength had also improved. Unlike iron alloys, Wilm discovered that aluminum alloys strengthened with age – in this case four days.[7] By 1911, Wilm was able to patent the new alloy and negotiated with the Durener Metalwerke for production rights. The new alloy was named after a contraction of the company's name and that of aluminum thus becoming "duralumin" or later simply "dural."[8]

Junkers quickly turned to this new, strong, lightweight metal alloy to build all of his subsequent aircraft. His Junkers armored attack aircraft fought successfully in the latter stages of World War I but, of far greater significance, his line of commercial all-metal dural transports made him famous. Using duralumin, Junkers corrugated the sheet metal to provide linear strength, using this on his highly efficient F.13 single-engine monoplane.[9] Subsequent designs led the industry through the 1920s and inspired many other, copycat designs, including the famous Ford Tri-Motor of 1926.[10]

Because of his experience with wood and with metal, Junkers made a compelling case for the use of the latter. Concerned only with finding the best material and unconcerned with popular impressions of modernity vs. tradition, Junkers laid out a logical and straightforward case for metal aircraft:

> Among the advantages the first is greater durability. Wood is subject to the dangers of fire and decay, and splinters when breaking; it bursts and warps from the effect of humidity and change of temperature and the glued joints split; finally it is attacked by insects. No wooden aeroplane, serviceable for any length of time in the Tropics, has been produced as yet. Metal is free from all such drawbacks . . . .
>
> Furthermore:
>
> Structural parts made in wood also change shape and size; they swell or warp under the influence of heat and humidity, making necessary a continuous re-setting and truing-up of the aeroplane. All this does not apply to metal, and

> a constancy of form is necessarily important in aeroplane wings, slight changes frequently producing a distinct deterioration of the aerodynamic qualities.[11]

Duralumin was first used in the construction of Germany's massive hydrogen airships – the Zeppelins which were employed as commercial airliners before the war and the first long range strategic bombers during the war. Quickly the new metal was incorporated into Junkers' and other pioneering German designs.[12]

As John Anderson states and Eric Shatzberg reluctantly agrees, metal aircraft construction was not widely adopted for another 10 to 15 years. Why? Schatzberg argues that that is because the acolytes of metal, with the backing of the military, navy, and federal government in the United States, pushed long and hard to overcome the problems of metal, deliberately ignoring the early failures of metal design while deliberately ignoring the advantages of wood because of the so-called progressive ideology of metal.[13] Anderson has a much simpler and rational explanation: aircraft designers are inherently conservative. They are not prone to making rash decisions and much prefer using what is known rather than what is not known. They prefer evolution to revolution. They are conservative because the consequences of failure are usually fatal to those operating the aircraft.[14]

This conservative approach produced a string of excellent, evolutionary aircraft during the 1920s. While the National Advisory Committee for Aeronautics (NACA), the predecessor to NASA, was actively researching metal and advocating its eventual use most designers were leery of the material. Indeed, for a while in NACA and in the British Ministry of Aviation, designers were directly discouraged from using duralumin. Some of this was the fear of the unknown and the conservatism of tradition – bound bureaucrats, but it was more a reflection on a potentially fatal flaw in duralumin – corrosion.

Pure aluminum is a remarkable metal in that is corrosion resistant. Unfortunately, aluminum alloys, especially duralumin and its imitators are highly subject to corrosion.[15] This unfortunate fact was not fully understood when Junkers' first series of popular duralumin aircraft entered the market. The Junker F.13, sold in the United States as the Junkers Larson JL-6, was initially sold to the United States Post Office for service on its air mail routes. The aircraft quickly developed an unfavorable reputation especially once intergranular corrosion was discovered throughout its structure.[16] Tests on the Junkers and other similar designs revealed that duralumin was highly susceptible to internal corrosion, which only revealed itself as a white powder on the metal's surface before failing. The lifespan of such an aircraft was less than four years.[17]

Designers wisely stayed away from duralumin until a solution was found in the late 1920s. In 1927 in Great Britain, G.D. Bengough and H. Sutton of the National Physical Laboratory developed a technique of anodizing alloys with a protective oxide coating.[18] While successful, and used on the world's first modern airliner, the Boeing 247 of 1933, it produced an unattractive, uneven finish. Many passengers thought the aircraft they were traveling on had been in numerous accidents as the metal sheets did not match in color.[19] A better solution was found through the collective efforts of the NACA and Alcoa. In 1927, Edward H. Dix of Alcoa patented a method of binding corrosion-proof pure aluminum to sheets of duralumin. This resulted in a beautifully finished, highly corrosion resistant alloy. This process of applying an aluminum cladding to sheets of alloy was made under the trademark of "Alclad."[20] This coupled with Alcoa's efforts to emulate German duralumin with an alloy of its own, at the insistence of the U.S. Navy, resulted in the first practical aluminum alloy for aircraft use – Alcoa 17ST.[21] Today, Alclad - based aircraft such as the Boeing B-52 and 747 have flown safely for decades and hundreds of thousands of hours of flightime.

With the problem of corrosion solved, what of the problems of drag? Metal is a very even, workable material, ideally suited for aircraft structure if used properly. In the eternal struggle to reduced weight while increasing the strength of aircraft structures, another German engineer and designer, Adolf Rohrbach, built the first all-metal, stressed-skin wing for his remarkable four-engine airliner, the E4/20 Staaken of 1920.[22] By allowing the aircraft's skin to carry most of the aircraft's aerodynamic load, this stressed-skin design eliminated the need for a complex, space-consuming interior structure, thereby saving a great deal of weight and opening up the fuselage for more payload. Underpowered and subject to the corrosion of unprotected duralumin, the Staaken was also seen as a potential military threat and eventually destroyed by the Allied Control Commission occupying defeated Germany. Nevertheless, the lessons of this aircraft quickly spread throughout the industry.

Other advanced European aircraft also used a radical method of fuselage manufacture that gave a low-drag streamlined shape coupling lightweight with great strength – ideal for metal construction. First used by the French before World War I, monocoque construction (more precisely semi-monocoque because of the use of strengthening stringers), from the French term referring to single-shell boat hull manufacturing techniques, greatly increased the usable volume of the fuselage. A shell of plywood strips was applied over a form. Once set, the plywood skin carried most of the structural load of the fuselage while reducing the weight of the airframe. Several World War I German combat aircraft used this construction technique as it allowed the use of cheap plywood rather than expensive and hard to find spruce. In June 1918, the experimental Dornier D-I fighter combined stressed skin with a metal monocoque fuselage.[23] Beginning in 1920, the NACA published German reports on these techniques which were closely read by designers throughout the American aviation community.[24]

Wood was a perfectly acceptable material for smaller aircraft. As aircraft grew in size the inherent problems with wood became increasingly difficult to overcome as its lightweight was more than offset by its limited life and unpredictability in various climates. Metal, while denser and, therefore, heavier, was readily formed into any aerodynamic shape and, after 1927, did not suffer from fatal corrosion.[25] Stressed skin monocoque construction greatly lightened airframe weight and increased usable interior volume while cantilevered wings combined to reduce drag significantly making metal competitive with wood. Metal's significant potential advantage lay in its ability to be used economically in ever-increasingly larger and higher performing designs. Just as steel made skyscrapers possible at the beginning of the twentieth century, duralumin, particularly Alclad 17ST and its immediate successor 24ST, made efficient large aircraft possible. These new designs could withstand the aerodynamic stresses of flight much better with metal. Bigger designs mean greater weight; greater weight requires greater power. The last problem to solve before all metal aircraft could be widely accepted was to find efficient, light, yet powerful engines to take advantage of the strength and durability of metal.

During the early 1920s, the U.S. Navy became increasingly interested in the air-cooled engines produced by the tiny Lawrance Aero-Engine Corporation of New York City. In the immediate post World War I years, the only engines producing enough horsepower for huge performance aircraft were bulky, unreliable water-cooled types. The Navy was anxious to find an engine that could produce sufficient power without the weight and maintenance problems of water-cooled motors. The aluminum Lawrance J series of engines seemed ideal for the task as they had no troublesome and heavy radiators, water pumps, or vulnerable cooling lines.[26]

Wishing to find a large company with enough resources to produce and develop these engines, the Navy threatened and cajoled the Wright Aeronautical Company into purchasing Lawrance in 1923.[27] It was a wise move. By 1924, the Wright J-3 and J-4 air-cooled radial engines, better known as Whirlwinds, were in service. Incorporating Englishman Samuel D. Heron's revolutionary sodium-cooled exhaust valves, which virtually eliminated the chronic problem of burned exhaust valves, the improved J-5 was the first aero engine to offer power and great dependability. This powerplant, the first truly reliable aero engine, made Charles Lindbergh's epic non-stop solo 33½ hour transatlantic flight possible in 1927 with no problems.[28]

The Wright company eagerly produced thousands of Whirlwinds but its upper management refused to invest in developing the design any further. Frustrated, president Frederick Rentschler and two others left Wright to form the Pratt & Whitney Company to build bigger radials, producing the landmark Wasp in 1925. The competition was on and, for the next two decades, these rivals fought to produce ever more powerful and efficient powerplants for the military and the airlines.[29]

The aviation industry now had the power it needed but one problem of drag remained. Air-cooled engines by definition require high volumes of air to cool the cylinders thus producing high-drag designs that must be exposed to the airflow. Water-cooled engines, by contrast, do not require this exposure so their designs are far sleeker except for the large radiator needed for cooling the water. The solution to this problem came once again from the NACA in the form of the engine cowl, a close-fitting aluminum structure that encased the engine while channeling air around the engine. The cowl improved cooling and lowered drag, thereby increasing speed. First used on the plywood monocoque Lockheed Vega in 1928, the NACA cowl, developed in large part by Fred Weick, made the radial engine the perfect choice for reliable aircraft power.[30] Incidentally, water-cooled engines received a new lease on life with the development of ethylene glycol as a coolant additive. Sold under the trade name "Prestone," ethylene glycol enabled engine designers to use much smaller radiators which greatly reduced the liquid-cooled engines' drag problem.

With the breakthrough in corrosion protection for aluminum alloys, the advent of the NACA cowling, and the increased awareness of new and more efficient methods of aircraft propulsion and construction, work began anew in the United States and around the world on all-metal aircraft.[31]

One of America's most avid enthusiasts of metal stressed-skin construction was John K. "Jack" Northrop. A brilliant designer consumed with eventually building a practical flying wing, Northrop designed and built the best wooden aircraft of the era, the Lockheed Vega. Sleek, streamlined, and made completely from plywood, the Vega was one of the fastest aircraft of its day and the aircraft of choice for many famous pilots including Wiley Post and Amelia Earhart.[32] Despite his thorough knowledge of wood, or perhaps because of it, Northrop became one of the loudest advocates for all metal construction.

When the corrosion problem was solved with the advent of anodized dural and Alclad, Northrop left Lockheed to start his own company, Avion, strictly to build metal aircraft. The first aircraft built under his name was the Northrop Alpha, a low wing all metal cantilevered single engine monoplane capable of carrying a large mail payload and up to seven passengers.[33] So impressed was William Boeing by this aircraft that he purchased Northrop's Avion Corporation and added it to his burgeoning United Aircraft and Transport Corporation empire. Bill Boeing had moved to the Pacific Northwest and established his aircraft manufacturing company there in order to be near the vast groves of spruce, thousands of acres of which Boeing owned. Ironically, and not at a small personal cost, Boeing became one of the leading producers of all metal aircraft after 1930. Northrop's fervent advocacy of all-metal aircraft had a lasting impact on the designs on Boeing and the other aircraft builders in the United Aircraft group. While Northrop's tenure at United was brief, his influence was lasting.[34]

This convergence of technologies in the late 1920s, driven by the development of Alclad, opened the market to all-metal aircraft. By 1930, new metal military and civilian aircaft were rolling from factories. Of great significance, in Seattle, Washington, the Boeing 247 all-metal, cantilevered, monocoque twin-engine airliner took to the sky on February 8, 1933.[35] This, the first modern aircraft, set the pattern for generations of airliners to come. With 50 percent less horsepower than a comparable Fokker or Ford Tri-Motor, the Boeing 247 cruised 60 percent faster. All of these advances, but particularly the adoption of metal construction, made this and the succeeding generations of aircraft possible. By the end of World War II, the United States alone had produced over 300,000 aircraft, virtually all of them metal.

Wood still had its place in a few important designs, such as the British de Havilland Mosquito bomber of World War II. A legend because of its versatility, the Mosquito was all plywood and built to relieve the problem of limited aluminum supplies to war production. It was, however, the exception that proved the rule.[36] Several German attempts to build wooden aircraft failed. While the Soviets built several successful wooden fighters, they were eventually supplanted by all metal designs when the aluminum supplies became plentiful.[37] More importantly, attempts by several countries, particularly Japan, to build wooden designs based on existing metal aircraft all failed because of severe weight problems.[38] Most tellingly, after the Mosquito, de Havilland turned to jet aircraft production – featuring all metal construction.[39] De Havilland's attempt to build a wooden airliner, the D.H. 91 Albatross failed because of structural problems.[40]

Even today, with the carefully adopted advent of even lighter composite materials, aluminum alloys will continue to be the primary material for aircraft in the coming years. New alloys are challenging the weight advantages of aluminum alloys. Regardless of which ever material prevails, the decision will be a rational one and not based on social or cultural pressures.

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Aluminum – A Modern Metal with Historical Importance

John Weritz

ABSTRACT. The most abundant metal in the earth's crust, aluminum has only existed as a free element for less than 200 years. Considered a precious metal until the end of the 19th century, aluminum has been part of every one of man's major achievements in aviation. From the Wright brother's first flight at Kitty Hawk to Neil Armstrong's first steps on the lunar surface, aluminum played an instrumental role in the design of the vehicles that made those feats possible. Aluminum has also played a major role in other forms of transportation and found useful applications as a building material, in packaging and countless others. High purity aluminum has properties that make it useful for a wide variety of applications, but the additions of alloying elements create materials that possess very different physical and mechanical properties. This paper will discuss the effects of these alloying elements and how engineers have used these different properties to create useful solutions to a number of design challenges. It will also include a review of the alloy designation system and typical applications of commonly used alloys to help in identifying the materials that were used to make different artifacts.

Keywords: aluminum, alloys, association, aluminum production

OVERVIEW

Unlike many of the materials commonly used today, aluminum has a relatively brief but important history. In less than 200 years, aluminum has evolved from a completely unknown element to the curiosity as a precious metal to the sustainable metal of choice for industries around the world. Today aluminum is the cornerstone of modern transportation, building construction and packaging industries.

A QUICK LOOK BACK

Aluminum existed as a free metal in 1825 when Danish chemist Hans-Christian Oersted successfully extracted it. For the next 60 years, scientists learned more about the metal and sought better ways to obtain it. Today, we can still see one of these early applications of aluminum as the capstone of the Washington Monument – 100 ounces of the light metal proudly rests at the apex of the monument today as it has since December 6, 1884.

In 1886, Charles Martin Hall in the United States and Paul Heroult of France simultaneously invented the electrolytic process for producing metallic aluminum from its oxide. Eleven years later, Austrian Carl Joseph Bayer invented the chemical process that refines alumina from bauxite. Together, these inventions contributed to the birth of the modern aluminum industry and are still used today by the alumina refineries and aluminum smelters around the world.

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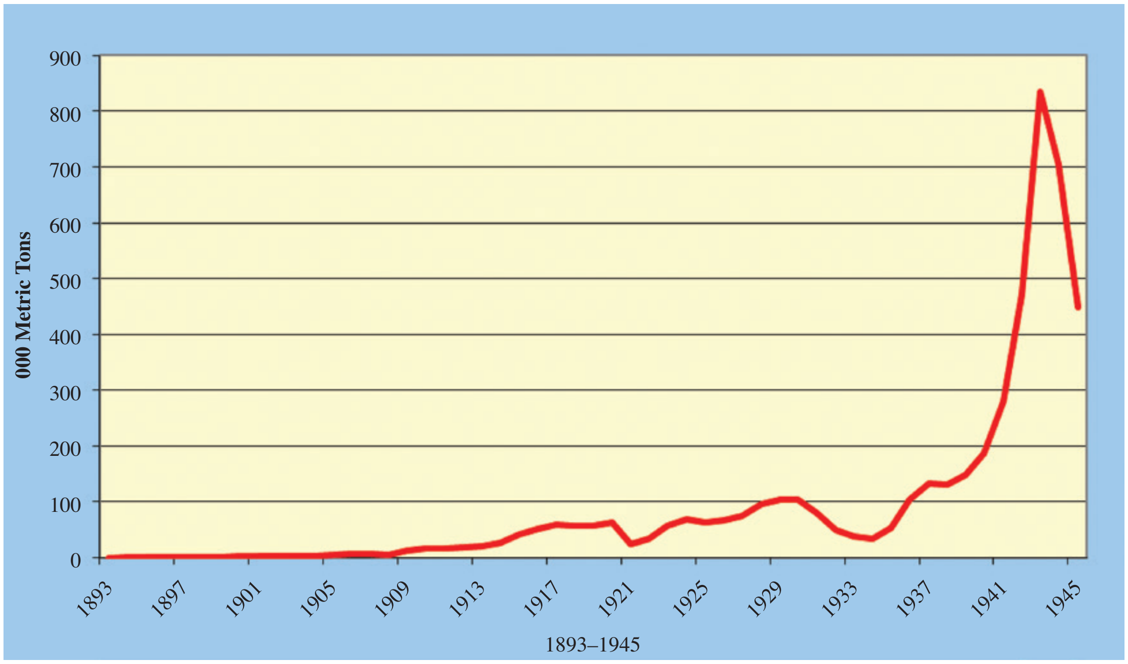

FIGURE 1. Production of primary aluminum in the United States from 1893 to 1945. The Aluminum Association.

As commercial use for aluminum increased, new applications took advantage of the high reflectivity and conductivity of pure aluminum, while other applications required alloy additions to improve the performance of castings or wrought products such as foil, sheet, plate, extrusions, wire and forgings.

Duralumin was a popular early application of the aluminum-copper-magnesium system discovered by Alfred Wilm in 1906. As a heat treatable, high-strength alloy, duralumin and derivative alloys found widespread use in military and commercial aircraft, which were evolving from fabric to metal skinned vehicles, a practice that continues to this day.

THE MODERN ALUMINUM INDUSTRY

As part of President Franklin D. Roosevelt's New Deal, Congress passed the National Industrial Recovery Act of 1933, asking each industry to establish codes and guidelines for fair competition. Representatives of 13 aluminum companies met in Pittsburgh to establish these codes and form what later became the Aluminum Association. At the first official meeting in New York in October 1935, the Association defined its purpose as "promoting the general welfare of the aluminum industry and its members".

The Technical Committee on Product Standards was formed to facilitate commerce in this new industry. It developed a standard nomenclature for designating alloys and tempers. The first step was renaming existing alloys to conform to the system. For example, Duralumin is now known as alloy 2017. This new naming system is formally recognized internationally by signatories of two dozen countries.

New alloys continue to be registered each year, and the list of wrought alloys currently stands at 520. The complete chemical composition limits for each of these alloys is contained in the Teal Sheets, freely available at: http://aluminum.org/. Industry experts continue to participate on the Technical Committee for Product Standards to this day and oversee this process to assure global adherence to the rules.

As the industry evolved and developed more competitive alloys, growth in aluminum production increased once again after WWI as new peace-time applications for aluminum were found.

STANDARDS: THE NEW NAMING SYSTEM

The Aluminum Association is the ANSI-accredited secretariat for maintaining the aluminum alloy and temper designation standard. The complete standard is ANSI H35.1, which is also included in a popular publication, Aluminum Standards and Data. Both of these have recently been updated and are available at http://aluminum.org/. A brief review of the aluminum alloy

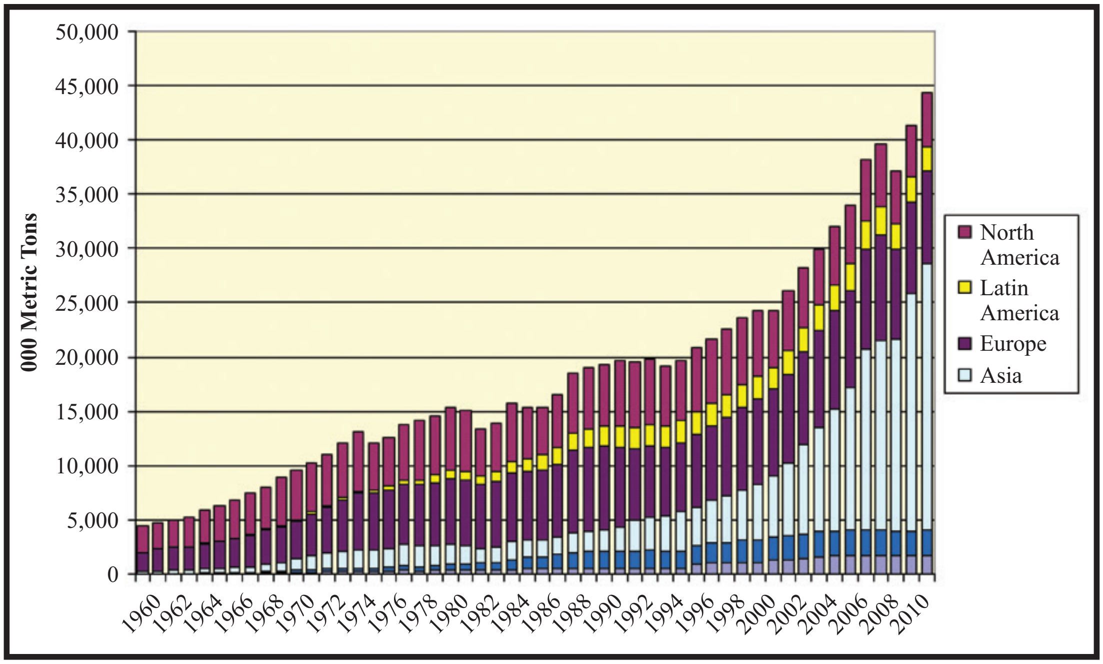

FIGURE 2. World primary aluminum production from 1960 to 2010. U.S. Geological Survey.

designation system along with some common applications of these alloys is described below:

1xxx series—Aluminum of 99% or higher purity has many applications, especially in the electrical and chemical industries. These compositions are characterized by excellent corrosion resistance, high thermal and electrical conductivity, low mechanical properties and excellent workability.

2xxx series—Copper is the principal alloying element in this group. These alloys require solution heat-treatment to obtain optimum properties. The alloys in the 2xxx series may lack corrosion resistance and under certain conditions, may be subject to intergranular corrosion. When the alloy is in the form of a sheet, it may be clad with a high-purity alloy which greatly increases resistance to corrosion. Alloys from this series are frequently used in many aircraft and aerospace applications. Some have also been used as automotive body sheet.

3xxx series—Manganese is the dominant alloying element in this group, which is generally non-heat treatable. One of these is the popular 3003, which is widely used as a general purpose alloy for moderate-strength applications requiring good workability. The ubiquitous aluminum can body is made from a 3004 type alloy.

4xxx series—The primary alloying element in this group is silicon, which can be added in sufficient quantities to substantially lower the melting point without producing brittleness in the product. Aluminum-silicon alloys are used in welding wire and as the cladding on brazing alloys, where a lower melting point than that of the parent metal is required.

5xxx series—Magnesium is one of the most effective and widely used alloying elements for aluminum. When it is used as the major alloying element alone or with manganese, the result is a moderate to high strength non-heat-treatable alloy. Alloys in this series possess good welding characteristics and special tempers have been developed to provide good resistance to corrosion in a marine atmosphere. Alloys from this series are extremely versatile and are often found in marine, chemical storage, architectural applications, armor and a host of other applications including the can end and tab which is a 5082 type alloy.

6xxx series—Alloys in this group contain silicon and magnesium in approximate proportions to form magnesium silicide, thus making them heat-treatable. The major alloy in this series is 6061, one of the most versatile of the heat-treatable alloys. Though less strong than most of the 2xxx or 7xxx alloys, the magnesium-silicon (or magnesium-silicide) alloys possess good formability and corrosion resistance, with medium strength. This series is very popular in the extrusion industry and in all wrought forms it possesses good formability, machinability and weldability and takes on a pleasing finish which is often an important element of design.

7xxx series—Zinc is the major alloying element in this group, and when coupled with a smaller percentage of magnesium results in heat-treatable alloys of very high strength. Many of the highest strength alloys are part of this series. Alloy 7075 has been used for decades, and somewhat more recently 7050 type alloys have gained favor. As with the 2xxx series alloys, this higher strength comes at the expense of corrosion resistance. In this case however, there are two popular methods to mitigate this problem. Cladding with a higher purity alloy provides galvanic protection as it does with the 2xxx series, but another popular method uses artificial aging for an extended time. Some of these alloys can be aged to peak mechanical properties by artificially aging to T6, but they can also be over aged to a T7 temper. Over-aging certain alloys significantly improves resistance to various forms of corrosion at a modest reduction in strength.

In addition to wrought alloys, another designation system is used for cast alloys as follows in Table 1. Alloys that don't fit into the above categories are given an 8XXX designation if wrought or a 9XX.X if cast.

TABLE 1. Major alloying element in each series

Series	Major Alloying Element
1xx.x	Aluminum, 99.00 percent minimum and greater
2xx.x	Copper
3xx.x	Silicon, with added copper and/or magnesium
4xx.x	Silicon
5xx.x	Magnesium
7xx.x	Zinc
8xx.x	Tin

CONCLUSION

It has been said that in our modern society, no one is more than two meters (six feet) away from something that is made of aluminum. This was certainly true at nearly every major historical feat of the past century – from Wilbur Wright flying at Kitty Hawk, Neil Armstrong making his small step on the lunar surface, to the International Space Station that has been continuously occupied as a home for astronauts since the year 2000. Aluminum will be on the vehicle that takes the first humans to Mars.

The public face of aluminum is the indispensable modern material used as packaging and in the production of vehicles used in all forms of transportation. By virtue of strength and beauty, it is also the backbone and facade of numerous structures.

In reality, aluminum is the base metal for hundreds of alloys, each produced in specific tempers designed to provide engineers, architects and consumers with the right solution for each specific end use. Understanding the characteristics of those products is important not only during the intended life of those products, but also in the preservation of those artifacts to be treasured for future generations.

Conservation of Aluminum Alloys Corroded under Water: From In-Situ Conservation through Storage to Exhibition

Ian Donald MacLeod

ABSTRACT. Corrosion problems inside the hull of the America's Cup winning yacht *Australia II* confirmed that without direct conservation intervention a bilge hull-plate, immersed in stale salty urine, would have perforated within months. Successful stabilization was achieved through soaking the interior in a 2 wt. % sodium silicate solution which extracted large amounts of chloride and passivated the series 5083 metal structure. The method developed for treating chloride infested corroded duralumin alloys in $NH_3/(NH_4)_2SO_4$ solutions demonstrated that it was possible to oxidize re-deposited copper from the remaining aluminum skin without any corrosion of the base metal alloy. The treatment ensured artifact stability for 30 years. Analysis of corrosion potential measurements on a wrecked WWII *Emily* flying boat in Chuuk Lagoon over five years has established that the aluminum alloys are corroding at a steady state after 60 years of immersion. Comparison with a similar wreck in Saipan Lagoon has confirmed that common corrosion rates and mechanisms are operating on both sites in the Pacific Ocean.

Keywords: Australia II, conservation, aluminum alloys, desalination, corrosion, WWII airplanes

INTRODUCTION

The corrosion of aluminum alloys used in the construction and maintenance of military and civilian aircraft in estuarine waters and in the open ocean is dominated by the presence of pitting reactions promoted by chloride ions. Just as the presence of chlorides manifests itself in bronze disease and causes iron artifacts to crumble, so too their impact on recovered archaeological aluminum alloys is often devastating. Without access to washing tanks to preserve the integrity of corroded metals, air drying of recovered corroded marine aluminum alloys can turn apparently sound objects into piles of crumbly, dusty, grey corrosion products within a short space of time (from months to a few years). Military and commercial aluminum aircraft wrecks that lie in fresh water lakes, with chloride levels 20 ppm or less, suffer much less corrosion than those objects recovered from brackish water or the ocean. Chloride ions not only penetrate defects in the protective Al_2O_3 film, which facilitates localized pitting corrosion; they also mobilize copper containing phases in the alloys, which lead to copper cementation on the external aluminum surface. This re-deposition reaction often occurs in the low oxygen microenvironment underneath the hold fasts of barnacles and other encrusting calcareous marine organisms (Figure 1). Cemented copper acts as an active cathodic site that facilitates the reduction of oxygen, which changes the rate determining corrosion step and the oxidation of the aluminum alloys in the underlying metal.

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FIGURE 1. Perforated duralumin skin from an Australian WWII Spitfire recovered from a French river estuary in 2011. Note the red-brown cuprite deposits under barnacle attachments and the blue-green copper-aluminium corrosion products. Photo West Australian Museum, Ian MacLeod.

FIGURE 2. Interior of *Australia II* showing the author examining the area where severe pitting almost perforated the hull. Photo WA Museum, Jon Carpenter.

CONSERVING THE AMERICA'S CUP YACHT AUSTRALIA II

On September 26, 1983, the 12-metre yacht *Australia II* won the America's Cup race and sailed into history, being the first vessel to beat the 132 year American hold on the Cup. The hull plates were constructed mainly from 5083 with 6061 frames to create a 2.5 ton hull, which had an 18 ton lead-antimony keel. The 5083 alloy contains 4½% magnesium, 0.7% manganese and 0.15% chromium and is frequently used in ship construction. The 6061 alloy has significantly less magnesium at 0.8–1.2% and is heat treatable, as it has manganese content of between 0–0.15% and 0.15–0.40% copper. Following construction the external hull plates were sandblasted, etch primed with a zinc chromate-hydrofluoric acid inhibitor before being coated with a high-build epoxy undercoat impregnated with micro-balloons. This surface was fared by a combination of hand and mechanical grinding with final polishing. The exterior of the completed hull was covered with 16 layers of paint that were rubbed down between each coating session. Details pertaining to the 19.7 meter long yacht have been previously reported (MacLeod and Kelly, 2001).

During a routine condition reporting exercise the removal of plywood flooring in the bilge revealed eight liters of a deep brown-grey entrained liquid, which was evolving copious bubbles of hydrogen. After five years in storage, salt water and urine residues had created an aggressive medium that assisted pitting of the hull plates. Rapid corrosion of structural aluminum alloys was occurring as a result of accumulated operational debris, which included fragments of insulated copper wiring, lying in the liquid (Figure 2). It is likely that some of the corroded copper wire would have been cemented on the surface of the metal (Annamalai and Hiskey, 1978). Cemented copper changes the corrosion rate determining step from being oxygen reduction on the alumina covered aluminum surface to anodic dissolution inside pits. Some areas of the 5083 hull plates had lost 2 mm, or 40% of the total original thickness. The corrosion potential, E_{corr}, of the pitting metal had a voltage of –0.397 V, relative to the Normal Hydrogen Electrode (NHE), at a pH of 2.67.

EFFECT OF CHLORIDE ON CORROSION

On pure aluminum the E_{corr} is directly related to the chloride concentration (Lowson, 1978) as shown in equation 1,

$$E_{corr} = -0.475 - 0.060 \, log \, [Cl^-] \qquad (1)$$

The voltages used in equation 1 relate to an Ag/AgCl reference electrode, and the chloride ion concentration is expressed in moles per liter. Using equation 1 to calculate the chloride ion activity associated with the observed E_{corr} of –0.397 volts gave a chloride activity of 1,770 ppm, which was of the same order as measured in the area of the pits with the flat surface chloride ion electrode. The chloride ion electrode readings in and around the worst of the pitting gave readings of between 800–2,200 ppm chloride. Gas chromatography confirmed that the solution found underneath the floor boards contained amino acids and a high content of urea which is consistent with sweat and urine residues from the crew. A map of the surface pH and E_{corr} of the hull plates between the 4th and the 14th frame from the bow was consistent with active corrosion of the alloys, as indicated by the regression equation 2, which had with an R^2 value of 0.9828,

$$E_{corr} = 1.21 - 0.22 \text{ pH} \quad (2)$$

The anodic dissolution of aluminum in the presence of chloride ions has been well documented in the literature (Despić et al., 1988). Electric field inversion, caused by the accumulation of negatively charged chloride ions, triggers the fast anodic dissolution of aluminum oxide films, since the primary electrostatic attraction between the metal ions and the negative oxides is fundamentally changed with the accumulation of chloride ions. Since chloride ions form soluble complexes with Al^{3+} ions, they also promote the overall corrosion reaction since they prevent the reaction sites becoming clogged with insoluble corrosion products (Richardson and Wood, 1970).

CONSERVATION TREATMENT

Initial attempts to passivate the hull involved an aqueous chromate solution but this failed to halt the corrosion because of the high relative humidity inside the hull and high level of adsorbed chloride (Oakes, 1973). Corrosion simulation experiments using an Amel 551 potentiostat in a linear polarization mode with logarithmic voltage vs. current plots were used to assess a variety of inhibitors. The electrode was made of a small section of original *Australia II* hull plate that had been sectioned during repairs of damage when the vessel collided during an anniversary race with a wharf in Cowes, England. The best results showed that inhibition could be achieved with a 2 wt.% sodium metasilicate (Na_2SiO_3) solution in deionized water. After two soaking treatments using almost 400 liters of the inhibitor solution, more than 220 grams of chloride had been extracted and the E_{corr} stabilized at –700mV after two weeks. The final chloride ion activity was estimated using equation 1 which showed a 280 fold reduction from 1770 to 6.3 ppm. Wet chemical analysis of the corrosion products on the 6061 frames had 14.5% sulfate and 1.3% chloride, which are due to selective adsorption of the divalent anion that results in a concentration factor of nearly 80 times over the ratios found in normal seawater (NACE, 1960).

AMMONIA LEACHING OF CEMENTED COPPER FROM DURALUMIN ALLOYS

In 1932, a duralumin skinned Junkers W33 aircraft crash landed on the far northwestern coast of Australia and the float *Atlantis*, which had been used by the crew in an escape bid, was recovered in 1978 after corroding on the shore of the Kimberley coast for more than 45 years. The dominant corrosion product was gibbsite $Al(OH)_3$; in addition, an unidentified light blue copper-containing material showed with a distorted alumina structure by X-ray diffraction analysis. The major calcium mineral was gypsum ($CaSO_4.2\ H_20$) with minor amounts of calcite ($CaCO_3$). There were significant areas of the metal surface that were covered with the original bitumen paint. The main alloy used in the *Atlantis* sea-plane float had the composition 92.8% aluminum, 4·12% copper, 0·44% magnesium, 0·31% iron, 0·77% manganese and 0·03% lead which is typical for Duralumin. Uncoated duralumin alloys in seawater can suffer from extreme pitting corrosion at more than 2 mm/year (Goddard et al., 1967).

The scanning electron microscope (SEM) images of a section of the float metal showed significant amounts of precipitation of intermetallic $CuAl_2$ which leaves grain boundaries depleted in copper and predisposed to localized corrosion – see Figure 3 (Dix et al., 1975). These corrosion issues are exacerbated by the presence of re-deposited copper (from corrosion products) on the surface of the alloy. Additional complications for historic aluminum objects is that phase changes occur over time, and this leads to complexities in the microstructure and different reactivity of the θ" and θ' phases, which alter the nature of the surfaces and the way in which the corrosion products react with chloride media (Muller and Galvele, 1977). Metallographic analysis of a solid section of the float skin revealed 150μm pits in the 500μm thick cross section. Up to 60% of the surface skin and structural members had severe pitting that led to perforation. Differential aeration cells due to the adherent red-brown clay were overcome by scrubbing the surface with a nylon bristle brush but the remaining tar coating was kept in place as it represented the original object and was inherently protective. The residual issue was how to remove a noble metal from the surface of a much more reactive alloy.

The treatment involved soaking the corroded float in pH 9.6 buffer solutions of 0.25 M NH_3 and 0.125 M $(NH_4)_2SO_4$.

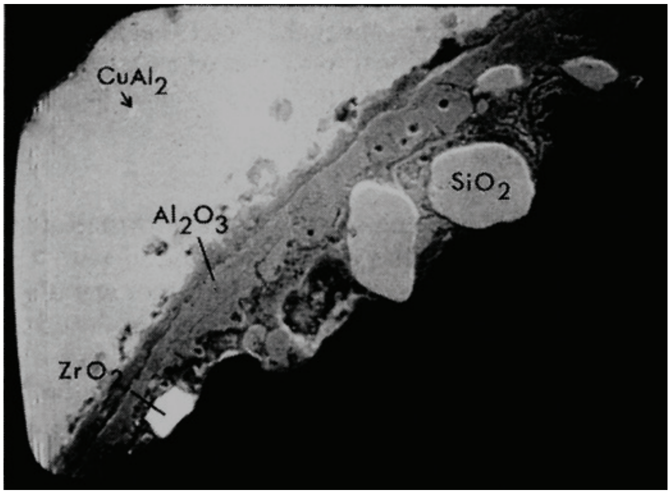

FIGURE 3. SEM image of a concreted section of the *Atlantis* sea-plane float showing pits, a thick oxide coating and adventitious zirconia and silica particles. The $CuAl_2$ intermetallic phases are seen as lighter colored spots. Photo WA Museum, Ian MacLeod.

The low viscosity and surface tension of ammonia in aqueous solutions facilitates the extraction of chlorides from pits and adsorption of SO_4^{2-} ions from the wash solutions actively assists in the hydrolysis of aluminum corrosion products. Ammonia readily reacts with copper (II) corrosion products to form stable $Cu(NH_3)_4^{2+}$ complexes which are no longer available for cementation reactions (Bartonicek and Lukasovska, 1969; Lowson 1974). The addition of ammonia fundamentally changes the thermodynamic stability of the re-deposited copper and allows it to be slowly leached from the surface through reaction with the dissolved oxygen present in the open fiberglass lined concrete tank. The unique positioning of copper in the periodic table permits both Cu (I) and Cu (II) to be stable in aqueous ammonia solutions. The electronic configuration of copper (I) is d^{10} and copper (II) is d^9 which provides good d-Π to p-Π back bonding in the ammonia molecules. The $Cu(NH_3)_4^{2+}$ ion also acts as an oxidant to remove metallic copper from the surface of the corroded metal. In this process the copper tetraammine ion is reduced to $Cu(NH_3)_2^{+}$, which is then oxidized by dissolved oxygen in the treatment bath back to the divalent state, and so the cyclic cleaning of the surface continued. Corrosion potential measurements of the float surface confirmed that the voltages were in the stability range for the copper (I) diammine ion. At the end of the leaching treatment adventitious iron stains from corroded ferrous components were removed by brushing with a solution containing 5wt% oxalic acid and 5wt% EDTA. The leaching buffer solution [NH_3 and $(NH_4)_2SO_4$] treatment used some 30 years ago has proven to be a cost effective method for stopping the cemented copper from accelerating the corrosion of aluminum-copper alloys, since the complex object is very stable today (MacLeod 1983).

IN-SITU CORROSION MEASUREMENTS ON WRECKED WWII AIRCRAFT

The Second World War in the Pacific between the Imperial Japanese Navy and the United States Navy produced thousands of aircraft wrecks, many of which lie in shallow and well oxygenated seawater. A great risk to the preservation of "intact" wrecks is that they appear to be structurally sound but the rolled nature of the aluminum skins and extruded frames makes them subject to significant sheet-like internal corrosion. In this condition of unseen major internal degradation, many well-meaning groups recover the wrecks, and almost without exception these artifacts within a few years are reduced to a pile of corrosion products compared with what once looked like "sound" aircraft. A feature of aircraft that crashed under power is their forward bending propellers; thus, on the wreck of the *Emily*, a flying bomber found in Chuuk (Truk) Lagoon in the Federated States of Micronesia, half of the four the engines were rotating and half were dead when the plane crashed into the sea. In-situ E_{corr} measurements on a series of Japanese aircraft inside the hold of the *Fujikawa Maru* in Chuuk Lagoon showed that the earlier model Claude fighter was skinned with duralumin, while later model Zeros had duplex skins of fusion-bonded pure aluminum on top of a duralumin, which improved their corrosion resistance (MacLeod, 2006).

During work for the US National Parks Service in 2002 and for the Earthwatch Foundation in July 2006, November 2006, and August 2007 a total of 50 sets of measurements were conducted on the wreck of the four-engine *Emily* flying boat bomber in Chuuk Lagoon. The measurements on the *Emily* in Saipan were made by Vicki Richards and Jon Carpenter in 2012 (V. Richards and J. Carpenter, WA Museum, unpublished report). The US Navy code named the aircraft type as an "*Emily,*" but they were Kawanishi H8K flying boats. It was a big shoulder-wing and sturdy aircraft that was well-armed, which flew long-range reconnaissance missions. It had a 38 m wingspan, length 28.13 m and a height of 9.15 meters and was driven by four Mitsubishi MK4Q Kasei 22 fourteen-cylinder air-cooled radials driving four-blade metal propellers. The aircraft crashed into the sea under power and lies several hundred yards off the southwest end of Dublon Island in three separate sections at depths varying from 12.6 to 16.7 meters (Figure 4). Although each set of measurements was done with different sets of equipment, each reference electrode had been calibrated against a secondary standard of the voltage of a pH 4 quinhydrone solution at a platinum electrode, which enabled the data to be directly compared across time. A summary of the results is given in Table 1 which shows that there were five different sets of correlations between the E_{corr} measurements and their observed dependence on water depth. The data was collected on fragmented parts of the massive planes in both Chuuk and Saipan lagoons.

FIGURE 4. Divers record in-situ corrosion parameters on the *Emily* flying boat wreck site in Chuuk Lagoon. Photo: Earthwatch, Bill Jeffery.

The average E_{corr} of parts of the wrecked planes in Chuuk and in Saipan, which had the same dependence on depth, were within 11 mV of each other, as shown by groups 1–3, indicating they had similar elemental compositions. Differences in voltage of ±4 mV is normal between batches of reference electrodes and so the E_{corr} differences are likely due to subtle changes in metallurgical structure during heat treatments and from mechanical deformation processes associated with the crash landing of the aircraft in the sea. The mean value of the corrosion potentials for the *Emily* bomber over five visits to Chuuk Lagoon was −0.469 ± 0.004 and these are associated with the bulk of the fittings on the aircraft that were readily measurable and are consistent with a 4% copper in solid solution which has an E_{corr} of −0.462 volts vs. NHE in seawater (Dix et al., 1975). The corresponding measurements on the plane in Saipan lagoon had a mean value of −0.473 ± 0.002 volts which is experimentally indistinguishable from the Chuuk data. The group 2 from Chuuk had an average E_{corr} of −0.485 is likely to be due to the presence of alloys such as a 4.5% copper in solid solution with 2.5% silicon. The E_{corr} of −0.538 is associated with sections of the plane that were either connected to or were cast alloys, as distinct from rolled sheet or drawn bars, and is experimentally indistinguishable from the E_{corr} of −0.542 volts reported by Dix et al. in the above publication for a cast alloy of 4% copper and 3% silicon.

When the data in Table 1 is viewed as a plot of the E_{corr} at mean depth against the rate at which the E_{corr} changes with depth some interesting trends emerge, as seen in Figure 5. The upper line (diamond shape) is given by the expression,

$$E_{corr} = -0.526 + 0.0073\,x,$$

TABLE 1. Dependence of the E_{corr} on depth for the *Emily* bombers in Chuuk and Saipan Lagoons.

	Group 1	Group 2	Group 3	Group 4	Group 5
Slope mV.m^{-1} Chuuk	7.4	15.0	14.2	13.2	21.4
Slope mV.m^{-1} Saipan	7.5	14.4	15.3		
E_{corr} V vs. NHE at mean depth Chuuk	−0.470	−0.485	−0.468	−0.538	−0.467
E_{corr} V vs. NHE at mean depth Saipan	−0.474	−0.474	−0.464		

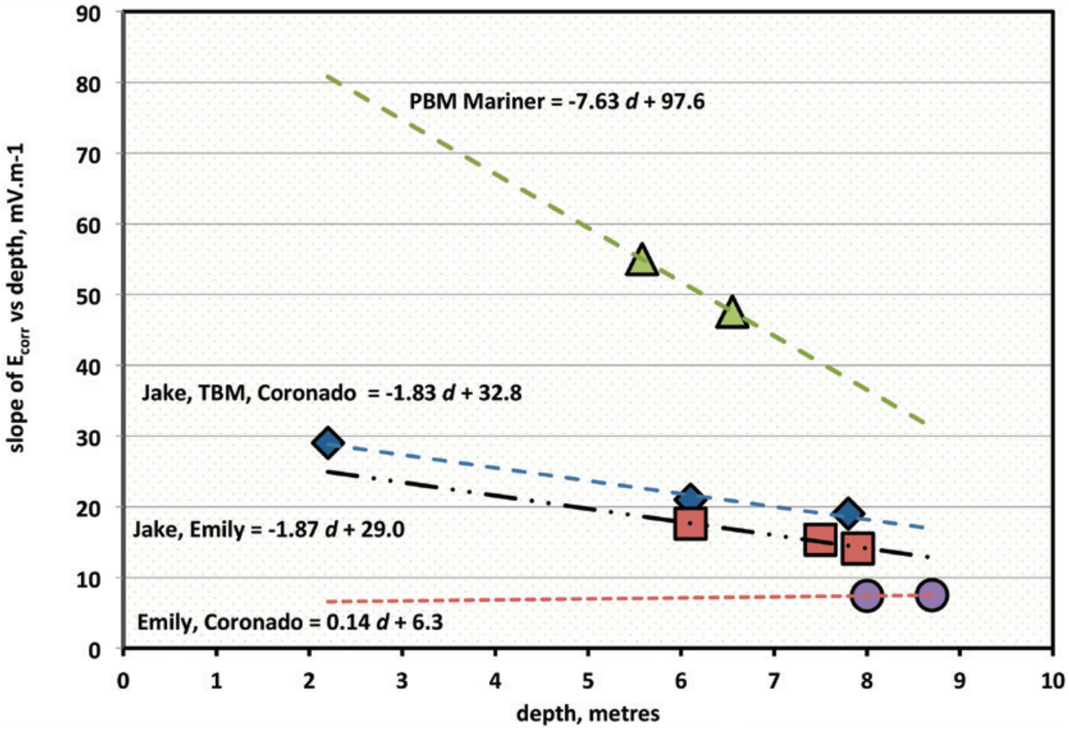

FIGURE 5. Plot of E_{corr} and their dependence on depth across wreck sites in Chuuk and Saipan.

where x is the depth dependence of E_{corr} on depth, in V/meter. The R^2 value for this regression is very high at 0.9984 so there is a high degree of confidence with the data which equates to an error of ±1% in the intercept and ±4% in the slope. The intercept of the relationship, the E_{corr} value at the point where it is independent of depth, is the E_{corr} for a 4.45% Cu, 0.85% Si and 0.4% Mn alloy (Dix et al., 1975). It is important to note that in the above relationship one of the data points was from the Saipan wreck and two measurement points were from the *Emily* in Chuuk Lagoon. The data indicate that the composition of the Al-Cu-Si-Mn alloy used in both planes was the same, which is not all that surprising. It is believed that this relationship shows that the materials from the crashed wrecks have the same composition and that their different sensitivities to water depth are reflections of the differences in the microenvironments. The second set of data (squares) has a mean value of −0.473 ± 0.009 which is typical of the common skin composition on the *Emily* bombers in both Saipan and Chuuk lagoons. The most negative E_{corr} data on the plot (equilateral triangles) of voltage vs. sensitivity to water depth has an intercept that is the same voltage as an aluminum alloy with 5% magnesium in it (Dix et al., 1975). The linear regression for these data points in this group followed the expression

$$E_{corr} = -0.650 + 0.0084\,x.$$

In this equation x is the depth dependence of the E_{corr} at the average depth of the wreck site in volts/meter. This data set had the same very high R^2 value of 0.9984 as the other alloys and all these points came from the *Emily* in Chuuk lagoon. The only reason why these data points were not recorded on the wrecked *Emily* in Saipan is that Richards and Carpenter only had one dive on the site in the 2014 visit (V Richards and J. Carpenter WA Museum, unpublished report). The opportunistic nature of the measurements on the Chuuk wreck site over four dives provided a better chance that all relevant parts of the aircraft would be recorded. The parts of the plane that the data represent are the sections of the aircraft that consisted primarily of cast sections, i.e., nose cones, engine components and other structural elements that were not extruded or rolled duralumin frames and skins. The greater slope of the cast Al-Mg alloy reflects its different composition compared with the Al-Cu-Si-Mn alloy. The difference in the slope of the two relationships, 7.3 and 8.5 mV/meter, is statistically significant at the two sigma level. In addition it is noted that the E_{corr} values measured on the wrecks are stable over a period of at least five years and that similar structural elements on the planes give the same voltage and so the macro-environment of the two wrecks in Chuuk and in Saipan lagoons is essentially the same. The average salinity at Chuuk lagoon was 35.3 ± 0.2 ‰ while the salinity in Saipan was slightly higher at 35.8 ± 0.2 ‰ and the respective temperatures were 29.2 ± 0.8°C and 27.4 ± 0.4°C which gives saturated dissolved oxygen levels of 4.52 ± 0.02 cm^3/liter. However within the corrosion microenvironment the apparent different sensitivities of alloys to depth can be rationalized as indicators of how the different alloys respond to the flux of dissolved oxygen.

There is sufficient data from the reports of the wrecked aircraft in Saipan and in Chuuk to begin to build up a handy reference of the characteristic voltages of different types of alloys that were used in the construction of the planes. From a combination of corrosion research data on aluminum alloys exposed to flowing seawater and archival research on the alloys used in the construction of the war planes on both sides of the Pacific conflict, it should be possible to provide archaeologists with a handy reference tool to aid them in the identification of heavily degraded aircraft wreck sites and to be able to determine whether the remains belong to planes of the Imperial Japanese or the United States Navies (MacLeod and Richards, 2014).

CONCLUSION

Corrosion of aluminum alloys in chloride containing media is a known contributor to the deterioration of cultural heritage objects. Poor design can lead to retention of fluids inside a container, such as hull of the America's Cup winning *Australia* II. When salty liquids and stale urine are combined with an accumulation of galvanically active debris underneath the floor boards accelerated corrosion occurs. Without intervention, this toxic brew would have resulted in hull perforation within two months. Rinsing with deionized water and soaking in a chromate bath were equally ineffective treatments of the hull plates. Soaking in several hundred liters of sodium silicate removed large amounts of chloride and stopped the pitting reaction.

A review of the surface of the duralumin *Atlantis* sea plane float from a Junkers W33 seaplane 30 years after treatment showed that the leaching of re-deposited copper and removal of chloride ions had been effective at corrosion prevention. Immersion of the float in $NH_3/(NH_4)_2SO_4$ solutions at pH 9.6 was effective because the alkaline solution helped flush out chloride ions from the pits and the ammonia changed the chemistry of copper from being a noble metal to one that was kinetically happy to dissolve and leave the surface of the aluminum alloy intact. When large electrolysis tanks are not available the $NH_3/(NH_4)_2SO_4$ leaching of corroded duralumin alloys is a cheap and effective method of stabilizing these culturally important items.

Analysis of a large Second World War wrecked aircraft in the ocean is a challenge due to operational constraints of diving time and access to the former military aircraft in locations which are normally remote from conservation laboratories and equipment. Collation of more than 50 sets of in-situ corrosion measurements on the *Emily* aerial reconnaissance flying boat from the Imperial Japanese Navy in Chuuk (Truk) Lagoon, Federated States of Micronesia, has established a new understanding of the long-term stability of E_{corr} values over 5 years. Additional data on the same type of aircraft wrecked in Saipan provided another 16 sets of readings of pH and corrosion potential as a function of water depth. Despite the opportunistic nature of the selection of measurement points, many key structures were measured several times and their E_{corr} values were steady indicating that after 60 years of immersion corrosion had reached a steady state. Comparison of data from the Saipan wreck has shown that the remains of the aircraft are corroding in the same fashion and that similar aluminum alloys were used in their construction. Literature values of the E_{corr} of aluminum alloys indicated that it is possible to characterize a wrecked aircraft from the analysis of the corrosion potentials of the fragmented remains. The apparently varying sensitivities of the aluminum alloys from both wreck sites in the Pacific Ocean have been shown that the microenvironment of the metals is consistent with the response of aluminum alloys to the flux of dissolved oxygen. Data analysis indicates that the most common alloys used in the construction of the *Emily* bombers were very similar in corrosion characteristics to duralumin style alloys, cast Al-4% Mg and wrought 4.4% Cu, 0.8% Si and 0.4% Mn alloys.

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Corrosion Characteristics of 3000 Series Aluminum Alloy Exposed in Different Climatic Conditions of India

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ABSTRACT. Corrosion characteristics of 3003 Aluminum alloy had been investigated by exposing samples under different climatic and pollution zones of India, namely Jamshedpur, New Delhi, Lucknow, Mumbai, Nagpur, Kolkata, Chennai and Palampur. Results indicated that amongst all the studied locations, the alloy corrodes at the highest and lowest rates respectively at New Delhi and Palampur. The presence of pollutants in the atmosphere, especially particulate matter under 10-micron size (PM_{10}), are noted to have maximum influence on the acceleration of corrosion rates. Electrochemical impedance spectroscopy (EIS) and direct current (DC) anodic polarization studies show that the film formed on metal surfaces exposed at Palampur was very protective. The samples exposed at New Delhi had a non-protective film and were prone to pitting corrosion. Raman spectroscopy was performed to characterize the corrosion products formed on the metal samples exposed at different locations. The film formed on the surface of the samples exposed at New Delhi had pitted layers of alumina, aluminum nitrate and sulfate of aluminum. In contrast, the Palampur exposed samples had a very uniform layer of alumina.

Keywords: aluminum alloy, atmospheric corrosion, India, electrochemical impedance spectroscopy

INTRODUCTION

Aluminum and its alloys are considered to be the materials of the future era. Their un-paralleled inherent properties such as being light weight, corrosion resistant, conductive, good formability and recyclable, vis-a-vis other available metals and materials bring them into the category of a standalone metal. Light weight and good formability as well as excellent strength make the alloys of aluminum very attractive for use in automobile bodies, utensils, electrical conductors, packaging materials, and many more. Due to the difficulty in refining the metal from its ore (bauxite) jewelry, cutlery and other items made from aluminum were initially considered as luxury items and available only for the well-to-do. After the discovery of a way to process and refine aluminum by electrolysis by the end of nineteenth century, the metal became one of the cheapest and most useful alloys for everyone to use (Hall and Héroult, 1983).

The corrosion resistance of pure aluminum is high, due to the formation of a very protective, compact and adherent alumina film on its surface. However, aluminum alloys suffer greatly from corrosive attacks in different types of environments. Being amphoteric in nature, the alumina film dissolves in acidic as well as in alkaline environments

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(Lindsay and Walthall, 1989). The presence of salinity and pollutants in the environment also deteriorates the passive film formed on the surface of aluminum and its alloys. Atmospheric pollutants such as SO_2, NO_x, and particulate matter greatly affect the nature of protective film formed on the surface. Keeping in view the wide spread applications of aluminum and its alloys in the making of utilitarian and other decorative items and the fact that they get exposed to varying degrees of environmental and climatic conditions during storage and use, it was proposed to study the corrosion characteristics of an important alloy of aluminum, namely 3003- a wrought aluminum-manganese alloy. This alloy is used in different parts of India having a great variability to environmental and climatic conditions. This type of alloy (designated as the 3000 series of alloy) exhibits high formability, corrosion resistance, joinability, medium strength (ultimate tensile strength range: 16–41 ksi) and is widely used for different applications such as in different types of tubings, aircraft components, builders' hardware, pressure vessels, storage tanks, heat exchangers etc. This paper explores the corrosion rate of this alloy and discusses the mechanism for the formation and deterioration of the film formed on aluminum coupons exposed at different locations of India. Although the data are generated by exposing these coupons in nine different pollution zones of India, the results may be extrapolated for the performance of the aluminum alloy exposed in other parts of the world where the pollution and climatic conditions are comparable to the places chosen in the present study.

EXPERIMENTAL PROCEDURE

The primary experiment of this study was the exposure of nine sets of coupons at different geographic locations of India. These locations were chosen because they represent different types of atmospheres where pollution levels in the air varied considerably. Mumbai is highly humid and saline, New Delhi is urban and polluted, Jamshedpur is industrially polluted and Chennai is the zone where all three of the above environments, namely coastal + urban + industrial pollutants exist. In contrast, Palampur is a location where pollution in the air is the lowest. Since the corrosion rate of the exposed coupons was determined after one and two years of exposure at these different sites, it was more pertinent to present pollution data as yearly averages, rather than monthly.

Samples in triplicate were exposed in the atmosphere of various cities of India namely Jamshedpur, New Delhi, Lucknow, Mumbai, Kolkata, Nagpur, Chennai, Palampur and Jorhat for durations of 1 and 2 years (January 2010 to December 2011). The locations of exposure sites are marked on the map of India as shown in figure 1. After the exposure period of 1 and 2 years, three sets of the coupons were taken out from the racks and brought into the laboratory for characterization.

The procedure for the atmospheric exposure tests followed the procedure as described in ASTMG50-76 (1992). The corrosion products on the exposed metal coupons were cleaned as recommended in ASTM-G1-90.

METAL COUPON PREPARATION

3000 grade aluminum alloy with nominal composition of Mn = 1.45%, Si = 0. 62%, Cu = 0.15%, Zn = 0.09%, balance Al, in sheet form was used to generate the data. The metal coupons of size 150 mm × 100 mm × 1 mm were hexa-cut from sheets. The surface of the coupons were belt polished and degreased in acetone prior to fixing them on exposure racks. The coupons were fixed to the racks utilizing porcelain insulators and brass hexagonal nuts and bolts to avoid galvanic contacts. The entire set of coupons were exposed on the steel racks fixed at an angle of 45° facing south.

RAMAN SPECTROSCOPY

After 1 and 2 years of exposure, the coupons were collected from the exposure sites and the corrosion products and passive films formed on their surfaces were characterized by Raman spectroscopy. Raman spectroscopy of exposed samples (bearing corrosion products) were performed by using an Almega dispersive Raman Spectroscope by exciting the He-Ne laser beam of 532 nm wavelength on the samples. The power of the laser was kept as low as possible (6 mw) to avoid the transformation of corrosion products due to the heating effect of the laser. The locations of the metal coupons to be studied were focused through an Olympus microscope at the magnification of 50. The sample holder had a motorized platform with the ability to jockey to a fine focus at a suitably desired part of the sample. The grating was 672 lines/mm, 25µm pinhole. Prior to the analysis of the coupons, the instrument was calibrated by using pure Silicon at the peak of 522.28 cm^{-1}. It is to be noted that to avoid repetition, the characterization of results of the films formed on the coupons, were exposed only at the most and least corrosive places are recorded in this paper.

DETERMINING RATES OF CORROSION

To determine the rate of corrosion, the corrosion products formed on the surface of the coupons were cleaned as described in ASTM G1-90. The average corrosion rates of three coupons exposed at the above stated locations were determined. The corrosion rates of different exposed samples varied in the range of 1.5% to 2.5%. The data were generated by performing three types of analyses; namely mass loss of coupons exposed at different locations, electrochemical tests and Raman spectroscopy of corrosion products formed on the surface of exposed coupons.

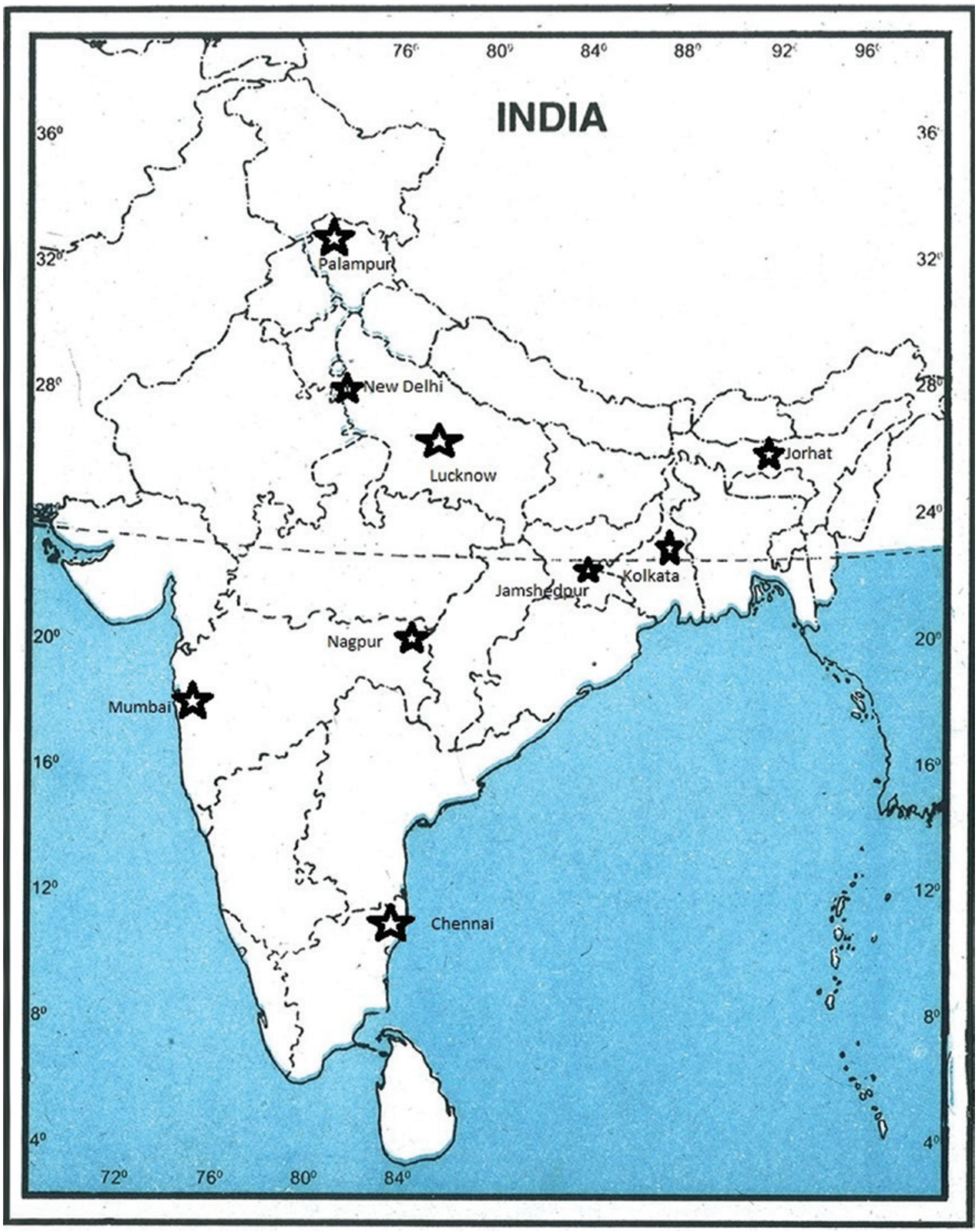


FIGURE 1. Sites of exposure of coupons at different locations of India. The location sites are indicated by star.

ELECTROCHEMICAL TEST

Electrochemical tests on the previously exposed coupons were carried out after exposing them in 1% sodium chloride solution for 2 hours (within this period of exposure in the chloride solution the steady state corrosion potentials of the coupons were stabilized. This helped to assess the protective properties of the film formed on the surface during the period of exposure at the different sites. For the sake of comparison, a control set of samples from each batch preserved in a desiccator in the laboratory were also tested.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

The electrochemical impedance spectroscopy (EIS) studies were performed by imposing 10 mV of sinusoidal voltage (with reference to open circuit potential) at the working electrode of the specimens (area of 2 cm^2) and varying the frequency from 100 KHz to 0.001 Hz. The polarization studies were performed at a scan rate of 0.1mv/sec. The electrochemical studies were carried out in a flex cell, exposing the working electrode to an area of 2 cm^2. Two graphite rods at two sides of the working electrode were fitted, acting as auxiliary electrodes. The reference electrode was a saturated calomel electrode (SCE). A lugging capillary was used to provide electrolytic contact between the calomel electrode and electrochemical cell. All the tests were performed at the temperature 30 ± 2°C. Electrochemical studies were conducted using a Gamry Potentiostat (supplied by M/S Gamry Instruments of USA).

RESULTS AND DISCUSSION

Corrosion rates of exposed aluminum alloy 3003 at different locations of India for the 1st and 2nd years of exposure are shown in Table 1. It is evident from the table, that the highest corrosion rate is noted at New Delhi, whereas the lowest corrosion rate is observed for Palampur during the 1st year of exposure. The trend is almost the same for the 2nd year of exposed samples, except at certain locations such as New Delhi, Mumbai and Lucknow, where the corrosion rate is observed to increase during the 2nd year of exposure. At other locations, the corrosion rate is inhibited during the second year of exposure. The increased corrosion rate of aluminum over time is uncommon, except in very corrosive environments where salinity and pollution in the atmosphere are very high.

Typical photographs of corroded samples exposed at New Delhi during the first and second years of exposure are presented in figure 2. Closer observations of the images illustrates that a localized type of attack has initiated during the first year of exposure (figure 2(a)) which became more visible after the second year (figure 2 (b)) of exposure. A similar trend was also noted for the coupons of Mumbai and Lucknow where enhanced rates of corrosion were recorded during the 2nd year of exposure.

The Palampur exposed coupons exhibit a decrease in corrosion rate over the passage of time, as recorded (Table 1) and did not show any trace of pitting on their surface. These results show that the increased rate of corrosion of the alloy over time exposed at New Delhi, Mumbai and Lucknow was related with the formation of an unstable film on its surface. This was confirmed by conducting Raman spectroscopy of the corrosion products formed on the surface of the exposed coupons. This aspect will be discussed more in detail in subsequent paragraphs.

The formation of a non-protective film on the aluminum alloy and its increased rate of corrosion over time at New Delhi, Mumbai and Lucknow may be linked with the pollution data generated at these sites during the periods of exposure. The pollution load in terms of SO_2, NO_2 and PM_{10} expressed in μg/m^3 are shown in Table 2.

It is evident from this table that SO_2 and NO_2 levels at New Delhi and Mumbai are within the acceptable limit, however the values for PM_{10} are alarmingly high at New Delhi, Lucknow and Mumbai in comparison to the other places. The PM_{10} in the environment is generated due to the burning of fossil fuels. The fine particles may incorporate various types of aggressive, ionic and molecular species and become deposited on the exposed specimens and act as a reservoir for moisture, chlorides and gases. Amongst the various aggressive materials, chlorides are the most harmful to the aluminum surface. This effect is manifested from the highest increased corrosion rate data observed at Mumbai. This is likely due to Mumbai's location by the sea. The proximity to sea air carries chloride-laden moisture, which is deposited on the surface of the exposed coupons.

The higher rate of corrosion at New Delhi is attributed to a high level of PM_{10}. New Delhi and its surrounding areas contain a cluster of industries and many of them are metal foundries who use fossil fuels as energy. It is reported that the majority of constituents in burnt fossil fuels are sulfur, silica, and iron oxides (Pollution Prevention and Abatement Handbook). These constituents generate an acidic environment, which tends to dissolve the protective alumina film formed on aluminum surfaces (Mears, 1976). Vernon has reported a synergism between SO_2 and particulate matter in accelerating the corrosion rate of metals and alloys. The very low corrosion rate recorded at Palampur located in the northern part of India, which is very thinly populated, cold and situated in a valley of the Himalaya, is attributed

TABLE 1. Corrosion rate (μm/year) of aluminum alloy exposed at different locations of India for 1st and 2nd year of exposure.

	Corrosion rate of metals/alloys (μm/year)							
Year	New Delhi	Lucknow	Mumbai	Nagpur	Jamshedpur	Chennai	Kolkata	Palampur
1	0.805	0.15	0.38	0.32	0.43	0.47	0.46	0.08
2	1.08	0.24	0.78	0.09	0.21	0.03	0.18	0.006

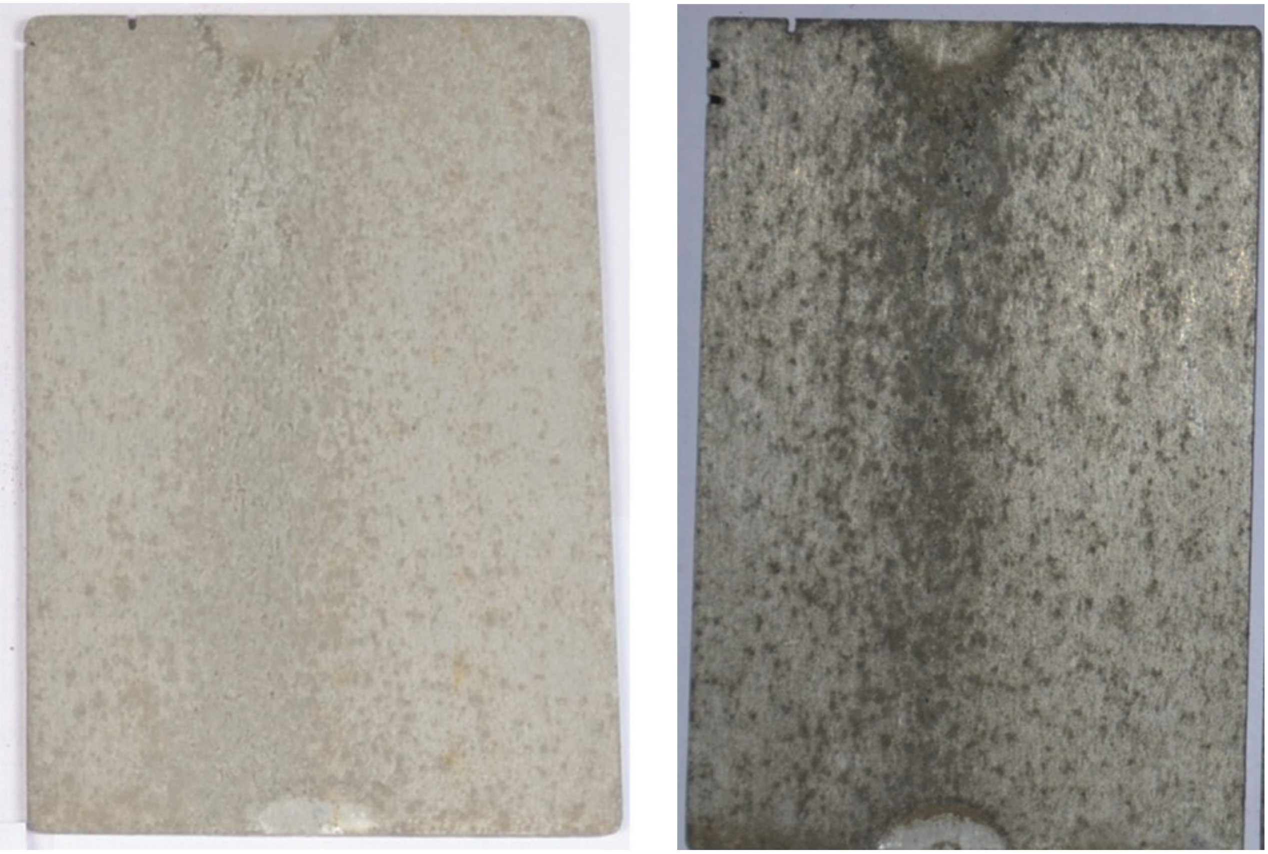


FIGURE 2. Images of corroded coupons after first year (a) and second year (b) of their exposure at New Delhi.

TABLE 2. Average pollution data (μg/m^3) collected from six locations in India from 2010 to 2012.

Locations	Year	SO_2	NO_2	PM_{10}
New Delhi	2010	5	55	261
	2011	6	61	222
Lucknow	2010	8	34	204
	2011	8	33	189
Mumbai	2010	4	19	97
	2011	5	33	116
Nagpur	2010	7	33	113
	2011	8	35	108
Jamshedpur	2010	35	48	153
	2011	36	48	152
Chennai	2010	9	15	59
	2011	9	24	92

to a comparatively clean environment at this site of exposure. Since no pollution monitoring system was installed at this location the pollution data of this location was not available.

To assess the protective properties of the film formed on the samples exposed at the most and least corrosive environments (New Delhi/Mumbai and Palampur respectively), electrochemical Bode log frequency – log modulus impedance plots for the exposed samples tested in a 1% Sodium chloride solution and the results are shown in figure 4.

The impedance values at a frequency approaching zero ($Imp_f \rightarrow 0$) in Bode's impedance plot is considered as polarization resistance (R_p) for the corroding interface. The R_p is related to corrosion current density (I_{corr}) by the Stearn – Geary equation:

$$I_{corr} = \frac{\beta_a \times \beta_c}{2.3(\beta_a + \beta_c) \times R_p} \tag{1}$$

Where β_a and β_c are respectively anodic and cathodic Tafel slopes. Thus, the higher the value of polarization resistance, the lower the corrosion rate.

It is seen from the above-mentioned figure 3(a) that the impedance value at the lowest frequency i.e. 0.01 Hz is the highest for the exposed samples of Palampur, followed by Mumbai and New Delhi. These results indicate that the protective film formed on the samples exposed at Palampur was considerably higher in comparison to the other two locations i.e. New Delhi and Mumbai. The log frequency – phase plots shown in figure 3(b) for the Palampur sample exhibits a single maxima at about 10 Hz. The Mumbai and Delhi exposed samples and the reference sample (shown as blank) show two maxima, one at 0.05 Hz and the other in the range of 10–50 Hz. According to the impedance theory, a pure capacitor and resistor exhibit maxima at –90°. However, in the present case, the maxima for all the samples, except that of Palampur, are noted at around –60°. The maxima noted in the impedance plots in the range of these phase angles are treated with a constant phase element in the equivalent circuit of the corroding interfaces. This is attributed to the distribution of defects and pore sizes in the film formed on the surface of the alloy exposed at Mumbai and New Delhi and the reference (blank) coupon. The Palampur exposed coupons have no such defects or pores and exhibit entirely different impedance plots.

The potentiodynamic tests on coupons removed after their two years of exposure were tested in a 1% sodium chloride solution and plots are shown in figure 4. The anodic part of the plots show that the New Delhi exposed samples exhibit a spontaneous increase in current starting from its corrosion potential. The plot for the Palampur exposed sample shows a strong polarizing tendency starting from its corrosion potential. A depolarizing anodic reaction of New Delhi exposed samples indicate that the corrosion products formed on its surface had an accelerating effect on the ionization of the aluminum metal into its cations. It will be evident from the Raman spectroscopy of the New Delhi exposed samples, described in the subsequent paragraphs that a conducting and non-protective layer of aluminum sulfate had formed on the surface of the metal exposed at this location.

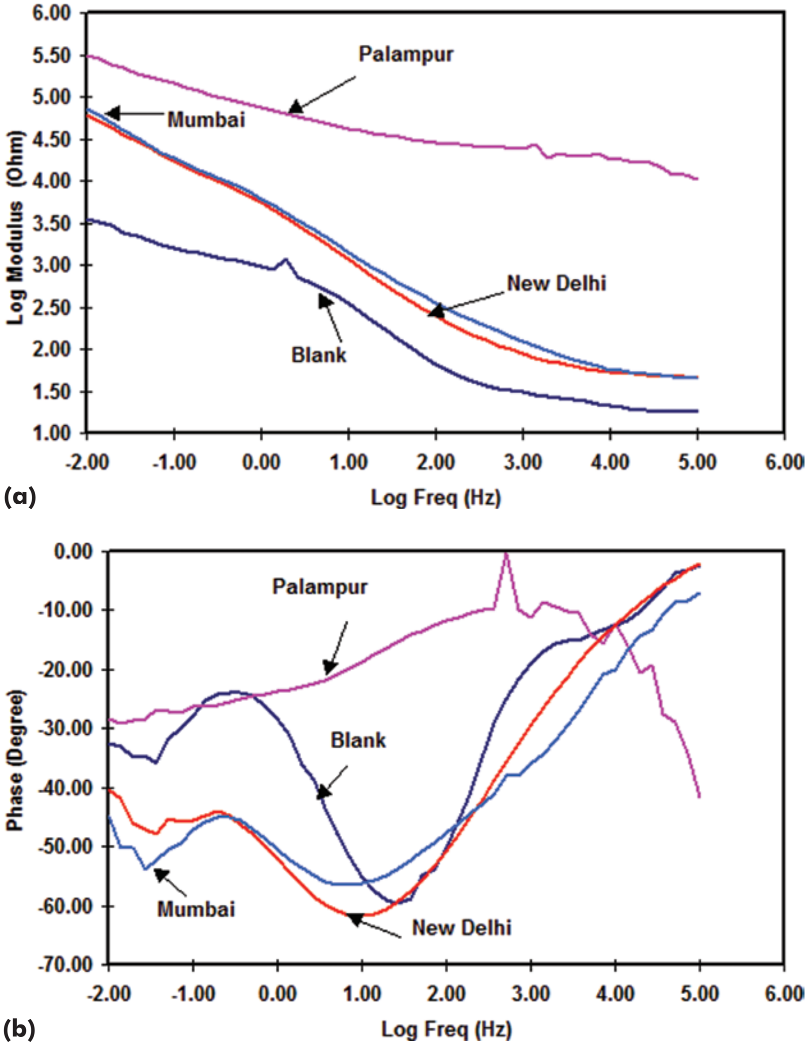


FIGURE 3. (a) Electrochemical Bode frequency, log modulus impedance plots for the exposed samples tested in 1% Sodium chloride solution. (b) Electrochemical Bode log frequency, phase plots for the exposed samples tested in 1% Sodium chloride solution.

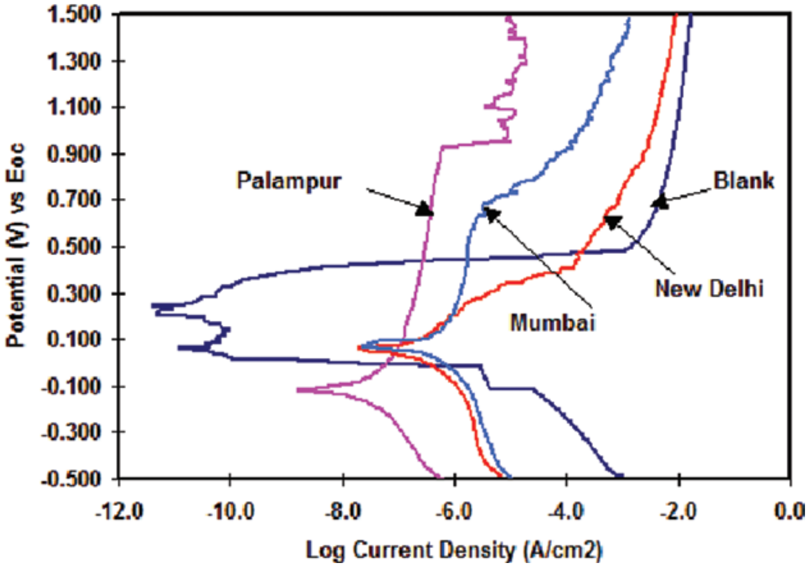
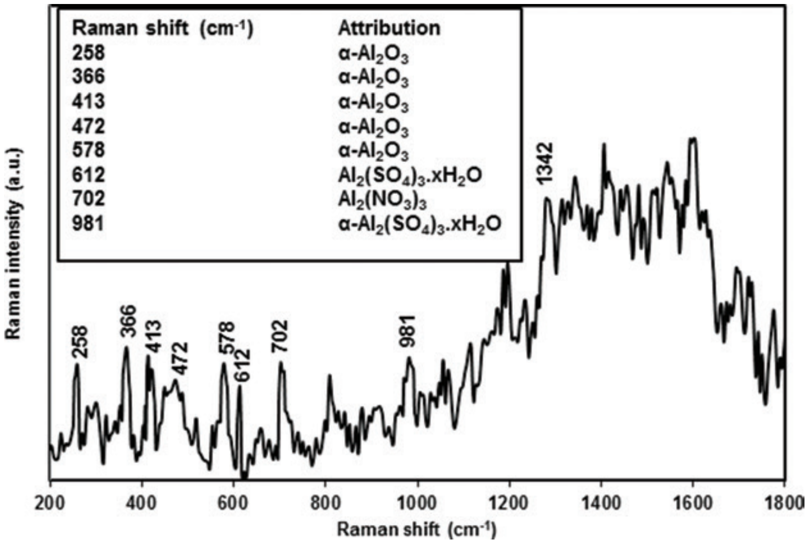


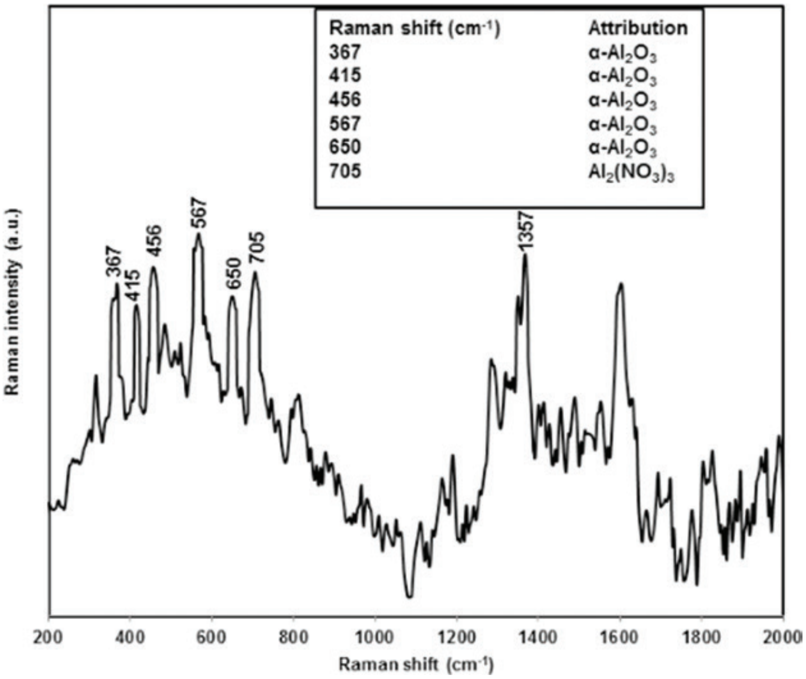
FIGURE 4. Aluminum plate removed after 2 years of exposure from different locations of India and potentiodynamic studies carried out in 1% NaCl solution after 2 hours of their exposure in the test electrolyte.

Raman spectroscopy for the corrosion products accumulated on samples at different locations as shown in figures 5–7 and their attribution to the observed peaks are embedded in corresponding figures. It is seen from these figures that in addition to the presence of alumina, which is a common corrosion product formed on aluminum and its alloys, many peaks attributed to aluminum sulfate and aluminum nitrate are recorded from samples exposed at New Delhi and Mumbai. It appears that the presence of these aggressive materials that came from the burning of fossil fuels is responsible for the accelerated corrosion rate observed at New Delhi. The corrosion products formed at Mumbai exhibit the peaks of alumina and aluminum nitrate. On comparing the peaks of the spectra of New Delhi and Mumbai exposed samples with that of Palampur it becomes evident that the Palampur samples have developed the only peaks of α-Al_2O_3 (alumina). No peaks corresponding to aluminum sulfate or nitrate are recorded on these samples. These findings suggest that the formation of soluble and conducting aluminum compounds on exposed surfaces were responsible for the enhanced corrosion rate of metal at New Delhi and Mumbai. A compact and defect free alumina film formed on exposed samples at Palampur protected the exposed samples and brought down the corrosion rate by more than one decade in comparison to the samples exposed at the other places. It is reported that aluminum sulfate is a very common corrosion product formed on the surface of aluminum and its alloys exposed in corrosive environments (Zhenhua Dan, Izumi Muto and Nobuyoshi Hara) (Graedel T.E., 1989), (Barton K., 1976). During the initial period of exposure, carbonate and other salts are nucleated on the surface followed by the formation of sulfate. During indoor storage of aluminum,



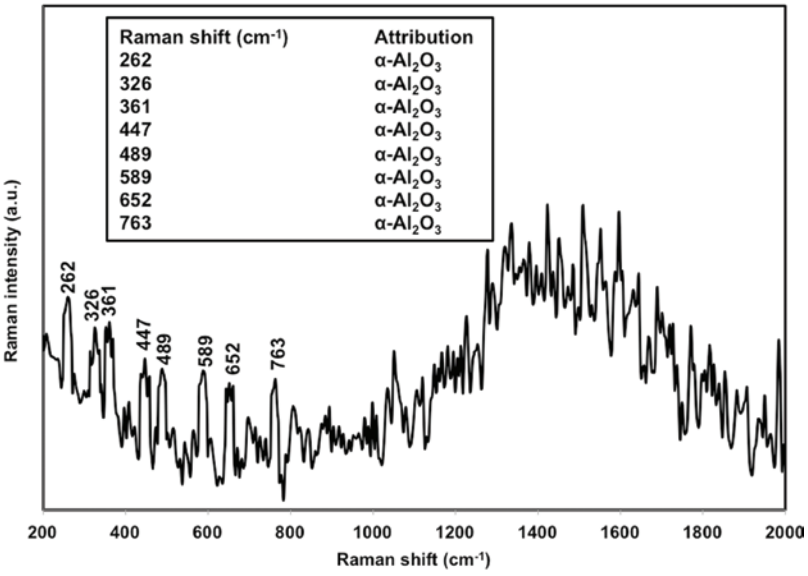
Raman shift (cm-1)	Attribution
258	α-Al_2O_3
366	α-Al_2O_3
413	α-Al_2O_3
472	α-Al_2O_3
578	α-Al_2O_3
612	$Al_2(SO_4)_3.xH_2O$
702	$Al_2(NO_3)_3$
981	α-$Al_2(SO_4)_3.xH_2O$

FIGURE 5. Raman spectra of corrosion products formed on aluminum alloy after removal from New Delhi.



Raman shift (cm⁻¹)	Attribution
367	α-Al_2O_3
415	α-Al_2O_3
456	α-Al_2O_3
567	α-Al_2O_3
650	α-Al_2O_3
705	$Al_2(NO_3)_3$

FIGURE 6. Raman spectra of corrosion products formed on aluminum alloy after removal from Mumbai.



Raman shift (cm⁻¹)	Attribution
262	α-Al_2O_3
326	α-Al_2O_3
361	α-Al_2O_3
447	α-Al_2O_3
489	α-Al_2O_3
589	α-Al_2O_3
652	α-Al_2O_3
763	α-Al_2O_3

FIGURE 7. Raman spectra of corrosion products formed on aluminum alloy after removal from Palampur.

ammonium (sulfate is the most common chemical ingredient deposited on their surface (Sinclair and Psota-Kelty, 1984). This deposition of anion may come either from SO_2 assisted corrosion or due to deposition of sulfate salts with particulate matters. Ammonium sulfate absorbs moisture from the atmosphere and after attaining saturation level it hydrolyses to generate acidic ammonium bi sulfate salt (Nikolic Cvetko, 1971) (Lobnig R.E., D. J. Siconolfi, J. Maisano, G. Grundmeier, H. Sfreckel, R. P. FrankenthaI, M. Stratmann, and J. D. Sinclair, 1986)

$$(NH_4)_2\,SO_4 \rightarrow NH_4HSO_4 + NH_3 \tag{2}$$

$$3Al_2(SO_4)_3 + 9H_2O \rightarrow 3Al_2O_3 + 9H_2SO_4 \tag{3}$$

In the active pH range, the alumina film formed on the aluminum surface and also the parent metal dissolve resulting in a localized increase in pH:

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O \tag{4}$$

$$4Al + 3O_2 + 12H^+ \rightarrow 4Al^{3+} + 6H_2O \tag{5}$$

$$Al + 3H_2O \rightarrow Al^{3+} + 3/2H_2 + 3OH^- \tag{6}$$

The dissolved aluminum ion or metallic aluminum reacts with $(NH_4)_2SO_4$ or ammonium bi sulfate (NH_4HSO_4) to form aluminum sulfate (Lobnig et al., 1986).

The mechanism suggested above appears to be validated in the present case. In corrosive environments of New Delhi and Mumbai, where the PM_{10} content in the environment are quite considerable, the corrosion products identified by the Raman spectroscopy on the surface of the exposed coupons are predominantly $Al_2(SO_4)_3$ (figures 5 and 6). This proposed mechanism was further established by analyzing samples from the corrosion products formed on the coupons exposed in aggressively corrosive environments by X-ray diffraction and scanning electron microscopy (*Pandya Achal et al*., 2015). The results observed by these authors showed that apart from aluminum sulfate, the phases of alumina and aluminum hydroxides also form on the exposed samples. The formation of aluminum hydroxide may form subsequent to the reaction (6) above and may be written as:

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \quad (7)$$

CONCLUSIONS

The corrosion rate of 3003 grade aluminum alloy exposed in different locations of India varies with the pollutants' load in the environment. It is noted that PM_{10} content in the environment has a dominant role on corrosion and the pitting attack on the studied alloy. It is suggested that the fine particulate matter deposited on the exposed coupons acts as a reservoir of corroding species by absorbing corrosive gases, moisture and anion and cation particles, resulting in the formation of corrosion cells. Amongst the studied places, the corrosion rate is the highest at New Delhi and lowest at Palampur. Electrochemical studies reveal the formation of a porous and poorly protective film on the surface of New Delhi and Mumbai exposed samples but a very compact and protective film on the Palampur exposed samples. Raman spectroscopy reveals the formation of a pure alumina film on samples exposed at Palampur but a defective film comprising of alumina and sulfate and nitrate of aluminum on New Delhi and Mumbai exposed specimens.

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The History of Orbiter Corrosion Control (1981–2011)

Richard W. Russell

ABSTRACT. This paper provides an outline of the history of the remarkable Orbiter Space Shuttles, which served America's space program tremendously for three decades, three times their designed life. The emphasis is on issues related to the use and maintenance of the spacecraft. The paper highlights problematic areas prone to corrosion, inspection methods, and how design and unanticipated events factored into the growth of corrosion. A brief discussion of corrosion preventive compounds tested for the preservation of components is included in addition to a discussion of the aging behavior of the primer used on the Orbiter. The goals, processes and accomplishments of the Corrosion Control Review Board (CCRB) are described in detail.

What made the Orbiter unique was its thermal protection and other systems designed for operation over a wide range of temperatures, pressures and stresses. Additionally, the Orbiter spent a good portion of its life in one of the world's most aggressive seacoast environments. A final challenge was that the Orbiter's structure and systems were not necessarily designed to be inspected or repaired.

Keywords: Space Shuttle, Orbiter, Corrosion, NASA

INTRODUCTION

The Space Shuttle Orbiter is a truly remarkable vehicle (Figure 1). As the first orbital spacecraft fleet designed for reuse, it was projected to have a life of 10 years or 100 missions but in fact served America's space program for three decades or three times the designed time span. The total number of missions was 135; with none of the space shuttle vehicles flying more than 39 missions.

The Orbiter is a complex vehicle, but its basic construction is not much different than a typical aircraft. What made the Orbiter unique was its thermal protection and other systems designed to operate over a wide range of temperatures, pressures and stresses. Additionally, the Orbiter spent a good portion of its life in Florida, one of the world's seacoast environments most aggressive to metals. Another challenge was the fact that the Orbiter's structure and systems were not necessarily designed to be inspected.

DESIGN CONSIDERATIONS

Many factors were taken into consideration when the original corrosion protection scheme for the Orbiters was developed by NASA (NASA, 1995). The majority of the Orbiter's life would be spent in Florida processing facilities, which were temperature and humidity controlled. However, when each vehicle moved to the launch pad, it would be subjected to almost constant salt spray from the ocean. High humidity would also allow for

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FIGURE 1. The Space Shuttle Atlantis on orbit.

the formation of condensation on all surfaces open to the atmosphere. While the condensation would evaporate in the vacuum of space, corrosive residues would be left behind. After landing, the Orbiter would be de-serviced and again exposed to harsh exterior environments. The duration of exposure would depend on the landing site. If the Orbiter landed away from the Kennedy Space Center in Florida, a ferry flight would be required, which would expose the vehicle to additional uncontrolled environments.

A detailed material control and corrosion protection plan developed by Rockwell, the design contractor, required an ‘A’ rating for corrosion and specifically stress corrosion of all materials. Metallic materials were required to meet MSFC-SPEC-250A (1977), class II requirements. If a material could not meet these requirements, it was evaluated and approved based on its use, location or protection scheme. The guideline document for stress corrosion cracking was MSFC-SPEC-522 (1987).

Galvanically dissimilar materials were required to not be in contact unless suitably protected against electrolytic corrosion. Faying surfaces of dissimilar metals were required to be sealed against water intrusion, or they were separated with a layer of corrosion-inhibiting epoxy or room-temperature vulcanized (RTV) silicone rubber. All fasteners were to be installed with a chromate epoxy primer. Special design features were to be implemented, such as a dry nitrogen gas purge system for interior spaces and drain holes to prevent water accumulation.

UNANTICIPATED EVENTS

As would be expected in any long-term operational program, unanticipated events occurred. The normal anticipated launch pad stay was approximately 31 days. However, flight delays often extended stays in the harsh coastal atmosphere. For example, Columbia spent 166 days at the pad prior to its tenth flight. This caused concern for the protection of exterior or unpurged areas such as the rubber speed brake, wing leading edge spar and external tank doors.

Other anticipated events included frequent use of the pad’s Firex system, which is activated when potential fire hazards are present. On one occasion, the Firex system was inadvertently activated in the Orbiter processing facility causing copious amounts of water to cover the Orbiter. A greater than expected amount of water intrusion was found during pad stays, ferry flight and mate/demate operations at the landing facilities. Finally, there were several cases of unanticipated spillage of hypergolic fuels and oxidizers.

CORROSION CONTROL REVIEW BOARD

In 1993, after approximately 10 years of operation, a Corrosion Control Review Board (CCRB) was formed by Orbiter management. The goals of the CCRB included assessment of the extent and causes of corrosion, the provision of both long term and short-term corrective actions, the generation and maintenance of an historical corrosion database, the development and implementation of methods for the detection of corrosion, and the development and implementation of corrosion training and certification programs.

The CCRB drew its core membership from the materials and processes discipline, Safety and Mission Assurance (S&MA) Engineers at the National Aeronautics and Space Administration (NASA), and the prime contractors. The CCRB also received regular support from structural engineers and specialists in the fields of chemistry, materials science and non-destructive evaluation at various NASA organizations.

The majority of corrosion inspections on the Orbiter were performed visually. Most inspections were documented in the airframe inspection section of the Operations Maintenance Requirements and Specification Document (OMRSD). Visual inspections were performed using aids such as flashlights, 5x–10x magnification, mirrors and borescopes. Requirements specified visual inspection not further than 18 inches away from surfaces. In some case removal of components and/or surface cleaning was necessary.

LIFE EXTENSION

The Orbiter project went through two major efforts to evaluate life extension beyond ten years. The first effort extended the Orbiter life to 20 years and the second to 30 years and beyond. During the second effort a program titled Aging Vehicle Assessment (AVA) was instituted, which included a separate corrosion control assessment partnered and directed by CCRB members from The United Space Alliance and Boeing. The AVA program provided a complete review of the Orbiter's corrosion control program and an extensive list of products for the remainder of the program (Russell, 2007).

Activities of the AVA program included a baselining effort to establish a starting point from which to compare corrosion. Next, prioritization was given to identifying and evaluating the top recurring corrosion problem areas. Prevention and detection methods were studied, and reaction and mitigation practices were evaluated. Patterns and trending were reevaluated, and upgrades to the database were made.

CCRB ACCOMPLISHMENTS

One of the cornerstone objectives of the CCRB was to suggest and implement improvements to process, tools and other means that would lead to life extension. One of the first tools developed in the early 1990s was the corrosion database, which represented an historical review of all Orbiter problem reports and corrective actions. The database was designed to be easily searched by keyword, and each entry was screened by CCRB members to assure adequacy.

The CCRB decided that visual inspection was adequate for general inspection, but it assisted in the development of specialized corrosion inspection training to assure consistency. For critical structural inspections, only inspectors who had received this specialized training were allowed to perform inspections.

In some cases, the CCRB advocated for more advanced non-destructive evaluation techniques, including eddy current, ultrasonic, dye penetrant, x-radiographic, infrared thermographic and terahertz testing. For example, eddy current was used for evaluation of corroded fastener collars, ultrasonic testing for internal corrosion of cold plates, infrared thermography for corrosion under paint, and terahertz imaging for corrosion under thermal protection tiles.

To further enhance operations the CCRB developed standard corrosion repair procedures consistent with commercial and military aviation practices (NASA, 1997). The procedures included specific instructions on the evaluation of corrosion, removal of corrosion by chemical or physical means, and repair of damaged areas.

CORROSION PREVENTATIVE COMPOUNDS (CPCS)

The use of corrosion preventative compounds (CPCs) is common in military and commercial aviation (Boeing, 2005). A CPC is a coating such as an oil or grease that provides corrosion inhibiting properties. For a CPC to be used on the Orbiter, it had to be stable in a space environment and not leave behind products that could contaminate the surfaces, and potential corrosion sites also had to be accessible. After a review of commercially available products, ten were selected for testing on aluminum alloy coupons. Testing included salt spray after vacuum exposure, seaside exposure, flammability, hypergolic compatibility, liquid oxygen compatibility and outgassing.

Based on the initial testing, three CPCs were selected for test application on Orbiters. A waxy hydrocarbon material was applied by spray on select interior surfaces such as the rudder speed brake, vertical tail, body flap and elevens; and by brush on vent doors, external tank door cavities (hydrogen side only), carrier panels and wing leading edge faying surfaces. A second material, a calcium grease, was applied to the rudder speed brake, body flap actuators, and elevon cover primary seal tubes. Finally, a fluid film was qualified for various ground support equipment applications.

A test program was performed to establish the mission life cycle of approved CPCs as part of the AVA program (Hale et al. 2007). All CPCs used on the Orbiter were tested in conditions to simulate multiple mission cycles. A mission cycle included four months in the Orbiter Processing Facility (OPF), three weeks in the Vehicle Assembly Building (VAB), one month at the pad and two weeks in low-earth orbit. For the purpose of the study the OPF and VAB stays were considered to have no life limiting effects. To simulate ascent and descent conditions, test panels were subjected to high and low temperatures. To simulate one mission cycle, it was decided to use four weeks at the beach facility or one week in salt spray atmosphere using a fog machine plus two weeks in a vacuum chamber. Metal coupons similar to the panels were also tested at two NASA centers with available beach sites, under a 10^{-2} Torr vacuum exposure at the Kennedy Space Center (KSC), and a salt fog machine and a 10^{-6} Torr vacuum exposure at Marshall Space Flight Center (MSFC). Four mission cycles were run at KSC and five at MSFC.

To further evaluate the performance of the CPCs applied to the coupons, electrochemical impedance spectroscopy (EIS) was used. EIS was selected because it measures both the deterioration of an organic coating caused by exposure to an electrolyte and the subsequent increase in corrosion rate caused by this deterioration. EIS detects changes in the coating in advance of any visible evidence. This study concluded that the waxy hydrocarbon material performed the best and would still be effective in protecting against corrosion after four mission cycles. The calcium grease also performed well and was expected to be effective for two mission cycles.

AGED PRIMER

One of the issues that plagued the Orbiter team was the inability to replace coatings. Depainting creates contamination, produces airborne debris, and is inherently difficult and expensive. Access for removing and replacing coatings requires a large amount of hardware disassembly and construction of special platforms. Schedule impacts are great. Over the life of the program only a few such operations were performed on select areas such as the rubber speed brake and wing lead edge spars.

Since replacement of coatings was problematic, aging studies were performed on samples of an aluminum access panel from the first Orbiter built, the Enterprise, which was coated with 30-year-old chromium containing Super Koropon primer (NASA, 2006). Corrosion on the aged coupon was observed after 500 hours of testing in a salt fog chamber, while a "control" coupon with freshly applied primer passed a 1500 hour test without corrosion. Scanning electron microscope (SEM) images of sample surfaces are shown in Figure 2. Even with the difference in magnification, the Enterprise sample appears very rough and flaky, while the control sample is smooth. Energy dispersive X-ray analysis (EDS) identified bright dots in both images as chromium. Additional examination found that the particle size and distribution of chromium particles varied widely, and some of the particles were larger than expected (Figure 3).

It was concluded that the poor performance of the 30-year old Koropon primer appeared to be directly related to both a reduced amount of chromium and an uneven distribution within the matrix of the film. The CCRB used these conclusions in building a rationale to either decrease the inspection interval of

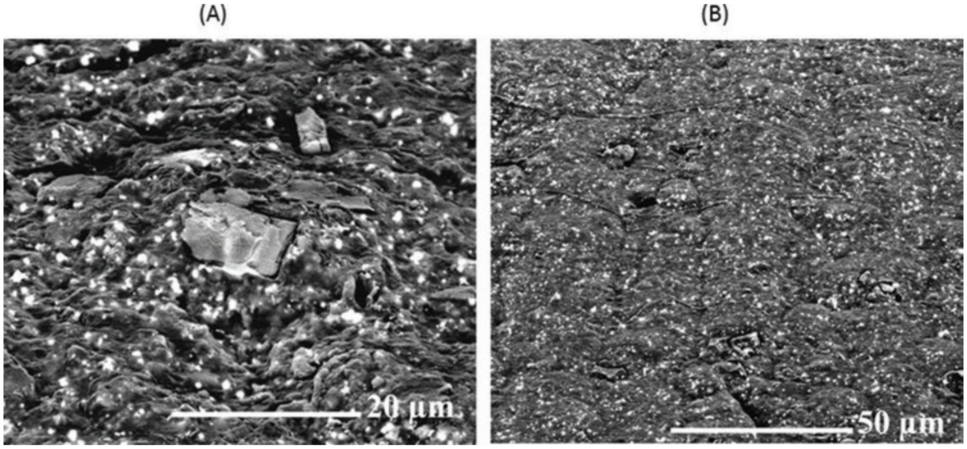

FIGURE 2. (A) Backscattered SEM image of the surface of the Koropon sample from the Orbiter Enterprise. (B) Backscattered SEM image of the surface of the Koropon from the control sample.

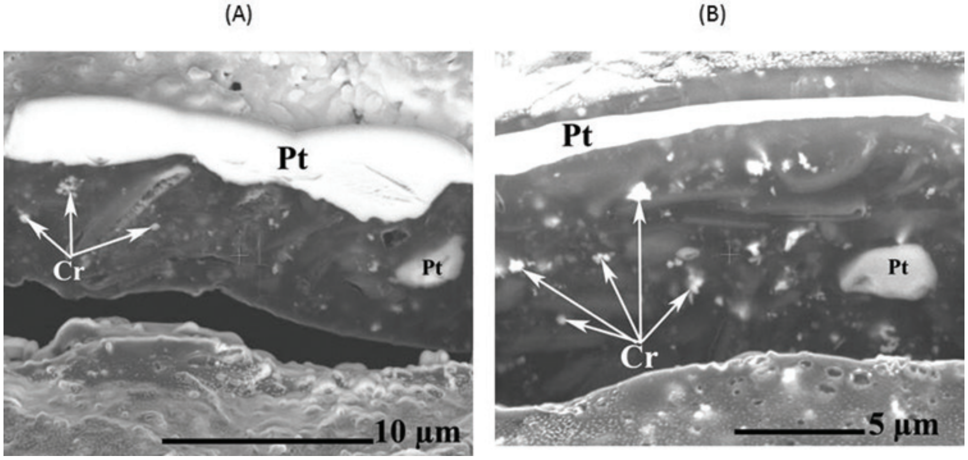

FIGURE 3. Backscattered SEM images at higher magnification showing distribution of chromium particles throughout matrices of the primer in cross-section (Pt indicates paint): (A) the Enterprise Koropon sample; (B) freshly applied Koropon on the control sample.

critical areas or strip and replace the primer. As a side note, in both commercial and military aircraft, no examples of a 30-year old primer are known. In most cases, primers are inspected and/or replaced in the five to seven year range.

SPECIFIC CORROSION ISSUES

Rudder Speed Brake

The Rudder Speed Brake (RSB) is deployed during landing to assist in slowing down the vehicle. The RSB is constructed from 2024 aluminum-alloy-honeycomb-skin panels and conventional aluminum ribs and spars. Two coating of Koropon primer and a topcoat were applied to the chemical-filled honeycomb face sheet. The assembly included Inconel trailing edge clips, which aided in door closure. The external RSB was exposed to unpurged/unconditioned air during OPF processing and to the seacoast air at the Pad.

Two major corrosion problems surfaced. Pitting corrosion found in the acreage and around fasteners was especially problematic because the face sheet was only 0.0279 centimeters thick (see Figure 4). Galvanic corrosion was found at the faying surface between the aluminum face sheet and Inconel clips. Besides implementing basic repair procedures, proactive measures included washing the RSB panels with water upon return to the processing facility. The CCRB also recommended that the panels be stripped and re-coated every six missions. For the Inconel clips, a barrier layer of room temperature vulcanized rubber (RTV) was applied on the faying surfaces.

Wing Leading Edge Spar Corrosion

The Wing Leading Edge (WLE) Spar was usually constructed of a corrugated aluminum-alloy panel approximately 0.1016 centimeters thick, but the Orbiter Columbia had a slightly different design with a flat honeycomb panel structure. Figure 5 shows the WLE spar of Columbia, Inconel thermal control system

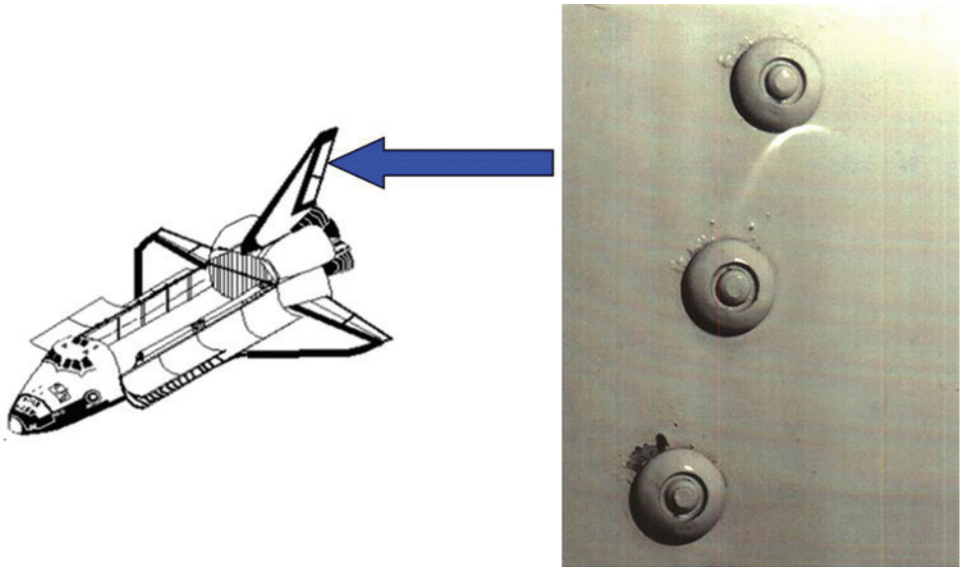

FIGURE 4. The Rudder Speed Brake highlighting pitting corrosion near fasteners.

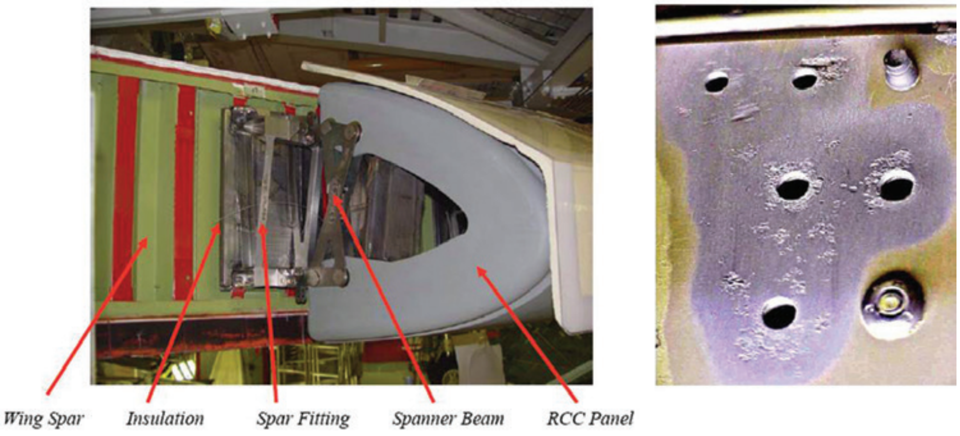

FIGURE 5. The basic construction of the wing leading edge and an example of pitting corrosion found.

blankets, Inconel fittings for attaching hardware (spar fittings) and reinforced carbon-carbon panels (RCC). The aluminum panels were chemical film treated and coated with three coats of Koropon primer. The WLE structure was not purged.

Because of galvanic dissimilarities between the WLE structure and the Inconel hardware fittings, pitting was observed near the fittings (Figure 5). As on the RSB panels, a barrier layer of RTV was applied to mitigate corrosion; after disassembly, depainting and repainting was instituted during the maintenance period. These protocols were not implemented on the Orbiter Atlantis, and an increase inspection protocol was instituted instead.

External Tank Doors Corrosion

Each Orbiter has two external tank (ET) doors on the underside of the vehicle, which closed after the ET and Orbiter separated during ascent into orbit. To maintain structural and thermal properties the ET doors were constructed from a beryllium alloy. Inconel support hardware was attached to each door, and over time the doors began to experience corrosion in both the open acreage and near or beneath the attachment hardware (Figure 6). Due to the unique metallurgical properties of these metal alloys, special care had to be taken when clean up or repair was performed. For shallow pits, the active corrosion product was manually and chemically removed, and the pits were filled with an epoxy and recoated. Special safety practices were employed for deeper pit removal, sanding on the surface, or primer removal. On galvanically dissimilar regions, an RTV barrier layer was applied.

Nose Cap Bulkhead Corrosion

Corrosion pitting was found during routine inspections of the aluminum nose cap bulkheads on both Columbia and Discovery (Figure 7). Titanium faying surfaces had been left bare to allow for the flow of an electrical current, creating a unique design challenge for the materials engineer. To mitigate corrosion, thin layers of a chemical conversion coating were applied, and joints were sealed with RTV fillets.

Figure 7 shows both the bulkhead and a close-up view of the footprint for one of these electrical bonds. Galvanic differences between titanium fittings and the aluminum bulkhead drove significant pitting, found in numerous locations on the outer perimeter. On both Orbiters corrosion was attributed to a breach in the RTV fillet seal. Several options were suggested by the CCRB to prevent this from occurring in the future. These included use of grounding straps, the addition of aluminum plating to the titanium faying surfaces, the addition of a conductive sealant and a

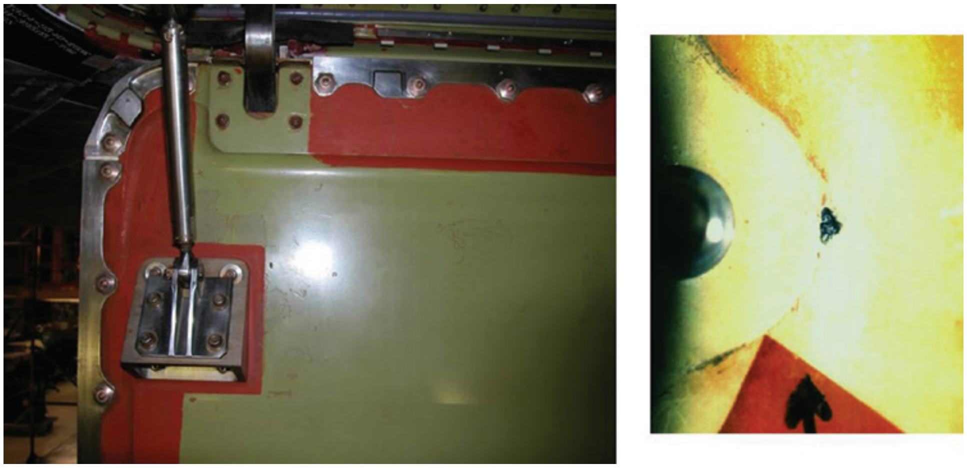

FIGURE 6. A closeup view of the attach hardware (right) on an External Tank door after the addition of an RTV barrier layer. Typical pitting is shown on the left.

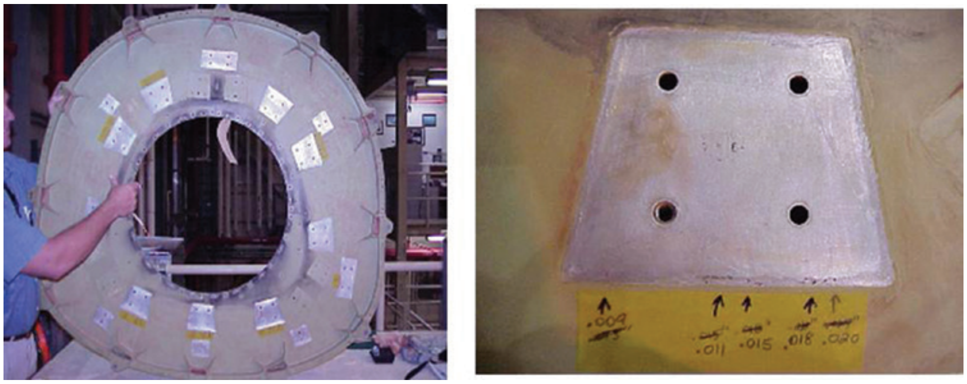

FIGURE 7. A nose cap bulkhead after removal. The bare areas represent faying surfaces left bare for electrical bonding purposes, as see in great detail on the right.

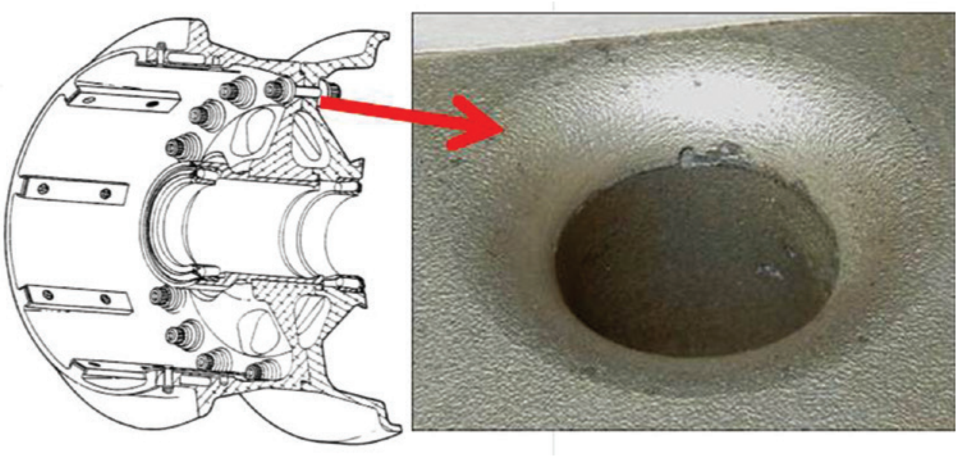

FIGURE 8. A schematic of the Main Landing Gear wheel designs and a close up of corrosion pitting observed adjacent to a bolt hole on the inner surface.

change of filling material. Unfortunately, none of these changes were accepted by the program, but the lessons learned may prove to be beneficial in future designs.

Main Landing Gear (MLG) Wheel Corrosion

The main landing gear (MLG) wheels were constructed of 7049/7050–T73 aluminum in a split-wheel design; 18 MP35N tie-bolts connected the inboard and outboard halves (Figure 8).

The left picture highlights pitting corrosion attributed to galvanic corrosion between the aluminum-zinc-magnesium-copper-alloy wheel halves and the nickel-cobalt-chromium-molybdenum-alloy tie bolts. A review also found contractor cleaning procedures to be inadequate. Of great concern was that the pitting could act as a stress concentration points that would lead to fatigue cracking and failure during landing.

Fracture analysis was performed, and critical flaw sizes were determined that limited the number of allowable cycles. To further alleviate concerns, testing was performed at Wright-Patterson AFB in Dayton, Ohio. Landing simulation tests were performed on a wheel that had seven notches cut into the outboard wheel half by EDM to represent a worst-case corrosion condition. Eddy current and dye penetration analysis after each test run found no crack growth. Design changes were made, and improved corrosion protection schemes, inspection techniques and cleaning procedures were introduced.

THE END OF THE PROGRAM

In 2006, using the tools developed during the AVA program, the CCRB developed a project plan that assumed a Space Shuttle Program end date of the end of fiscal year 2010. The goals were divided into three categories: near term (approximately one year), mid-term (approximately three years) and continuous (end of program).

The near-term project goals include creating a CCRB website, finalizing recommendations for implementation of non-chromium based primers and performing life cycle testing of CPCs. The mid-term goals were defined as completing the development of any NDE (e.g., for corrosion under the thermal protection system) and finalizing a recommendation for development of laser de-painting. Finally, continuous goals were defined as documenting lessons learned, maintaining the database, revising a Fair Wear and Tear document, updating the CPC specification, networking and benchmarking.

CONCLUSION

After 135 missions and 30 years, the Orbiter fleet was retired in 2011. Working with Orbiter project management and a world class engineering team, the CCRB was successful in providing sustained engineering support that allowed the Orbiter to operate for an additional period of approximately 20 years. Lessons learned from the Orbiter program have aided NASA and contract engineers in the design and manufacture of new spacecraft so that exploration of space can continue. The Orbiters are proudly being displayed for all the public to see in New York City, Washington D.C., Los Angeles, and at the Kennedy Space Center in Florida.

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Finding a Suitable Method for Chloride Removal and Preventative Storage of Spacesuit Gloves at the National Air and Space Museum

Lisa Young[1], Aaron N. Shugar[2], Malcolm Collum[1], and Christina L. Simms[2]*

ABSTRACT. The National Air and Space Museum has the largest and most complete collection of spacesuits in the world. The collection contains suits that made history- such as Neil Armstrong's Apollo 11 Lunar suit as well as one-of-a kind suits used for training, engineering prototypes and developmental designs that allowed humans to live and work in space. Spacesuits are complex, composite objects that were constructed to allow humans to withstand the harshest environment of space and still be able to live and work safely and comfortably while doing so. Spacesuit gloves are the single most important part of the suit. In order to fit the astronaut's hand, each glove was custom made to allow intricate work to be completed for long hours at a time yet be easily removable via a precisely manufactured disconnect. Each glove is constructed of layers of synthetic and natural materials with an interior pressure bladder adhered and fastened to an anodized aluminum wrist disconnect.

A survey of over 300 gloves in the NASM collection showed that approximately half of them are suffering from advanced forms of aluminum corrosion at this mechanical disconnect. The corrosion is more prevalent on the interior surfaces of the metal disconnect and at the interface where the soft materials are joined to the aluminum. Previous research and analysis were undertaken using sacrificial glove components from the Gemini and Apollo period in order to characterize the corrosion types present and to investigate and identify the composition of the aluminum alloys and anodizing. Analysis was performed by staff at the Museum Conservation Institute and Suny, Buffalo State using Optical Microscopy (OM), X-ray fluorescence (XRF) spectroscopy, scanning electron microscopy (SEM) accompanied by energy dispersive X-ray analysis (EDS), X-ray diffraction (XRD), Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy.

Two main contaminants were identified in the corrosion layers during analysis: chlorides and acetates. Hydrochloric acid gas caused by deteriorating rubber components and astronaut sweat are the likely source of the chlorides. FTIR identified acetates in all samples indicating another form of corrosion, most likely coming from the nickel acetate used in the anodizing process. Testing confirmed that soft goods, and in particular the rubber bladder, are continuing to off-gas even after 45 years. This paper will briefly review our findings from the survey and analysis of the aluminum alloy, corrosion products and contaminants. Characterization of the chlorides and how they participate in the corrosion process will be examined. Research on HCl scavenging products to achieve a suitable passivating atmosphere for storage and display of spacesuit materials will be reported. Investigation into developing treatment protocols for the removal of chlorides and corrosion as well as stabilization of the metal without damaging the anodized layer will be discussed. The results of this research will inform future treatments of composite artifacts containing aluminum alloys.

Keywords: aluminum alloy, spacesuit, corrosion, chlorides, Smithsonian

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INTRODUCTION

More than 50 years ago, President Kennedy presented a challenge to the United States to land a man on the moon and return him safely to Earth (Figure 1). Not only was this challenge met, it paved the way for many other accomplishments in manned spaceflight. Early spacesuit designs were engineered to meet the demands of this fast-paced race to the moon. Suits used during early Mercury and Gemini missions were adapted and modified flight suits worn by Naval and Air Force pilots who performed rigorous high altitude flights at fast speeds. With the first American spacewalk by Ed White in 1965, suit engineers were pressured to find new materials to ensure survival both inside and outside the craft. As the Apollo program drew closer, the spacesuit was redesigned again to utilize over twenty-one new materials layered together (DuPont™ 2012). The layers protected the astronaut from the harsh environment of space while still allowing him to perform mission-critical tasks on the lunar surface.

FIGURE 1. Buzz Aldrin explores the surface of the moon during Apollo 11. Photo credit: NASA.

SPACESUIT GLOVE HISTORY

Historians and aerospace engineers have long noted that gloves are the most complex and essential part of any spacesuit. More design changes have been made to the gloves than to any other component of the suit. Astronauts need to be able to grip tools and have tactile sense, and the gloves must be able to flex, bend, and be repeatedly, quickly and easily attached and detached from the suit (Figure 2).

The glove design incorporates three main elements: from the hand outward, the first layer of the glove is the bladder, which is designed to retain a pressurized environment. The next layer is the restraint system. This component of soft goods is responsible for carrying all the pressure as well as man-induced loads during operational use. The final outer layer is the thermal protection garment designed to provide a buffer from temperature swings and to guard against the impact of hyper-velocity particles (Stein, Ross and Kosmo, 2001). A fourth design element is the anodized aluminum quick-disconnect system, which attaches the glove to the suit and allows the astronaut to take off his or her glove while maintaining residual pressure in the suit.

Incorporation of wrist bearings and ring locks on the sleeves began in 1961 with Grissom's Mercury suit used aboard Liberty Bell 7. Previous suits utilized gloves that were zippered onto the suit, preventing the astronaut from easily rotating his wrists and donning and doffing his gloves in a timely manner. The

FIGURE 2. EVA gloves in the National Air and Space Collection. Left to right: Ed White's Gemini 4 gloves; Gene Cernan's Apollo 17 gloves; and Kathy Sullivan's Shuttle mission gloves. Photo credit: National Air and Space Museum, Smithsonian Institution.

new design consisted of a male-female lockable mating system that attached a male connector on the glove to a female locking ring on the arm of the spacesuit. A non-detachable, sealed rotation bearing was incorporated into the glove next to the male connector, and a pressure seal was provided by an O-ring on the female side (NASA 1971). Air-Lock, Inc., has remained the prime contractor for the glove disconnects since the 1950s. Soft glove materials, including a Neoprene rubber bladder, fabric components and adhesives, were designed and assembled by the David Clark Company (DCC) in Massachusetts and by the International Latex Corporation (ILC) in Dover, Delaware. (Ayrey 2007). We were fortunate to be able to collaborate with industry experts at both organizations – material and suit engineers – to help with historical research throughout our project.

SURVEY OF THE NASM COLLECTION

The National Air and Space Museum (NASM) preserves the largest and most complete collection of spacesuits in the world. The collection contains historical suits such as Neil Armstrong's Apollo 11 lunar suit as well as engineering prototypes and developmental designs (Young 2009). In 2013, a comprehensive condition survey of over 300 gloves in the NASM collection was undertaken. The main purpose of the survey was to document the materials used in the construction of the gloves, record their history and identify corrosion types.

The large survey sample allowed us to identify where corrosion was most often located, find patterns relating to the corrosion, and determine to what extent the patterns related to operational use. The results showed that 50% of the gloves suffer from advanced forms of aluminum corrosion at the mechanical disconnect, with significant loss to the metal and anodized surface (Figure 3). Most glove corrosion is more prevalent on the interior metal ring at the interface with soft goods. Historical documents confirmed a surface treatment at this interface during glove assembly using air abrasion to remove the anodized coating for better adhesion of the rubber bladder (Litton Industries 1969). Two primary forms of advanced corrosion were found on the gloves: pitting and exfoliation (Figure 4). (Young, Simms and Shugar 2013). Secondary forms of surface corrosion were noted as well, including gloss loss, oxidation discoloration of the anodized layer and etching manifested in finger prints (Figure 5). Some surfaces appear stable, but it is unclear if they are protected by a layer of passive corrosion, have not yet been exposed to high levels of contamination, or present initial stages of more advanced forms of corrosion.

Storage of the gloves in the past apparently contributed to corrosion. Up until three years ago, the gloves were subjected to environmental fluctuations, excessive handling and inadequate storage and display supports. The majority were stored upright on their wrist disconnects so that the very fragile soft goods would not be damaged. This seems to have led to greater corrosion on the interior of the gloves by its creation of a micro-climate with little or no air movement inside the glove. A build-up of hydrochloric acid gas almost certainly led to the attack of the

FIGURE 3. Corrosion on the interior wrist disconnect of an Apollo-era glove appears light colored where red anodizing has failed.

FIGURE 4. Exfoliation corrosion on the exterior surfaces of the wrist disconnect with gold anodizing.

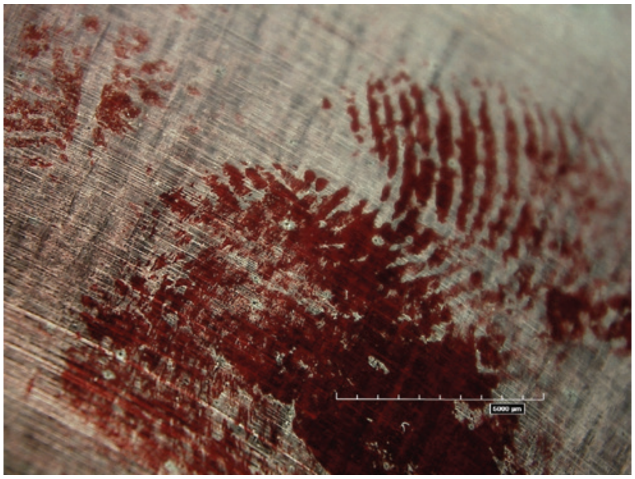


FIGURE 5. Fingerprint etched into the anodized aluminum alloy surface.

metal surfaces. Currently the gloves are stored in far better conditions at NASM's Udvar-Hazy facility in a newly constructed environmentally controlled room at 63 degrees and 35% relative humidity (Young and Young 2001). They are mounted in storage boxes that obviate microclimates inside the gloves.

ANALYSIS AND RESULTS

Research and analysis were undertaken using deaccessioned glove components from the Gemini and Apollo period with similar corrosion patterns. Industry documents provided information on the gloves, and the fabrication methodology of the aluminum prior to anodizing was confirmed through optical microscopy. Aluminum-alloy sheet metal was extruded and turned on a lathe to form the end product. Although we cannot be 100% certain, we believe that the high shine of anodized areas indicates an electro-polish pre-treatment to smooth out the surfaces prior to anodizing. This practice is common in industry during the processing and anodizing of aluminum alloys to clear the metal surfaces of remaining flaws.

Instrumental analyses conducted at the Smithsonian Museum Conservation Institute and Suny, Buffalo State College provided further information. Scanning electron microscopy (SEM) accompanied by energy dispersive X-ray analysis (EDS) and X-ray fluorescence spectroscopy (XRF) confirmed the presence of the elements in aluminum alloy 2024, the copper-aluminum alloy specified for the gloves; sulfur used in the anodizing process; and nickel associated with the sealing process (figure 6).

The 2000 series of aluminum alloys, which contain relatively high levels of copper, are known to suffer from both pitting and exfoliation corrosion. Both forms of corrosion on the gloves were found to be contaminated with chlorine, with higher concentrations located in the corrosion pits. The two most likely sources of the chlorides are the nearby neoprene rubber, which breaks down to hydrochloric acid gas, and contamination from astronaut sweat during use. Chlorinated pool water can be ruled out, since none of the objects in NASM's collection were used for testing in NASA swimming pools. Further testing using A-D acidic testing strips in enclosed storage boxes and cabinets confirmed that the neoprene rubber bladder and adhesives are continuing to off-gas acidic byproducts even after decades in storage. Fourier transform infrared spectroscopy (FTIR) was utilized to identify organic components of the surface corrosion. Samples of corrosion from a fingerprint showed an unexpected presence of acetates, consistent with the nickel acetate sealing used in the anodizing process. All of the corrosion samples were too amorphous for any conclusive results using X-ray diffraction (XRD).

Using a Hirox 3-d digital microscope, grooves machined for the glove disconnect were imaged on both corroded and uncorroded surfaces of all samples (figure 7). Based on a recent NASA paper on similar glove disconnects (Christoffersen et al., 2009), pitting on the disconnects is likely the result of imperfections during machining before the metal was rinsed and anodized. The NASA scientists found pitting where the edge of the tool cut grooves in the metal, which was otherwise uncorroded. It was

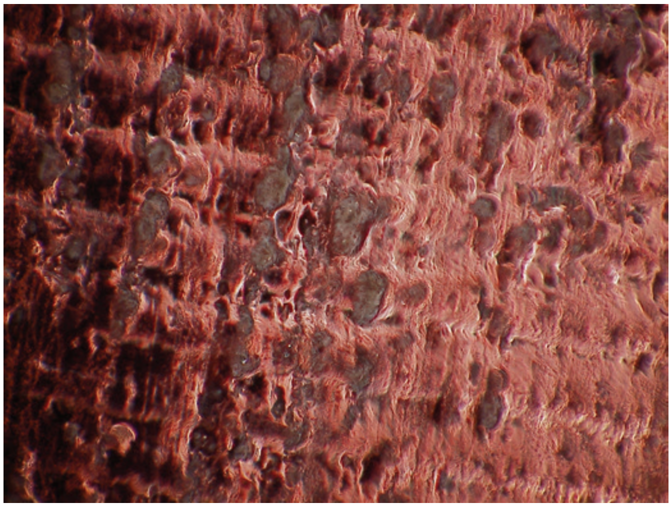


FIGURE 7. Uncorroded sample of red anodized glove disconnect showing vertical grooves in the surface from the machining process.

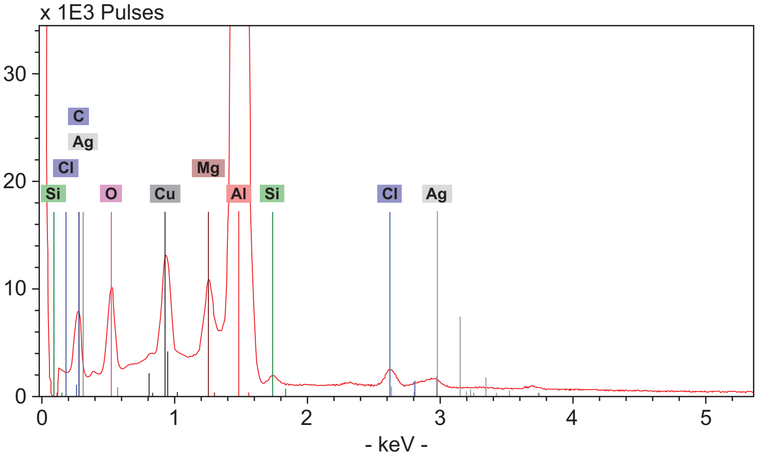
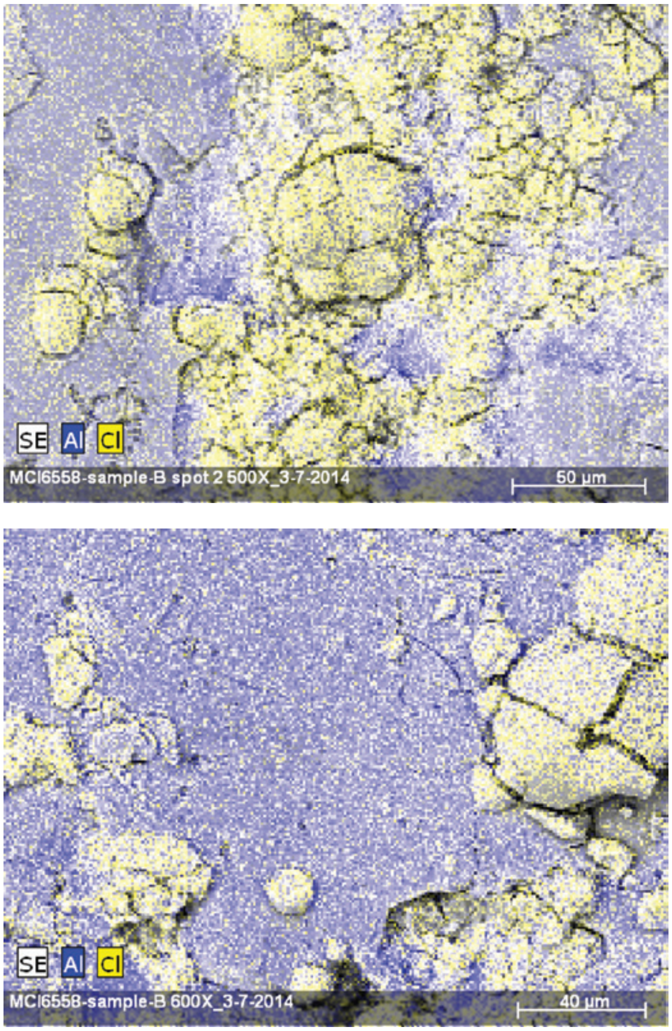


FIGURE 6. SEM EDS spectrum showing elements in the corrosion pits of a glove sample. Photo credit: Museum Conservation Institute, Smithsonian Institution.

concluded that the imperfections led to breaks in the anodized coating that allowed contaminants to penetrate the oxide layer and start the corrosion process.

In order to develop a treatment methodology for the gloves, we thought it was essential to better define where the chlorides were distributed and how they participate in the corrosion process. Additional research using SEM EDS confirmed the presence of chlorides localized to the corrosion pits in the classic pattern described by Selwyn (this volume). Many pits have circular debris fields surrounding corrosion blisters (Figures 8 and 9).

The blister, or cap over the pit, is comprised of aluminum hydroxides with hydrochloric acid showing a concentration of chlorine in this area. The pH of the corrosion blisters and pitting measured between 4 and 6. Considerations for a treatment methodology led to two distinct research paths: active treatment and preventative treatment.



FIGURES 8 and 9. SEM image mapping of elements related to pits in the anodized surface of an aluminum alloy wrist disconnect. Blue identifies aluminum (in the form of aluminum oxides), and yellow identifies chlorides. Photo credit: Museum Conservation Institute, Smithsonian Institution.

ACTIVE TREATMENT CONSIDERATIONS

A number of factors were considered as we approached finding an active treatment solution for removal of chlorides and stabilization of active corrosion, without causing further harm to the anodized surface coating. With over 300 gloves in storage and approximately half as many more on display at NASM and other organizations, treatment methods would ideally be cost-effective, repeatable and effective. A single treatment approach might not be adequate or applicable to differing levels of preservation and types of corrosion, but every object could not undergo the same level of analysis that our samples were afforded, which could negatively affect results.

Traditional chloride removal techniques were considered, such as desalination, electrolysis and those utilizing basic solutions, chelating agents and corrosion inhibitors. The majority of relevant published information on aluminum treatments for museum objects currently falls under archaeological materials or corrosion science, however, and there is little reference material related to multi-media or technical objects. Many successful chloride removal methods for metal alloys must be excluded from use because the gloves are composite objects. The fragile condition and historical value of many of the gloves makes it impossible to consider disassembly as part of an ethical treatment approach.

Preserving the anodized layer in situ was also found to limit active treatment solutions. Retention of original anodizing is considered important to slow down or halt unstable corrosion of adjacent areas before, during and after treatment. Moreover, the colors used to dye the anodizing are historically significant. All flight gloves were colored to indicate use by right (red) and left (blue) hands. In addition, early on in the program different shades of blue represented different suit manufacturers (not that lighter blue colors represented fading).

Industry restoration techniques – such as stripping off the anodizing, treating the corrosion and re-applying a new anodized surface – were found to be unsuitable for long-term preservation of the gloves at NASM. Each of the gloves tells its own story: for instance, lunar dust is trapped inside some wrist bearings on Apollo mission gloves, and others show evidence of wear and use, which may have altered the glove surface. Preserving these primary sources of historical information and the subtle historical changes in the evolution of each glove was ultimately determined to be more important than such interventive treatments.

PREVENTATIVE TREATMENT CONSIDERATIONS

As we are not yet confident in an active treatment approach for the corrosion, our focus has turned to preventative conservation. Rather than risking corrosion removal, this places emphasis on slowing down the rate of future corrosion. Similar to our approach with the active treatment, preventative treatment requires a number of factors to be taken into account before deciding which system will be used. The preventative treatment needs to be cost-effective, easy to maintain, and reliable without draining staff resources. A prototype will need to be set up in storage to evaluate the effectiveness of the scavenger in slowing down or halting corrosion. A holistic preventative treatment of the entire collection may find a way to stop chloride contamination now and in the future, given improved storage conditions for the gloves.

We have been undertaking research to capture off-gassing in both storage and display areas using suitable scavengers, including pollution and oxygen scavengers. Even if gloves could be treated successfully, they would potentially be exposed to the inevitable aging of attached rubber that would contaminate them with chlorides in the future. The difficulty is finding a medium that will be able to capture the very small hydrochloric gas molecules. We are currently looking toward industry for products that are already being used and commercially available. Three products are being considered for evaluation through testing and determination of the ease of working with them. The first is the material created for respirator cartridges that protect a person while working with hydrochloric gas, although it requires active air movement to trap the gas. The second utilizes passive air filtration and relies on the natural diffusion of air through a membrane to collect the gas. The third is a new product that seems promising for museum application – a modified silica-gel containing amines to attract and capture acidic gases. Ideally the scavengers or other materials chosen should be analyzed before and after use to determine their effectiveness in trapping the small hydrochloric gas molecules.

An alternative to use of scavengers may be to increase ventilation in storage and on display. Now that the levels of relative humidity have been dropped to 35% and are no longer fluctuating, ventilation of the spaces may solve the problem of future chloride contamination.

CONCLUSION AND FURTHER WORK

As with so many conservation projects, what started as a small research question about one type of object quickly evolved into a multi-phase project. At NASM, we have the privilege and challenge of working on unique, one-of-a-kind, multi-faceted objects such as the spacesuits. We often make light of the fact that most of the objects we deal with are not the sort of objects or materials conservators are trained on in graduate school or would find in other museums. As we move forward, we hope to find a way to treat these unique materials and to use this information to inform the treatment methodology of composite aluminum alloy objects in our collection. We will be happy to report on our results and will continue to engage our colleagues from this conference as our research and treatments are finalized. We anticipate collaborating with industry experts further in this endeavor as a way to bridge the gap between the field of conservation and colleagues from other professions.

The NASM conservation team is often asked why a spacesuit built to withstand the harsh environment of outer space is not able to survive on Earth. Many of the materials used in the aerospace industry were new and chosen for a one-time use. No one ever expected them to last fifty years or more. This case study of corroded aluminum alloys on spacesuit gloves is just one small example of all the aluminum alloy objects we care for at NASM, many of which have flown to high altitudes or orbited the Earth. As technology evolves and we find better solutions to slow down the evitable aging of modern materials, we will be continually challenged to preserve the objects in our collection-some of which are the only primary evidence of man's space race to the moon and back.

ACKNOWLEDGEMENTS

I would like to acknowledge the organizing committee for spearheading this conference and bringing together expertise from around the globe to engage in conversations about the conservation of aluminum alloys. And to all of my colleagues at NASM, who challenge us to solve problems and step outside the box with our approach to find treatments for such unique materials. I would also like to thank Bill Ayrey of ILC and Shane Jacobs at AirLock for searching for and recovering historical documents pertaining to the manufacturing and production of spacesuits. And lastly, I would like to thank Nicole Little and Jennifer Gaiccai at the Smithsonian's Museum Conservation Institute for assisting with the project and helping us to run analysis on our samples.

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Characterization and Electrochemical Behavior of Aluminium Corrosion Layer Systems on Air and Space Museum Aircraft

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ABSTRACT. Since the 1920s, aluminium alloys have been widely used in the fields of transport and architecture. As a consequence, an increasing number of aluminium artifacts are registered in museum collections, especially in technical museums like air and space museums. The great size of these objects often requires storage outdoors or in partially sheltered environments such as hangars, so that the artifact remains in uncontrolled atmospheric conditions, increasing the corrosive processes on the aluminium components. The purpose of the present work is to characterize the corrosion morphology observed on early aircraft and to study the reactivity of aluminium alloy corrosion layer systems by electrochemistry. This data is of primary importance to better understand and evaluate the risks encountered by aluminium made collections.

Keywords: Aluminium, Corrosion, Cultural heritage, XANES, Electrochemistry

INTRODUCTION

Aluminium is second to iron as the most widely used metal in the world. Its use rapidly increased at the beginning of the 20th century mainly in the transport industry because of its low density. As a consequence, an increasing number of aluminium alloy materials are nowadays registered in museum collections, especially in technical museums like air and space museums but also in modern art collections.

The Air and Space Museum of Le Bourget near Paris has one of the more important and comprehensive aircraft collections representing aviation history from its origins to the beginning of the 21th century. In fact, light aluminium alloys with good mechanical properties were used in the earliest aircraft. Unfortunately, aluminium alloys are very sensitive to corrosion phenomenon. For the aeronautic alloys, the corrosion behaviour is related to the presence of intermetallic phases in the aluminium matrix mainly composed of aluminium, copper, manganese/iron and magnesium (Davis, 1983). In the preliminary steps of the degradation process, the aluminium corrosion is mainly localised in pits spread across the entire surface (Blanc, Lavelle, and Mankowski, 1997); then over time the development of thick corrosion layer, more or less adherent, is observed. This corrosion phenomenon is responsible for a large loss of material and eventually leads to the degradation of the mechanical properties of the aluminium structure.

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When faced with thick corrosion layers on aluminium, conservators and curators are most of the time without good solutions. The complete removal of such corrosion layers is often impossible because it is too expensive, especially on large aircraft, both because of the vast surfaces that need to be treated and because the corrosion layers could retain historical markings that need to be conserved.

To get a clear evaluation of the risks encountered by collections containing aluminium artifacts and to propose the development of a coherent conservation strategy, the influence of the thick corrosion layer on the corrosion rate of the underlying metal has to be understood. Two main questions must be investigated: (1) is the corrosion layer a threat to the preservation of the remaining metal and (2) can the phase composition of the corrosion layers affect the reactivity of the corrosion system as is observed in the case of iron corrosion layers (Dillmann et al., 2004; Hoerlé et al., 2004; Monnier et al., 2008)?

The initial purpose of the present work is to analyse and study different kinds of aeronautic aluminium artifacts contained in the collections of the Air and Space Museum of Le Bourget in order to reliably diagnosis the degradation of aluminium alloys. Then it is to try to establish a correlation between the physicochemical characteristics and the electrochemical behaviour of the corrosion products constituting the thick corrosion layers of aluminium alloys.

EXPERIMENTAL METHODS

In this study we present the results for three samples representative of those for 30 samples collected from five aircrafts produced from 1930 to today (Table 1).

After embedding the samples in epoxy resin and polishing as previously described (Rocca et al., 2003). Metallographic examination was performed on uncoated samples with a FEG-SEM (Hitachi S4800) using an acceleration voltage of 1 kV to 2 kV. The elemental chemical composition was analyzed by Electron Probe Microanalysis (EPMA) at 15 kV (Cameca SX100).

A combination of micro-X-ray fluorescence (μXRF) and micro-X-ray absorption spectroscopy (μXANES, for X-Rays Absorption Near Edge Structure) at the Al K-edge was performed with high spatial resolution and high sensitivity on the LUCIA beamline at SOLEIL Synchrotron (Flank et al., 2006). Measurements were done at room temperature under vacuum (10^{-2} mbar) with a beam size of 3.5×6 μm^2. The energy of the double crystal KTP(011) monochromator was calibrated by setting the first inflexion point of an aluminium foil spectrum at 1559.6 eV. First, μXRF maps of the zones of interest were obtained above the edge (1580 eV) with 20 μm steps and 1 second intervals; these maps determine the nature and location of the chemical elements present in the corrosion layers. Then, on different parts of the corrosion layers, the energy scans were measured from 1.52 keV to 1.68 keV, including pre-edge and near-edge features. These XANES spectra were carried out with a step size of 2 eV and a counting time of 3 s in the pre-edge region, 0.2 eV and 3 s in the edge region and 1 eV and 3 s in the post-edge region. All measurements were collected in the fluorescence (FY) signal, using a silicon drift detector.

For the electrochemical measurements, the noted standard corrosive solution in American Society for Testing and Materials (ASTM) D1384-87 was used. It has the following composition: 148 mg/l Na_2SO_4, 138 mg/l $NaHCO_3$, 165 mg/l NaCl (ASTM Standard D 1384, 1988).

The electrochemical measurements used to characterize the corrosion behaviour of the "metal/corrosion products" system were performed in a three-electrode electrochemical cell connected to a potentiostat and driven by a computer in reference corrosive water as previously described (Georges et al., 2008). A circular and horizontal working electrode (2.8 cm^2) was placed at the bottom of the cell under the counter electrode. The reference electrode was a KCl-saturated calomel electrode (Hg/Hg_2Cl_2, E = +0.242 V/SHE); all working electrode potentials are given versus this reference electrode. Recording of the potentiodynamic curve, i = f(E), was performed from –250 to 1300 mV versus the open-circuit potential (or corrosion potential, E_{cor}) with a sweep rate of 1 mV/s. For each sample the measurements were carried out on both polished samples (bare metal) and as-received samples, i.e. the overall "metal/corrosion products" system, after 24 hours of immersion in the corrosive solution.

RESULTS

The first samples analysed were collected on an inspection hatch of a French supersonic bomber Dassault Mirage IV aircraft (Figure 1a). SEM images of the cross-section of the exterior and interior faces in Figure 1b and Figure 1c reveal the development of intergranular and lamellar corrosion processes. On the exterior face, a thick laminated corrosion layer formed (averaging about 500 μm). Because aluminium oxide and hydroxide are more voluminous than aluminium metal, growth of the corrosion products inside the metal induces significant mechanical stresses in intergranular regions, as can be seen in Figure 1b. In contrast, the metallographic cross-section for the inner face of the hatch shows a much thinner corrosion layer in Figure 1c. In this case, better conservation conditions have allowed the preservation of the initial anodized layer. The regular thickness of this layer (about 10 μm) and homogeneous presence of several percent sulphur proves that this piece has been anodized in sulphuric acid that is the traditional anticorrosion treatment of Al alloys (Thompson et al., 1983).

Elemental analysis performed by EPMA showed that the aluminium matrix contains 3.8 wt. % of copper and 0.66 wt. % of manganese. A large number of intermetallic precipitates can be seen in the metal with a chemical composition of Al (Cu, Fe, Mn) and Al_2Cu. This composition is very close to the AA2024 aluminium alloy composition (Korb, 1987).

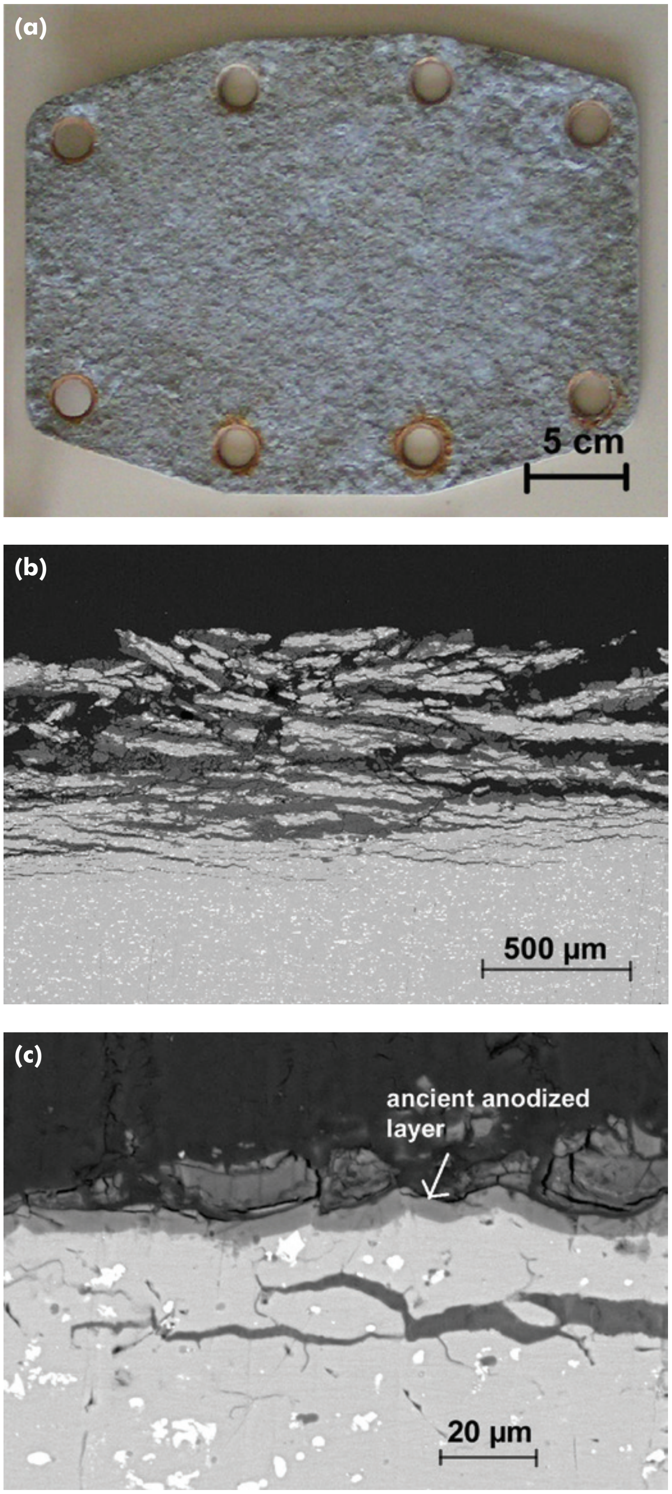

FIGURE 1. Mirage IV: (a) macroscopic aspect of the inspection hatch under the delta wing (exterior face); (b) SEM image of a cross-section of the hatch's external face; (c) same as previous, internal face.

Figure 2 presents macroscopic and microscopic images of a sample taken from a spar of the SNCASO Vautour aircraft (1956), which is characterized by a very thick layer of lamellar corrosion. As can be seen in Figure 2b, long-term corrosion is clearly foliated and lamellar. SEM images in Figure 2c show that the growth of the corrosion products at the grain boundaries leads to the destruction of the metal (Eckermann et al., 2008). EPMA analysis confirmed that the metal is an Al–Cu alloy with 3.75 wt. % Cu and trace amounts of 0.1 wt.% Fe and 0.6 wt.% Mn.

The 'Point d'Interrogation' aircraft, a Breguet XIX (1923–1929) presents a third type of corrosion morphology. In the macroscopic image displayed in Figure 3a, the sample appears to present only spots of corrosion, but SEM images in several locations revealed significant internal corrosion at the grain boundaries of the alloy. Figures 3b and 3c show that half of the original thickness of the metal is affected by internal oxidation. On the surface, the homogeneous presence of sulphur, detected by EDX, proves that this piece has also been anodized. The EPMA analyses of the metal reveal that the alloy has approximately the same composition as the Vautour (3.8 wt. % Cu and 0.38 wt. % Mn). It is important to note that this kind of intergranular corrosion is as destructive as the lamellar corrosion observed in the Vautour samples, but the piece has preserved its original size as a whole.

The XANES analyses (Figure 4) demonstrate that for all the samples, aluminium atoms are coordinated in an octahedral arrangement; no tetrahedral coordination was revealed (Table 1). Moreover, Al-VI coordination is observable throughout the corrosion layers. The majority of spectra detected an aluminium metal contribution at around 1559 eV, certainly correlated with small particles of aluminium remaining in the corrosion layers.

Close examination of the XANES spectra found three main groups in all samples, but the proportion of each group could be different for each aircraft. The first type of spectra, mainly found in the Vautour samples and to a less extent in the Mirage IV samples, is presented in figure 4a. The white line consists of a broad peak (8–9 eV wide) and two main absorption features, with B at 1571 eV more intense than A at 1568 eV. One oscillation of lower intensity is visible at a higher energy, C, at about 1590 eV. These spectra are clearly close to that of gibbsite used as a fingerprint.

The second type of XANES spectra, mainly for corrosion layers of the Breguet XIX, are presented in figure 4b. In this case, the white line also consists of a broad peak, but the intensity of the two peaks is reversed: A at 1568 eV is more intense than B at 1571 eV. This increase in the intensity of the A peak suggests the presence of boehmite, a type of local structure that contains aluminium atoms in a distorted octahedron.

The last group of spectra shows in a general manner the same features at the same energies in figure 4c: A at 1568 eV, B at 1571 eV, and C at 1590 eV. However, for these spectra a broadening of the white line is clearly observed, and the two

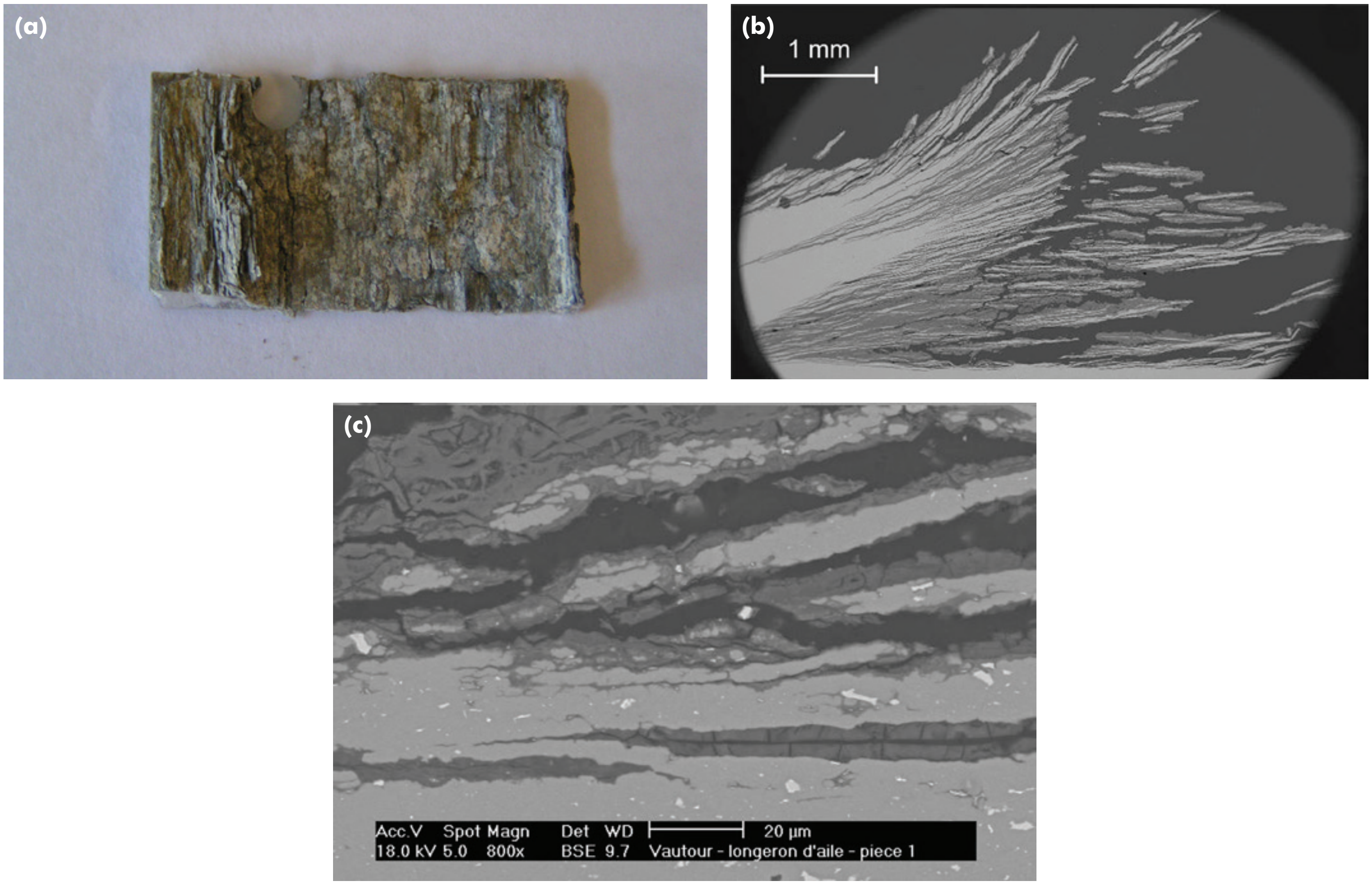

FIGURE 2. Vautour aircraft samples: (a) obverse, (b) and (c) SEM images of cross-sections.

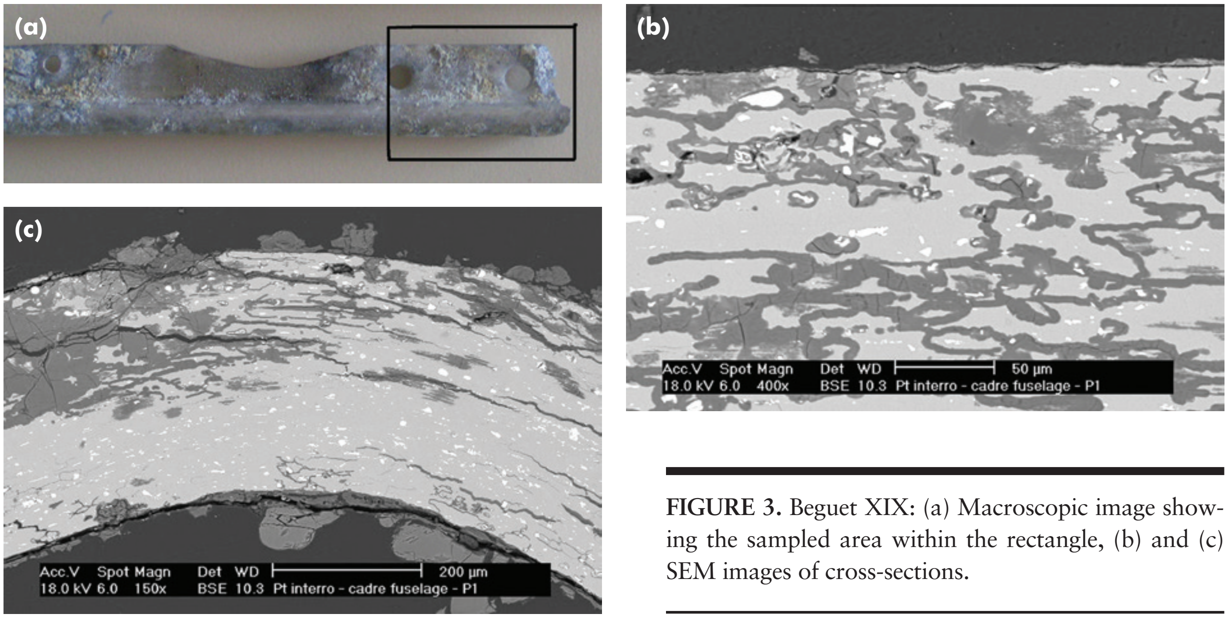

FIGURE 3. Beguet XIX: (a) Macroscopic image showing the sampled area within the rectangle, (b) and (c) SEM images of cross-sections.

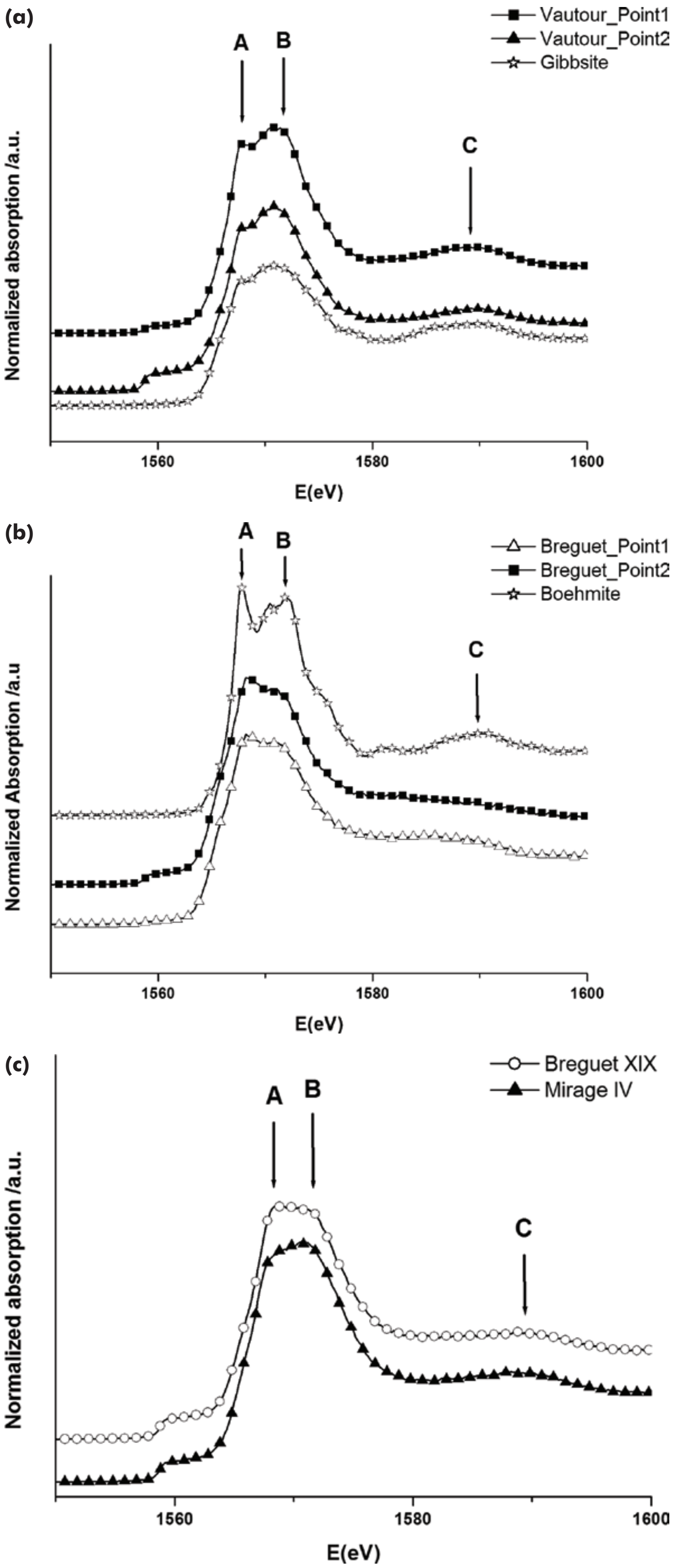

FIGURE 4. XANES spectra: (a) gibbsite type, with A < B, (b) boehmite type, with A > B, (c) third type, with A = B.

TABLE 1. Description of the aircraft samples and summary of XANES data collected

List of Aircrafts	Operational deployment	Positions in energy of the two main resonances in the Al K-edge spectra	Intensity of the main resonances in the Al K-edge spectra listed by order of occurrence	Al coordination
Breguet XIX	1923–1940	A : 1568 eV	A > B	VI
		B : 1571 eV	A = B	
			A < B	
Douglas A26 Invader	1942–1959	A : 1568 eV	A = B	VI
		B : 1571 eV	A > B	
			A < B	
SNCASO Vautour	1956–1970	A : 1568 eV	A < B	VI
		B : 1571 eV	A = B	
			A > B	
Dassault aviation MirageIV	1964–2005	A : 1568 eV	A < B	VI
		B : 1571 eV	A = B	
			A > B	
Bermuda Short	1938–1958	A : 1568 eV	A < B	VI
		B : 1571 eV	A = B	
			A > B	

main peaks A and B are less resolved in intensity. The same type of spectra was observed by Rocca *et al.* for accelerated ageing of anodized layers after 500 hours in a salt spray chamber (Rocca, 2012) in that case, ageing promoted formation of amorphous hydrous aluminium oxide [$Al(OH)_3 \times H_2O$]. This last group of spectra suggests a mixture of more amorphous aluminium hydroxide phases with a more disordered local aluminium octaedral arrangement, in comparison with the gibbsite and the boehmite ones.

The electrochemical measurements were performed both on polished samples without corrosion products and the overall "metal/corrosion products" system. As can be seen in figure 5, the potentiodynamic curves after 24 hours of immersion in the ASTM water are almost identical with and without corrosion layers on the Breguet XIX, Vautour and Mirage IV. In the group of the samples collected, the presence of thick corrosion layers did not modify the corrosion potential of metal and the corrosion current density in both anodic and cathodic regions.

In others words, the presence of a thick corrosion layer on aluminium alloys has little effect on the electrochemical activity of the corrosion phenomenon in immersed conditions. If we consider that the apparent surface may be underestimated, the thick corrosion layer can be considered as slightly protective from an electrochemical point of view. This result is very different from what has been observed for iron artifacts, for which the composition of the corrosion layer can greatly influence the corrosion rate of iron underneath the oxide layer.

DISCUSSION AND CONCLUSION

Our work has demonstrated the effect of long term exposure of Al–Cu alloys collected from a range of aircraft. The aluminum alloys are covered by very thick corrosion layers and are characterized by significant intergranular corrosion inside the metallic pieces, which can lead to the crumbling of the metal and complete disintegration of components. This phenomenon can be either very easily detectable or completely hidden. Therefore, the diagnosis and the assessment of objects are often complex and can require several samplings and analyses.

XANES analyses provides new information at a micrometric scale about the nature and distribution of aluminium phases of corrosion systems formed over time in atmospheric conditions for different historic aircraft. Data confirmed that corrosion products in thick layers are mainly composed of poorly crystallized or amorphous phases in which the aluminium is six-fold coordinated, rather than four-fold coordinated. In all cases the corrosion products consisted of more or less crystallized aluminium oxyhydroxides or hydroxides.

Whatever the manufacturing period of aircraft, our electrochemical experiments demonstrated that the Al–Cu alloys seem to have similar corrosion behaviour and that the presence of thick corrosion layers has little influence on the corrosion rate of the bare alloy. Despite small structural changes, the fact that the three oxyhydroxide aluminium phases are distributed homogeneously at a larger scale explains why the thick

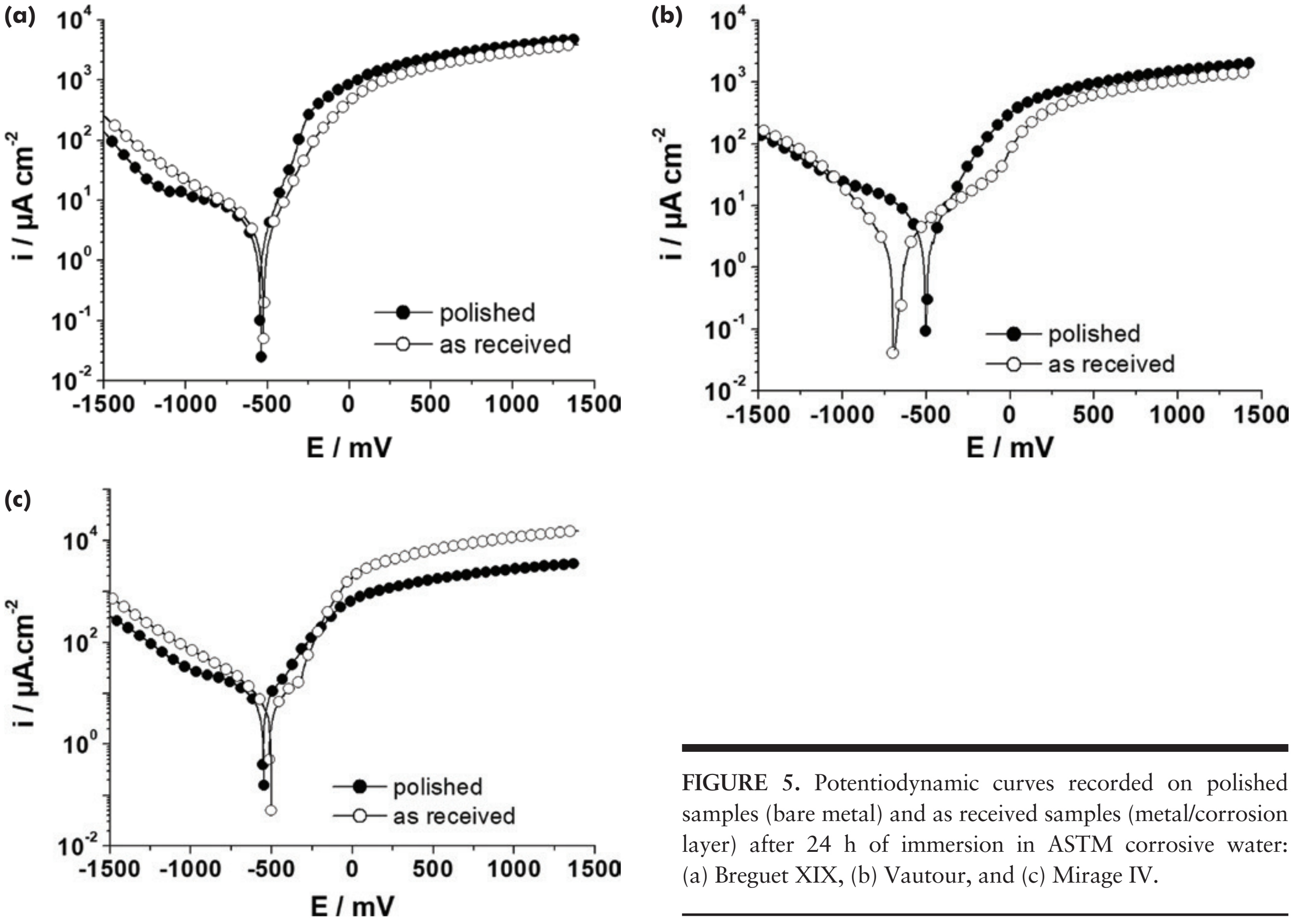

FIGURE 5. Potentiodynamic curves recorded on polished samples (bare metal) and as received samples (metal/corrosion layer) after 24 h of immersion in ASTM corrosive water: (a) Breguet XIX, (b) Vautour, and (c) Mirage IV.

corrosion layers have no impact on the corrosion behaviour of Al-Cu alloys. Contrary to long-term corrosion of ferrous alloys, the aluminium corrosion layer does not contain oxidant species similar to Fe (III) compounds or conductive compounds, such as Fe_3O_4.

From a practical point of view, “corrosion diagnosis” of aeronautic artifacts is often uncertain and difficult because of the significance of internal corrosion. The characterisation of the reactivity of the ‘aluminium alloys/corrosion layer’ complex systems in immersed conditions by electrochemical measurements has to be confirmed by further research devoted to the study of hydration or swelling of aluminium corrosion products with humidity, which seems to be the cause of crumbling and destruction of many pieces. Nevertheless, data obtained for the first time on the corrosion layers of aluminium alloys can be used to model the behaviour of such systems during the ageing process and to propose new coherent conservation strategies based on stabilization of aluminium hydroxide compounds versus hydration processes.

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Characterization of Two Propeller Blades from Submerged World War II-Era Wrecks

Yolaine Tissier[1]*, *Elodie Guilminot*[2], *and Sylvie Bergès*[3]

ABSTRACT. This paper focuses on the characterization of two World War II propeller blades, one extracted from brackish water of Lake Biscarrosse and the other from the saline Bay of Brest. Aircraft wrecks dating from the First and Second World Wars are regularly located and removed from crash sites. Of important historical value, they need to be preserved and exhibited without risk of further damage. To find the appropriate stabilization treatment it is essential to have a good understanding of the alloys used during this era. The research presented here characterizes the aluminum alloy and the corrosion products with optical microscopy (OM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and hardness measurements. The alloy for both blades was consistent with the composition of Duralumin, which was in widespread use at the time; it is similar to contemporary 2XXX series aluminum alloys such as 2024. This study concludes with questioning the necessity of dechlorination as a treatment step for aluminum alloys.

Keywords: Aluminum alloys, Duralumin, metallography, corrosion, aerospace

INTRODUCTION

Aluminum is a relatively new material (Selwyn, 2004). Friedrich Wöhler first isolated this metal from minerals in bauxite in 1827, but it is only from 1886 onwards that the use of aluminum spread, thanks to the Hall-Héroult electrochemical process (Hardouin Duparc, 2005). As aluminum production became easier, the metal started to be used by industry, especially because of its lightness and ease of shaping. During WWI, stronger aluminum alloys were developed with copper as the main alloying element. Duralumin was widely used during the first part of the 20th century (Pubellier, 1951). It is similar to modern 2XXX aluminum alloys that contain about 4 wt% copper (Cu), 0.5 wt% magnesium (Mg) and 0.5 wt% manganese (Mn). According to records searched at the archives of "Musée de l'Air et de l'Espace" (air and space museum) at Le Bourget Airport near Paris, this alloy was used in the construction of spars and the fuselage of several aircraft including Junkers J4 (a German WWI aircraft), Devoitine D520 (a French WWII aircraft) and Mustang (a U.S. WWII aircraft). Duralumin propeller blades, the focus of this study, were developed between the two World Wars and extensively used during WWII (Anonymous, 1954). The wide use of Duralumin can be explained by its combination of low density imparted by aluminum and good mechanical properties due to alloying with copper. Since the addition of other components makes it more sensitive to the corrosion of aluminum (Vargel, 2004), however, it is important to analyze the composition of artifact alloys and identify fabrication processes to understand corrosion behavior. To accomplish this, samples were removed from the two propeller blades for characterization using optical microscopy (OM), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), X-ray diffraction (XRD), chloride detection, and hardness testing.

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MATERIAL AND METHODS

Two aluminum alloy propeller blades were studied from wrecks submerged in water in France. The first was extracted from the brackish (45 mg/L chlorides) "lac de Biscarrosse" (Lake Biscarrosse) and provided by the Musée de l'Hydraviation (seaplane museum) in Biscarrosse. The second was extracted from the saline (36,000 mg/L chlorides) "Rade de Brest" (Bay of Brest). No serial numbers were found on the blades, but according to the Musée de l'Hydraviation and the DRASSM (Direction des Recherches Archéologiques Subaquatiques et Sous-Marines) it was assumed that both dated from WWII, since they were made from aluminum alloys.

SAMPLES

For examination by OM and SEM-EDS and for hardness measurements, a severely corroded and a slightly corroded sample were cut, using a circular saw, to the size in the range of 20 mm by 7 mm from each of areas #1, #2 identified in Figure 1 and area #1 identified in Figure 2. The six metallographic samples used for OM, SEM-EDS and hardness measurements were embedded in epoxy resin (Araldite resin DBF and hardener HY956) and polished using a series of silicon-carbide papers up to 4000 grit and a 1 µm diamond paste.

Corrosion products were sampled for XRD with a scalpel and ground using a mortar. On the blade from Brest, which was more severely corroded, they were removed from an area about 5 mm in thickness and in diameter (area #1 in Figure 1); blue and white colored corrosion products were collected separately. On the blade from Biscarrosse, mixed corrosion products about 1 mm thick were sampled from an area about 10 mm (area #1 Figure 2). Corrosion products (0.2 g) were also sampled for chloride measurements from 0.1–0.5 cm^2 areas on the blades; three samples were taken from each of four or five areas on each blade (areas #a, #b, #c, #d and #e in Figure 1 and areas #a, #b, #c and #d in Figure 2).

FIGURE 1. Areas sampled on the propeller blade from the museum in Biscarrosse, indicated by numbers #1 and #2 for examination by optical and scanning electron microscopy and for hardness measurements, and indicated by letters, #a, #b, #c, #d and #e, for chloride measurements. Photo credits: Jean-Gabriel Aubert.

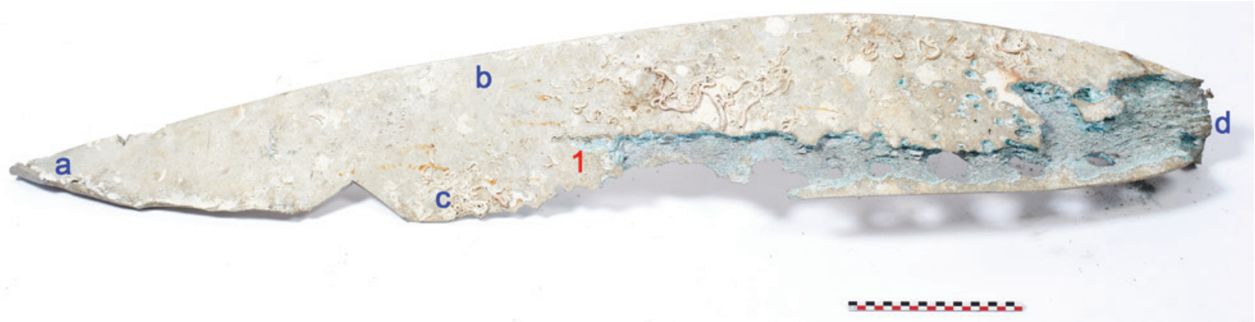

FIGURE 2. Areas sampled on the propeller blade from the Bay of Brest, indicated by number #1 for examination by optical and scanning electron microscopy and for hardness measurements, and indicated by letters, #a, #b, #c, #d and #e, for chloride measurements. Photo credits: Jean-Gabriel Aubert.

ANALYTICAL TECHNIQUES

Two acid solutions were tested for etching and OM examinations. Etch solution #1, 0.5 mL HF (40 wt%) in 100 mL deionized water, is recommended to highlight precipitates (Habraken, *et al*., 2007). Etch solution #2 was Keller's reagent [2 mL hydrofluoric acid (HF, 40% w/w), 3 mL hydrochloric acid (HCl, 37% w/w) and 5 mL nitric acid (HNO_3, 65% w/w) in 190 mL of deionized water]. Each acid solution was first tested individually and then they were combined. Etch solution #2 proved to be more effective than solution #1, which did not appear to yield any additional information, and only results obtained using solution #2 are presented here. The 10-second etching time recommended by Degrigny (1990) for 2XXX alloys was insufficient for the propeller samples, which instead required 50 to 110 seconds to acquire grain coloration. After etching, samples were rinsed in deionized water and dried with a hairdryer. Optical microscopy was performed on the metallographic samples using a ZEISS Axiotech 10HD microscope with 10× and 20× objectives.

Scanning electron microscopy was performed on the metal samples using a JEOL 5800LV at 20 keV, accompanied by energy dispersive spectroscopy. Samples were carbon coated. Images were obtained using a back-scattered electron detector. Six compositional measurements each on the matrix and inclusions were averaged.

Vickers hardness measurements (1 kN) were performed on the metallographic sections using a Mitutoyo MVK-H3 microdurometer. To assess the accuracy of the measurements, six hardness tests were performed on a standard (163 Hv1). The average result was 146 Hv, an error of about 10% compared to the expected value. The standard deviation was about 25 Hv.

XRD was used to analyze the composition of the corrosion products samples. The powders were placed on sample holders and analyzed using a D8 Advance diffractometer (geometry Bragg-Brentano type) equipped with a copper anode and a front monochromator that selects Cu $K\alpha_1$ radiation. Each measurement was performed at 40 kV and 40 mA for 1 hour.

Argentometry–potentiometry was used for chloride measurements. Samples were dissolved in 10 mL of 10% w/v sodium hydroxide (NaOH) for 24 hours, and the chloride measurements were repeated six times for each sample. Since chloride concentrations were near the detection limit, a chloride standard solution (25 mg/L) was systematically added before titrating. Two mL nitric acid were used to acidify the solution (to pH ≈ 1), so that silver chloride would precipitate. Solutions were assayed as follows: the blank consisted of 25 mL standard solution, 75 mL distilled water and 2 mL nitric acid; the dissolved sample solution (filtered to avoid interference with the electrode) consisted of 2 mL nitric acid, 25 mL standard solution and distilled water to make 100 mL. Chloride concentrations (mg/L) were related to the corroded surface areas of the samples (μg/cm²) as a more appropriate parameter than the volume of the dissolved solution.

RESULTS

METALLOGRAPHIC CROSS-SECTIONS

Optical microscopy showed that grains in all samples were strain hardened but that grain sizes varied among the samples (Figure 3). Grains on the Brest blade measured approximately

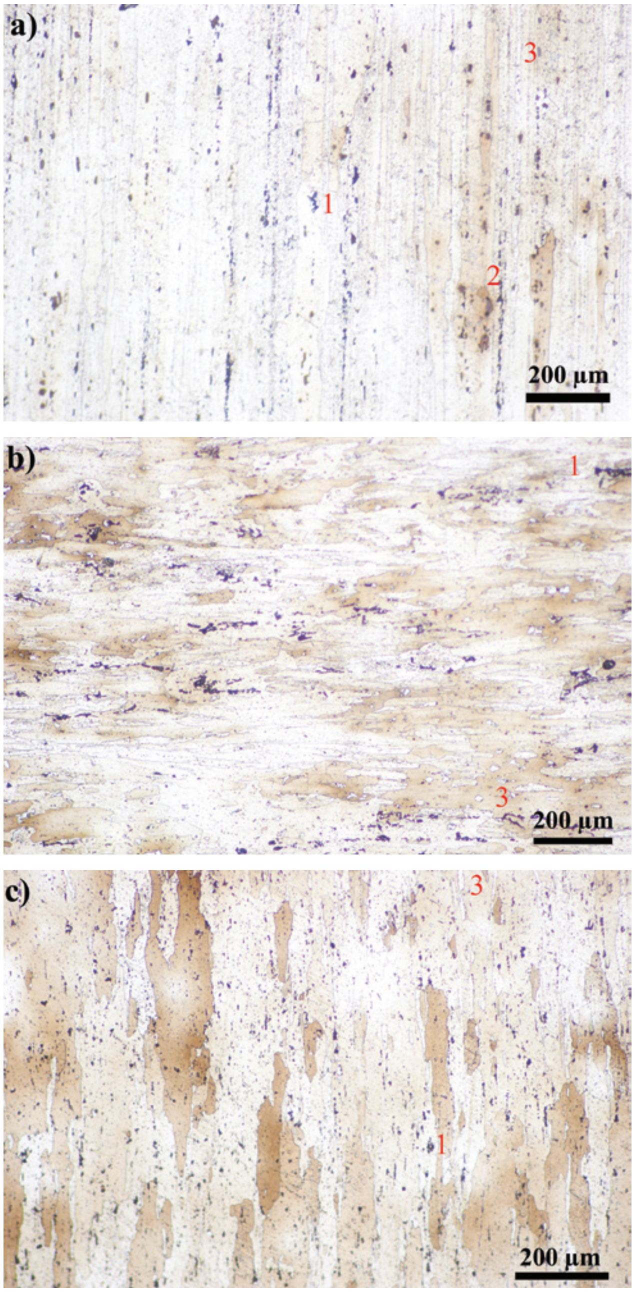

FIGURE 3. Optical microscopy of metal samples taken from: a- the extremity of the Biscarrosse blade, b- the center of the Biscarrosse blade, and c- the inner side of the Brest blade. #1 indicates black inclusions; #2, large brown; #3, white. Photo credits: Yolaine Tissier.

450 µm by 80 µm (Figure 3c), while those on the Biscarrosse blade grains were narrower, about 30 µm in width for the most corroded area at the blade extremity (Figure 3a, 3b). Brest blade samples exhibited predominantly small inclusions in large numbers (density around 1250–1300 particles/mm^2), which were distributed uniformly. Biscarrosse blade samples showed fewer inclusions (density 500–1500 particles/mm^2) with very heterogeneous distribution. Three types of inclusions were identified: #1, black; #2, large (about 15 µm in diameter) brown; and #3, white. Biscarrosse blade inclusions appeared to be concentrated at grain boundaries (Figure 3a), while they were not on the Brest blade sample illustrated in Figure 3c. These differences between the two blades might be explained by different alloys and/or shaping methods.

SEM images revealed different distributions of inclusions for each sample (Figure 4). On more corroded samples from the Biscarrosse blade, inclusions were clearly oriented (Figure 4b), while they were more randomly distributed on slightly corroded samples (Figure 4a). They were homogeneously distributed on the Brest blade sample, and two types of inclusions were identified on the samples (Figure 5): #1, small (around 5 µm in diameter) round; and #2, larger (around 20 µm) and variously shaped.

SEM-EDS results for the matrices showed that the blades were made of the same alloy, for which copper was the main alloying element (Table 1). They correspond to what was known at the time as Duralumin and in the current nomenclature is the 2XXX series, with the proportions appearing to correspond to the 2024 alloy. The composition of inclusions was variable (Table 2). The Biscarrosse blade mainly contained inclusions whose composition corresponds to the theta (Θ) phase (Al_2Cu) of the Cu-Al phase diagram. Some inclusions near the Biscarrosse blade's slightly corroded hub contained manganese and silicon. On the Brest blade, inclusions (Θ phase) were very small (around 10 nm) and distributed homogeneously. On the sample

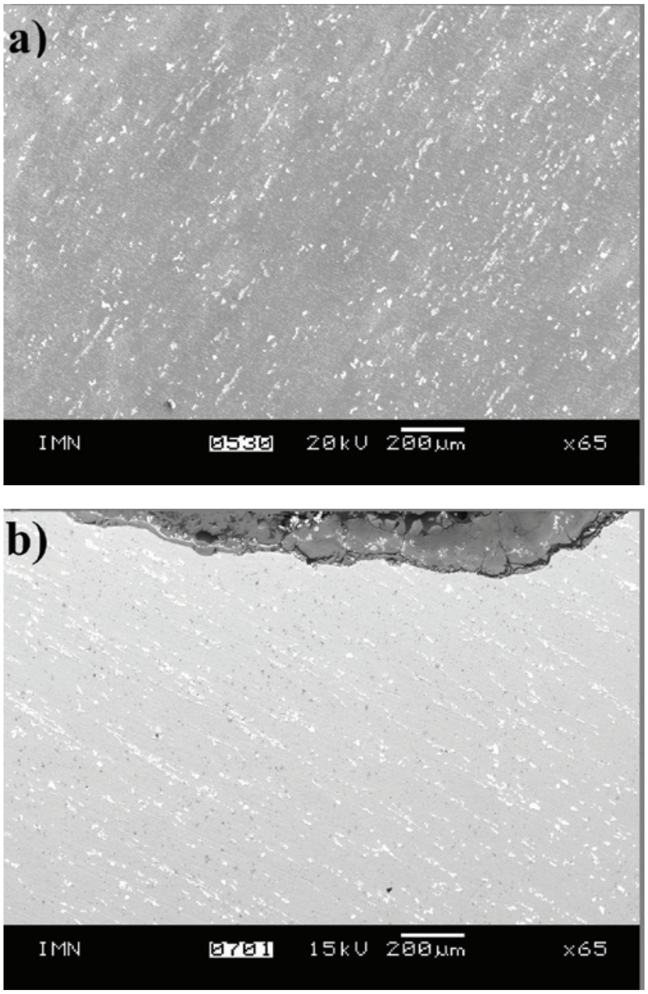

FIGURE 4. SEM images of samples from the Biscarrosse blade: (a) from a slightly corroded area, (b) from a severely corroded area.

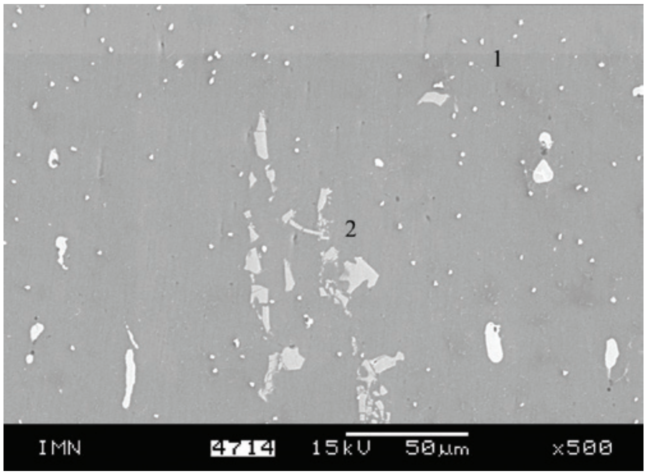

FIGURE 5. SEM image of a slightly corroded area from the Brest blade. (#1) small round particles, (#2) larger variously shaped particles.

TABLE 1. Matrix composition of the propeller blades from Biscarrosse and Brest as determined by SEM-EDS

	Biscarrosse			Brest		
	wt%	at%	Standard deviation	wt%	at%	Standard deviation
Al	94	95	2.6	94	95	2.4
Cu	3.7	1.6	0.8	4.0	1.7	0.0
Mg	1.1	1.2	0.3	0.9	1.0	0.2
Mn	0.6	0.2	0.1	0.6	0.3	0.1

TABLE 2. Composition of inclusions of the propeller blades from Biscarrosse and Brest as determined by SEM-EDS (*element was not present in all 6 measurements)

	Biscarrosse		Brest			
	Inclusions		Inclusions (slightly corroded area)		Inclusions (corroded area)	
	wt%	at%	wt%	at%	wt%	at%
Al	50.5	69.7	58.4	71.7	83.7	90.0
Cu	47.3	27.8	8 to 55	5 to 30	6.7	3.0
Mg	0.8	1.2	traces	traces	1.0*	1.2*
Mn	traces	traces	6.5*	3.9*	3.0	1.6
Fe			15.6*	9.2*	6.3*	3.3*
Si			0.2 to 5.4	0.2 to 6.3	2.4	2.5

from a slightly corroded area of the Brest blade, half of the six inclusion measurements showed the Al_2Cu type and the other half, the Al-Cu-Fe-Mn-Si-Mg compounds, while on the sample from the more corroded area all six measurements showed the latter compound. Lower quantities of magnesium were found in highly corroded areas, which could be explained by the fact that magnesium is usually the first compound to be dissolved, since it is less noble than the other elements present. Up to about 1 wt% chlorine was detected in inclusions.

Microdurometer results are presented in Figure 6. Values were generally near 100 Hv (mean values between 93 and 105 Hv). The standard deviation for each sample was less than 25 Hv. Therefore, measured differences fell within the error for the standard calibration. However, it should be noticed that results obtained on the slightly corroded sample of the Brest blade showed a less important dispersion which could be explained by a more homogeneous material as observed in previous results.

Different results for the two blades corresponded to what one might expect from the records search in the archives of air and space museum at Le Bourget regarding propeller manufacture during WWII era. As stretching of the metal occurred during fabrication of the blades, work hardening of grains may have been induced to a greater or lesser extent through plastic deformation. Particularly on the Brest blade, the very small inclusions were distributed homogeneously, which could be due to a heat treatment, annealing, quenching and aging that would improve mechanical properties of the alloy; for example, 2 hours at 525°C, quenching, and 17 hours at 160°C [the 525°C annealing temperature is between the stability limit of the α phase (approximately 475°C, depending on the amount of copper) and the eutectic temperature (549°C)]. On the Biscarrosse blade, in contrast, the inclusions varied in size and were concentrated at grain boundaries, as shown in Figure 3a and 3b. These differences could be explained by a limited knowledge of suitable Duralumin manufacturing processes which were still improving at the time, in the case of Biscarrosse Blade. Regarding Brest blade, results obtained suggest a better process control.

CHARACTERIZATION OF CORROSION PRODUCTS

Corrosion layers examined using SEM-EDS showed different surface appearances. Figure 7a shows pitting corrosion on a sample from the extremity of the Biscarrosse blade (area #1 Figure 1), while Figure 7b shows more homogeneous and widespread corrosion on the Brest blade (area #1 Figure 2), which was also found in the area closer to the hub of the Biscarrosse blade (#2 Figure 1). Light areas identified as #1 in Figure 7 corresponded to the matrix; grey areas (#2) were mainly composed of 65 wt% aluminum and 35 wt% copper (probably $CuAl_2$). Darker areas (#3 Figure 7a, 7b) on the corrosion layer of the analyzed samples were rich in oxygen (about 3 atoms: 1 aluminum atom) and may contain sulfur (up to 5 wt% in Brest blade). Chlorine was found in corrosion layers on both blades, around 1 wt% on the sample from the extremity of the Biscarrosse blade, about 3 wt% on the slightly corroded sample closer to the hub of the Biscarrosse blade and up to 4 wt% on the more corroded Brest blade.

XRD analysis of all corrosion products samples showed major peaks characteristic of gibbsite ($Al(OH)_3$), which corresponds to the composition of corroded areas found by EDS, e.g., 3 atoms of oxygen to 1 atom of aluminum. A chlorinated copper compound was identified in the blue colored corrosion products taken from the Brest blade, but only one chlorinated aluminum compound (chlorinated aluminum hydroxide) was identified among residual peaks in corrosion from the Biscarrosse blade.

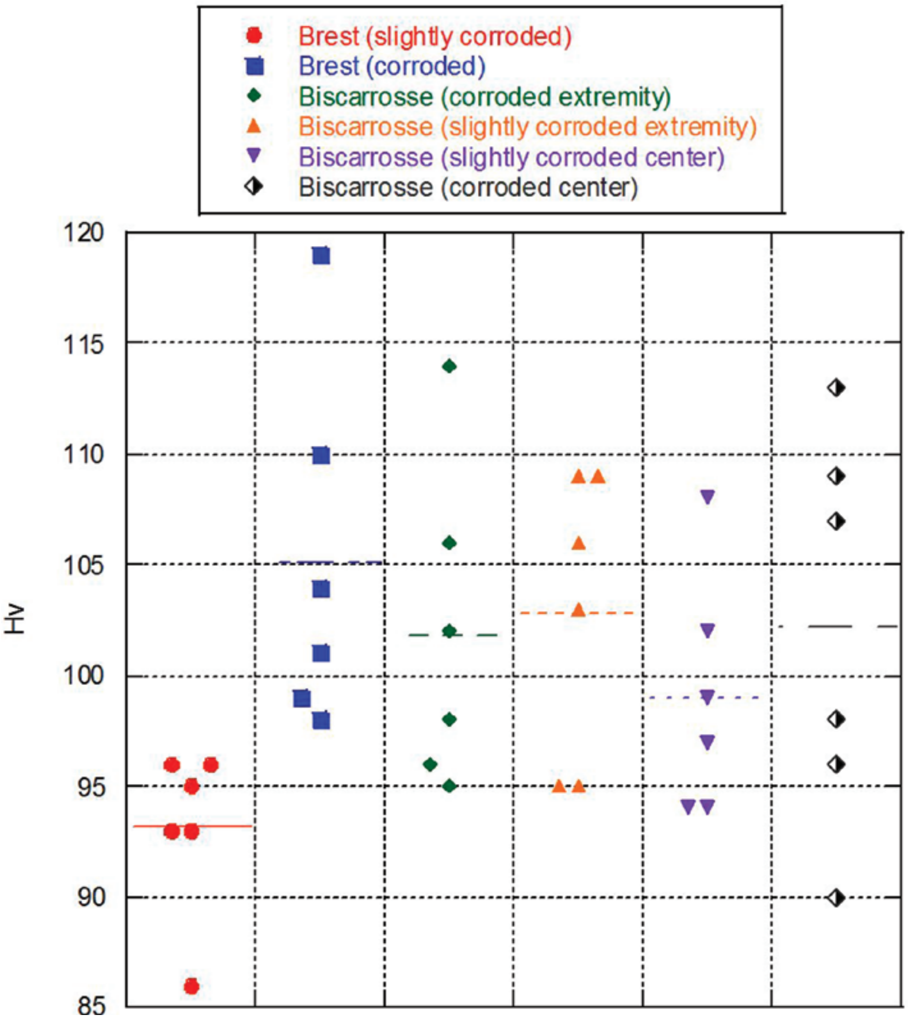

FIGURE 6. Results of Vickers hardness measurements (1 kN) on the propeller blades from Biscarrosse and Brest.

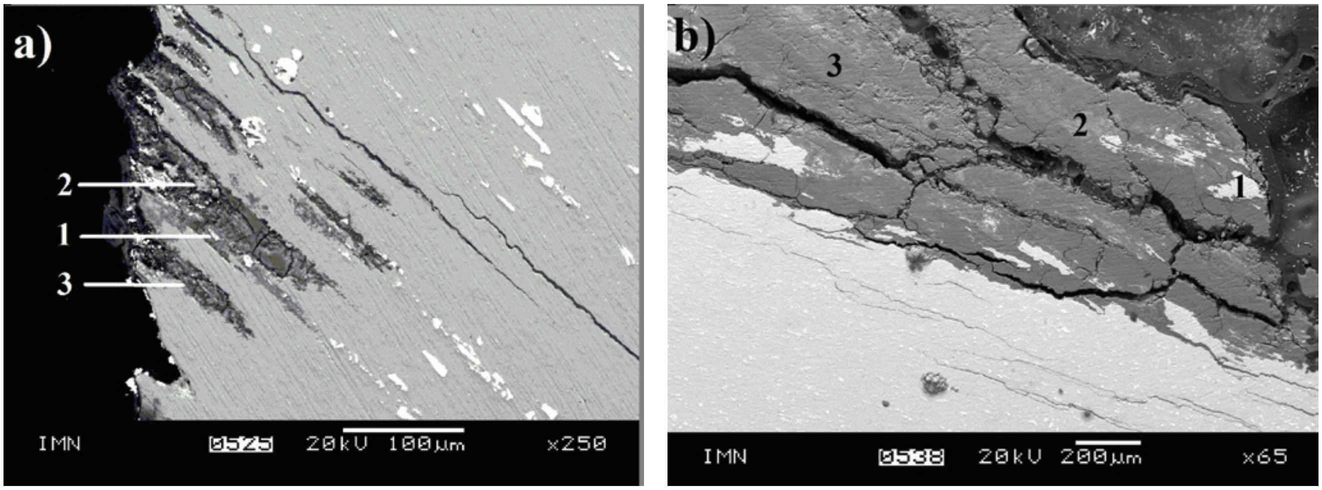

FIGURE 7. SEM images of corrosion layers on samples from: (a) the Biscarrosse blade and (b) the Brest blade; #1 identifies a light area, the matrix; #2 a grey area composed of 35% Cu/ 65% Al; and #3 an oxygen rich dark area.

TABLE 3. Chloride measurements by argentometry-potentiometry of samples from propeller blades

	Biscarrosse		Brest	
	Concentration (µg/cm^2)	Average (µg/cm^2)	Concentration (µg/cm^2)	Average (µg/cm^2)
Area 1 in the extremity	1270 ± 150	1900 ± 1300	1820 ± 220	2900 ± 2100
	1780 ± 240		2910 ± 470	
	2540 ± 300		3890 ± 840	
Area 2 in the extremity	2630 ± 410	2430 ± 300	-	-
	2310 ± 310			
	2340 ± 360			
Area 3 in the other extremity	990 ± 80	1100 ± 400	-	-
	1050 ± 100			
	1400 ± 150			
Area 4 near the hub	4640 ± 700	3700 ± 1900	1950 ± 190	1600 ± 1700
	3760 ± 560		580 ± 40	
	2700 ± 400		2330 ± 270	
Area 5 in the center	2050 ± 300	2200 ± 400	3550 ± 700	3000 ± 1900
	2160 ± 320		3900 ± 900	
	2400 ± 360		1510 ± 180	
Area 6 in the center	-	-	2250 ± 360	1700 ± 1000
			1740 ± 230	
			1230 ± 130	

Chloride Measurements

Chlorides were mainly localized in corrosion products on the blades, and chloride measurements of dissolved corrosion samples (Table 3) indicate low amount of chlorides. Considerable disparities in chloride values correlate with the corrosion thickness in particular areas. Chloride variation was limited on samples from slightly corroded areas of the Biscarrosse blade (standard deviation of about 300 µg/cm^2), for example, while it varied by a factor of two or more on severely corroded surfaces on both blades. Near the hub of the Brest blade, the smallest value corresponded to a quarter of the highest value (standard deviation of about 1,700 µg/cm^2). In any case, the quantity of chlorides was generally low even though the blades had not been treated and the Brest blade came from water containing high amounts of chloride ions (Bay of Brest 35,000 mg/L).

CONCLUSION

Analysis of propeller blades from Biscarrosse and Brest indicate they are made of Duralumin, an alloy representative of early metal aircraft. Duralumin combines good strength and low density, explaining its widespread use in the production of aircraft. Its improvement of mechanical properties over pure aluminum is mainly due to the addition of copper. SEM-EDS analyses showed that the propeller blade compositions approximate those of the current aluminum alloy 2024. Both propeller blades exhibited round particles corresponding to the intermetallic Al_2Cu phase. The Brest blade also contained coarser particles of the Al-Cu-Fe-Mn-Mg-Si type. These results are consistent with a distinction reported between hardening precipitates and coarse intermetallic particles in the 2024 alloy (Augustin, 2008). According to Augustin, the coarse Al-Cu-Fe-Mn-Mg-Si particles form during solidification, cannot be redissolved, and have an adverse effect on corrosion resistance. The heterogeneous corrosion of the Biscarrosse blade and more homogeneous corrosion of the Brest blade may be correlated with different distributions of inclusions. In addition, the more severe corrosion of the Brest blade can be explained by its exposure to the more corrosive environment of salt water.

Analysis of the corrosion products mainly revealed aluminum hydroxide $[Al(OH)_3]$. A copper compound was also identified in blue colored corrosion products. Chloride quantities were low, even on the heavily corroded Brest blade retrieved from highly chlorinated seawater. It has been stored in Arc'Antique for fifteen years without any changes observed during that time. Thus, questions about dechlorination arise. Should we treat these objects by dechlorination? Is it safe to keep residual chlorides in these objects? Whilst copper-rich phases promote corrosion, do chlorides also participate in the evolution of corrosion? Can we speak of active corrosion? Following this study, it appears essential to determine the chloride threshold beyond which corrosion is active. Therefore, the question of when and how to remove chlorides remains open. Cleaning the surface and using inhibitors could prove to be sufficient. The impact of the storage or exhibit environment should also be analyzed more precisely, including the relative humidity and presence of chlorides. Control of storage conditions may be easier to implement and less risky than dechlorination.

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The Conservation of Historical Marine, Terrestrial and Industrial Aluminium Objects: A Review

Christian Degrigny

ABSTRACT. Only recently (since the 1980s) have conservation professionals become interested in the conservation of the most modern of our heritage metals: aluminum. If the first aluminum alloys in the nineteenth century have good corrosion resistance and are usually well preserved, those produced in the twentieth century are often poorly conserved and require conservation treatment. The level of intervention depends strongly on the nature of the artefact, its size and the message to be conveyed. On large industrial objects, damaged original materials are often replaced by new materials. In a few cases the most innovative conservation techniques (laser cleaning, chronoamperometric, polarization) have been applied to preserve original material through cleaning and stabilization by extraction of aggressive species.

Keywords: Aluminum alloys, pitting, cathodic corrosion, conservation, stabilization, composite artefacts

INTRODUCTION

References in specialized literature to the good condition state of artefacts and architectural structures made of aluminum alloys produced at the end of the nineteenth century and exposed outdoors were and are still laudatory. Industrial objects (such as aircraft and components) produced afterwards have not received the same attention. They are even cases of neglect due to their large quantity. Aluminum metal was regularly scrapped during restoration, and it is only after historical remains became rare that a more conservative approach has been developed. Still, damaged components continue to be replaced with brand new materials except when traces of their use has historical significance, such as bullet holes or painted pictograms on aircraft fuselages.

This paper will review the way conservation approaches on aluminum artefacts have progressed and current knowledge of treatment. Different options, such as partial or full restoration and stabilization, will be illustrated through representative case studies. The pros and cons of each treatment will be discussed in the light of the most recent advances in the field.

HOW RECENT SEARCH FOR MYTHICAL ICONS BOOSTED THE CONSERVATION OF ALUMINUM-BASED ARTEFACTS

Until the 1980s, no mention is made in the conservation literature of the corrosion and conservation of heritage aluminum alloys. For many conservation professionals, aluminum alloys are considered rather stable. Their use in daily life, even in the

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most aggressive marine environments, supports this general idea (Vargel, 1979).

The first aluminum alloy objects (purses, opera glasses, office accessories, cigar and medicine cases, jewelry) were produced from 1855 to 1890 with the expensive Deville chemical process and are piously conserved in museums or by private collectors (Plateau, 2003). They have always been considered precious objects and preserved in controlled environments. Since their condition state is often excellent, these objects do not usually require any conservation treatment. This applies as well to the largest chemically produced aluminum piece installed at the top of the Washington Memorial in Washington DC in 1884. The cast-aluminum apex, which contains 1.7% Fe and 0.5% Si, is still in good condition (Binczewski, 1995).

By the end of the nineteenth century, the cost of aluminum was reduced significantly because of the new electrochemical method of extraction, which produced larger quantities of the metal. A few well-known heritage artefacts or monuments have confirmed the corrosion resistance of aluminum alloys produced at this time. The most famous is certainly the *Eros* of Picadilly Circus (1893) made of 98% cast aluminum; it has suffered several times from vandalism and benefited from seven restoration campaigns (Clarke, 1993). Another example is the cupola of the 1898 San Giocchino Church in Rome, the oldest aluminum roof in the world, which is exposed to a polluted urban atmosphere but has never been restored (Vargel, 1979).

The first industrial use of aluminum was for ship building, more particularly racing yachts. Copper was added to produce a harder metal alloy, but it decreased corrosion resistance of sheets applied to steel structures. The galvanic cell thus produced caused failure of the aluminum-alloy as well as the end of an era, which started at the very end of the nineteenth century, did not continue beyond 1901, and left few historical remains (Renié and Charles, 1990). The First and Second World Wars boosted development and production of aluminum alloys in the car and aircraft industries, particularly aluminum-copper alloys.

After World War II, tons of aluminum alloys from aircraft wrecks were recycled by scrap dealers. As time passed, wrecks became invaluable witnesses to the development of technology between the wars. Since most of terrestrial wrecks had disappeared, enthusiasts were obliged to look for wrecks that were rather inaccessible, notably those that were submerged. Everywhere new groups of wreck hunters were created.

Pictures of the remains of poorly conserved aircraft have been published in journals for aircraft lovers: since 1973 in the United Kingdom by *After the Battle* (www.afterthebattle.com) and between 1969 and 1975 in France first by *Le Fana de l'Aviation* and afterwards by *Pégase*. Often references are made to the recovery process, and in some cases the result was rather successful since it was immediately followed by conservation work (Flower, 1986). In others, the process was less thoughtful and the whole metallic structure was eventually scrapped (Bousquet, 1981). In these journals, the description of corrosion processes is very limited, and in most cases conservation work consists of the replacement of heavily corroded aluminum components. Indeed the shared approach of the volunteers was to get the aircraft back to the way it used to be.

It is only in 1985 after the recovery of an aluminum megaphone and soap dish from the famous *Titanic* (1912) wreck that a larger audience became aware of the need to conserve aluminum alloys (Montluçon and Lacoudre, 1989) and that funding became available to develop innovative conservation treatments for aluminum alloys.

THE IMPORTANCE OF DAMAGE EVIDENCE

Over time, metal artefacts may be mechanically or (electro) chemically damaged by corrosion, often reflecting part of the history of the materials.

Mechanical Damage

The conservation of the motorized tricycle fabricated in 1920 by Béchler and owned by the Musée du tour automatique et d'histoire (Museum of Automatic Lathe and History) in Moutier, Switzerland, provides a good example of historical mechanical damage (Figure 1a). When the artefact was entrusted to the Haute Ecole Arc Conservation-restauration (HE-Arc CR) in Neuchâtel in 2011, it was proposed to return it to operating conditions, as is usual for such objects. During the condition survey it appeared that the two-stroke engine was equipped with a clutch prototype inserted in a case made in an aluminum alloy containing both Cu (4.4%) and Sn (4.5%). This alloy is very porous and fragile, and cracks had formed in stressed areas (Figure 1b). The crankcase is made of a different aluminum alloy containing 10% Zn and 2% Cu, which is less porous and in much better condition. It seems then that the aluminum alloy used to make the clutch case was inappropriate compared to the alloy used for the crankcase, showing a lack of expertise in aluminum alloys and the lack of standardized compositions at the beginning of the twentieth century. The Al-Cu-Sn alloy of the clutch case is one of these alloys that were once used but later abandoned due to the production of better performing alloys. It is important to conserve such alloys either on the artefact itself or separately. In both cases, they are witnesses to technological developments.

Pitting Corrosion

While aluminum and its alloys are often found in rather good condition due to protection by oxide films, aggressive species such as chlorides may initiate localized corrosion (pitting) in the presence of an aqueous medium. Figure 2 shows the development of a new pit on the surface of an aluminum-based artefact immersed in a slightly chlorinated solution (Degrigny, 1990).

Depending on the microstructure of the metal, larger pits might develop that sometimes spread through the metal thickness (transgranular corrosion) or at grain boundaries (intergranular corrosion).

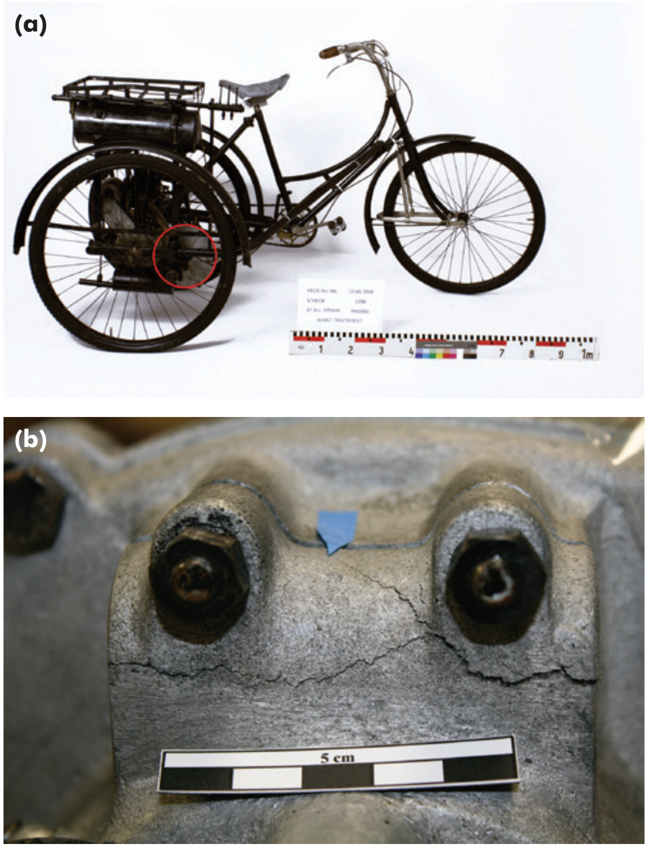

FIGURE 1. Béchler motorized tricycle from the Musée du tour automatique et d'histoire in Moutier, Switzerland. (a) Overall image with the clutch indicated by the red circle. (b) Detail of cracks in the clutch case where the metal is stressed. © HE-Arc CR.

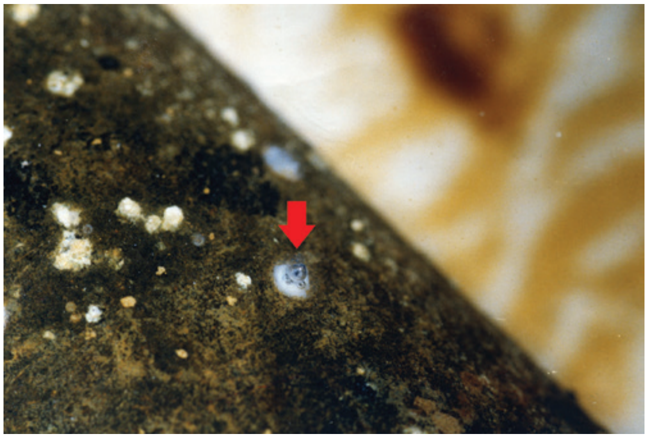

FIGURE 2. Formation of a pit is indicated by the red arrow on an aluminum-based artefact immersed in a slightly chlorinated solution.

When grains are elongated, intergranular corrosion degenerates into exfoliation. At that stage the metal has lost most of its mechanical strength. If a metal component is under permanent load, it is a risk to limit treatment to stabilization by extraction of chlorides; the component may need to be replaced for safety reasons.

Galvanic corrosion

Aluminum alloys are rarely found alone on heritage artefacts. On most industrial objects like cars, ships and aircrafts they are combined with more noble metals, such as copper and iron alloys, and/or reducing metals like magnesium alloys. Aircraft engines are good examples of these composite artefacts.

Specific corrosion forms are found on such composite metal artefacts. Galvanic corrosion may occur with the consumption of aluminum parts to the benefit of copper- and iron-alloy components. It is limited on the World War II Focke Wulf (FW) 190 BMW 801D-2 radial engine seen in figure 3, recovered in 1990

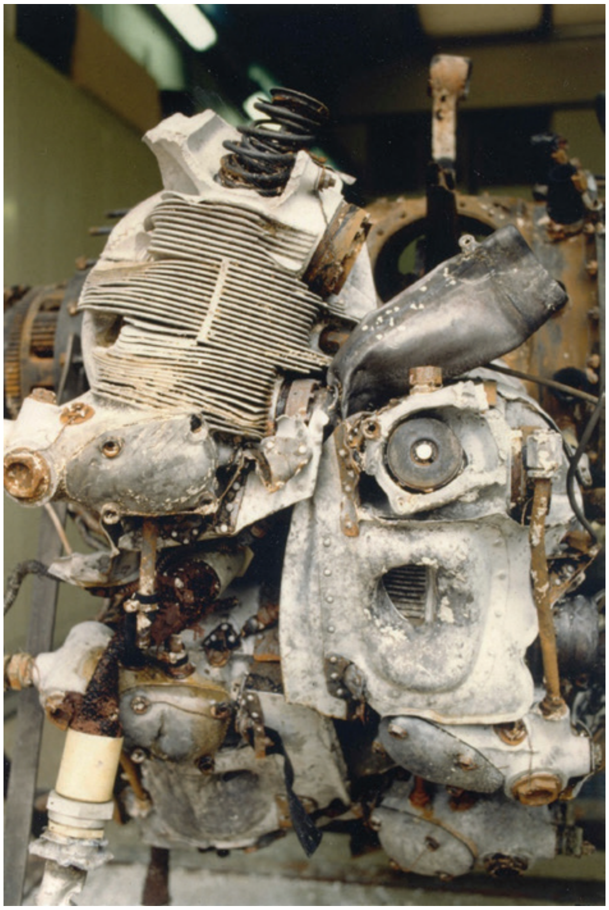

FIGURE 3. BMW 801D-2 radial engine from a FW 190 aircraft shot down in 1944 and recovered from the Loiret river in France in 1990, before treatment. The cast Al-Mg-Si alloy cylinder heads are in direct contact with iron-and copper-based components.

FIGURE 4. Detail of a radial engine from a CAMS 37 (1930), recovered in the 1980s from Cazaux Lake in France, before treatment. The cast Al-Cu cylinder heads, indicated by arrows, are fully mineralized.

from the freshwater Loiret river near Orléans, France. Galvanic corrosion may develop in more aggressive seawater or brackish environments and in uncontrolled storage areas, such as that housing a CAMS 37 radial engine (1930) recovered in 1980 from Cazaux Lake in the Landes region of France (Figure 4). Still both engines convey a message: in 1944, the German Air Force was significantly weakened when the FW 190, a legendary German fighter, was shot down. Similarly, the engine of the CAMS37 is one of the few remaining in its category.

Cathodic Corrosion

Aluminum parts should normally be preserved when in contact to more reducing metals such as magnesium components, but cathodic corrosion occurs. It can take different forms, either localized or general. This corrosion is due to a localized alkalization of the aqueous medium next to the metal surface when it is polarized cathodically. Corrosion is favored above metal inclusions where the oxide film is thinner (Figure 5a). Reduction of the aqueous medium produces not only hydroxide anions locally that consume the aluminum oxide, but also accentuates the alkalization process under hydrogen bubbles that adhere to the metal surface, eventually provoking the removal of the metal inclusions (Figures 5b and 5c). This form of corrosion needs to be further investigated by conservation professionals, particularly those in charge of the maintenance of aircrafts in uncontrolled atmospheres where condensation phenomena often occur. Indeed the risk of damage to composite artefacts containing aluminum components still connected to more reducing magnesium or other metals, such as landing gears, should be evaluated.

FROM TRADITIONAL TO THE MOST INNOVATIVE CONSERVATION TECHNIQUES

When conserving modern artefacts containing aluminum alloys, different options may be considered depending on the objective of the conservation project (Mikesh 1998). If the artefact has to be restored to its original appearance, damaged aluminum components may be replaced. When metal is preserved in-situ, surface treatments may be required to match the original appearance of the metal. On the other hand, if the goal of the conservation project is to preserve traces of the artefact's use, limited interventions are preferred, and any original paint, evidence of damage and remaining corroded metal may be preserved. Naturally the conditions of exposure of the artefact (outdoor or indoor, controlled or uncontrolled) will have a strong influence on the treatment selected.

The choice of one approach over another not only depends on the philosophy of the institution that owns the artefact but also on the size of the artefact and availability of the expertise required to carry out a successful conservation project. If the institution can only rely on volunteers or non-trained conservation professionals who might have been involved in the maintenance of aircrafts in operating conditions on a daily basis, the tendency will be to replace damaged components with brand new ones or to fully clean them to the polished state. The conservation of the *Concorde 001*

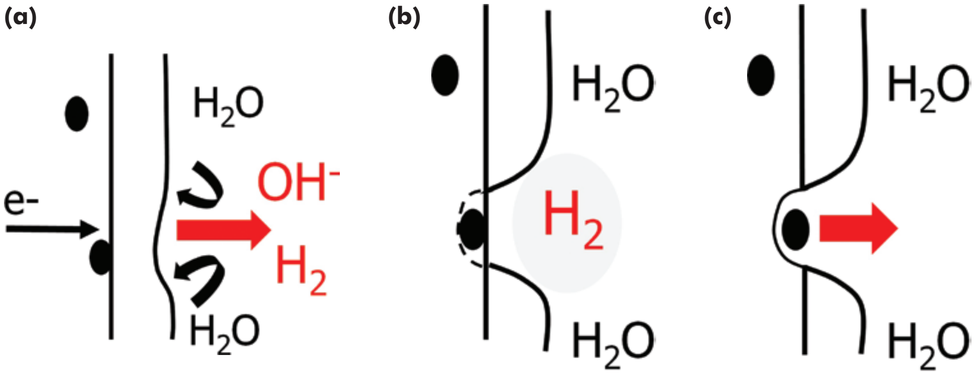

FIGURE 5. Mechanism of cathodic corrosion of aluminum alloys in a non-buffered solution. (a) Initiation, (b) development, and (c) removal of a metal inclusion.

built in 1969 is a good illustration of this approach. After its last flight in 1973, it was stored on one of the platforms of the Bourget airport near Paris, at the Musée de l'Air et de l'Espace (Air and Space museum). The metallic structure, constituted mainly of an Al-2%Cu-MgNi alloy, suffered from filiform corrosion under the paint layer, crevice corrosion and sediment deposits on the wings. The conservation treatment decided upon in 1993 involved degreasing the aluminum alloy surfaces, chemical removal of surface coatings, mechanical cleaning of damaged metal surfaces and inhibition of corrosion with potassium chromate. After rinsing with fresh water, the metal surface was repainted with a more recent and effective paint system based on polyurethane instead of the acrylic and polyester resin coatings used and the *Concorde* was installed in 1995 in a closed hangar (Magnin et al., 1995).

During the 1980 and 1990s, other innovative treatments were tested on corroded aluminum alloys. A few are presented below.

LASER CLEANING

Laser cleaning has been applied with success to mechanically remove crusts that formed with time on aluminum artefacts exposed to polluted urban environments. The *Eros* in Sefton Park in Liverpool, United Kingdom, was made in 1932 as a copy of the *Eros* in Picadilly Circus in London. Cast in a less pure 93.2% aluminum alloy than the original statue, the copy became heavily corroded with time and eventually was covered with a thick crystalline crust of calcium sulfate that had migrated from the core. The statue received conservation work in 1991 in the Conservation Center of National Museums Liverpool (Larson, 1995). Since the metal was rather porous, it was thought that water-based solutions and chemicals for cleaning would not be appropriate. Laser cleaning was tested because it was dry, controllable and would not interact with the chemistry of the aluminum. Not only were dirty layers vaporized, but layers of salt crystals were also detached using the ultrasonic effect of the beam. Furthermore, the laser left the naturally oxidized patina on the surface intact. The *Eros* is now exhibited inside the Conservation Center, while a replica has been installed in Sefton Park.

CHEMICAL PROCESSES

In 1983, MacLeod published the first scientific paper on the chemical stabilization of a heavily chlorinated aluminum alloy artefact: a duralumin seaplane float from a Junkers W33 that crashed on land in tropical northwest Australia in 1932. It was rediscovered in 1978 and treated in the conservation laboratories of the Western Australian Museum (MacLeod, 1983). The treatment consisted of a simple washing procedure that aimed to remove aggressive species (Cu cations and Cl anions) contained in corrosion layers. The buffered ammonia-ammonium sulfate solution (pH 9.6) used to produce $Cu(NH_3)_4^{2+}$, was renewed three times. In total the treatment lasted 425 days, and the metal surface was scrubbed down with fresh water between each step. A total of 53 g of copper cations and 110 g of chloride ions were ultimately removed, and after one year no further corrosion had occurred on the artefact (see also MacLeod, this volume).

ELECTROLYTIC STABILIZATION PROCESSES

In 1985, the Valectra division of Electricity of France was contacted by the curator of the Musée de l'Hydraviation (seaplane museum) at Biscarrosse in the Landes region of France to provide expertise on stabilization of aluminum-based artefacts recovered from Lake Biscarrosse (slightly chlorinated at 28 ppm) used before and during the Second World War as a German flying boat base. A PhD research project was launched with the objective of designing an innovative electrolytic stabilization process, different from the ammonia-ammonium sulfate procedure used by MacLeod, which was considered rather hazardous at that time for treating large aluminum structures (Degrigny, 1990).

The electrolytic treatment had to be carried out in neutral solution within the passivation field for aluminum alloys in an aqueous medium; that is, a pH between 4 and 9 and a potential between the two diagonals of stability of the aqueous solution (a and b on figure 6). Risks of recorrosion were investigated in this field, corresponding to the red dashed circle on figure 6. Indeed chlorides extracted from the chlorinated alloys might provoke new forms of pitting corrosion in the upper part of the diagram, while cathodic corrosion might occur in the lower part due to the cathodic polarization applied to accelerate the extraction process (Degrigny, 1991).

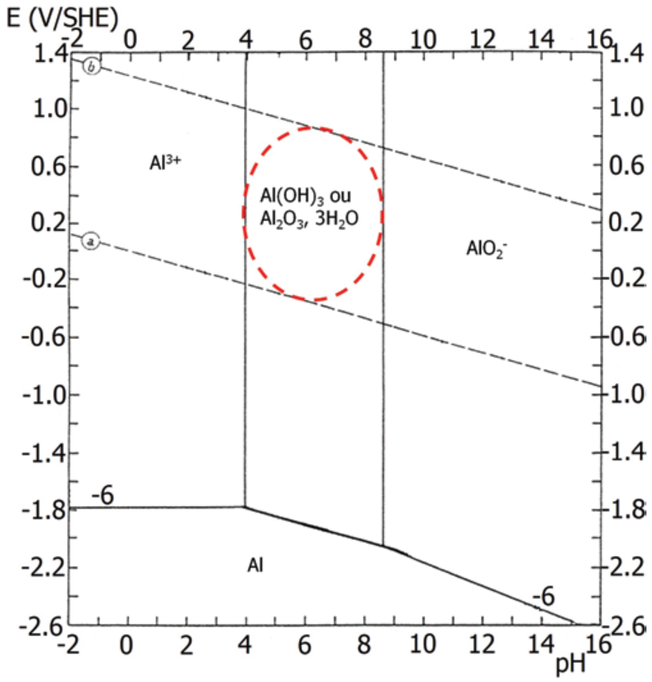

FIGURE 6. Potential-pH diagram of the system Al-H_2O at 25°C and Al species < 10^{-6}M (Pourbaix, 1963). Potentials are versus the Standard Hydrogen Electrode (SHE).

Probability of Pitting Corrosion

Pitting corrosion occurs on aluminum alloys in presence of chlorides at a certain potential known as the pitting potential (E_p). At the E_p, corrosion current increases tremendously; the E_p is also not a reproducible value. Two potentials are then defined: the potential of low ($E_{p.\ inf}$) and high probability of pitting ($E_{p.\ sup}$). Above $E_{p.\ sup}$, the probability of pitting corrosion is 100% while below $E_{p.\ inf}$ it is 0. Figure 7 shows how the concentration of chlorides and the buffering of the solution might affect the sensitivity to pitting corrosion of alloy 6082 (Al –0.8%Mg – 1%Si– 0.7%Mn). Obviously E_p increases with decrease of the chloride content, while buffering of the solution tends to slow down pitting corrosion.

When studying the same sensitivity to pitting corrosion at pH between 4 and 9 and in a buffered solution containing 30 ppm chlorides, an amount usually found during stabilization treatment, a modified potential-pH diagram can be constructed (Figure 8). It appears that the risk of pitting corrosion of 6082 aluminum in a neutral solution is least around a pH of 6.7.

The corrosion potential of aluminum alloys immersed in a neutral solution containing 30 ppm chlorides slowly increases and after a few hours runs the risk of pitting corrosion. Therefore, the risk of pitting corrosion is real for chlorinated artefacts left without cathodic polarization in neutral solutions.

Risk of Cathodic Corrosion

Cathodic corrosion occurs when the potential of aluminum alloys decreases artificially (cathodic polarization). It is characterized by two parameters: $E_r l$, potential of localized rupture of the oxide film where corrosion remains limited to a few pits, and E_r, potential of rupture where corrosion is generalized. In slightly acidic buffered solutions, initiation of cathodic corrosion through localized alkalization is difficult to achieve. Corrosion develops in two steps, as indicated in figure 9 for the 6082 alloy in chrono-amperometric plots at different cathodic potentials in unstirred and de-aerated buffered sodium citrate solution (10.56 g anhydrous citric acid + 4.84 g NaOH per liter of

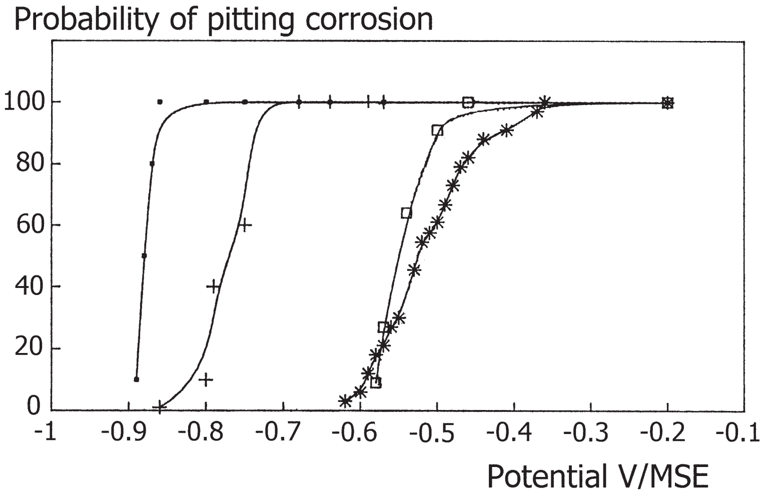

FIGURE 7. Influence of a buffer (sodium citrate, pH 5.4) and concentration of chlorides on the sensitivity to pitting corrosion of alloy 6082. (■: 150 ppm Cl^- in deionized water, +: 150 ppm Cl^- in buffered solution, □: 50 ppm Cl^- in deionized water and *: 50 ppm Cl^- in buffered solution). Potentials are versus the Mercury Sulfate Electrode-MSE (0.66 V/SHE).

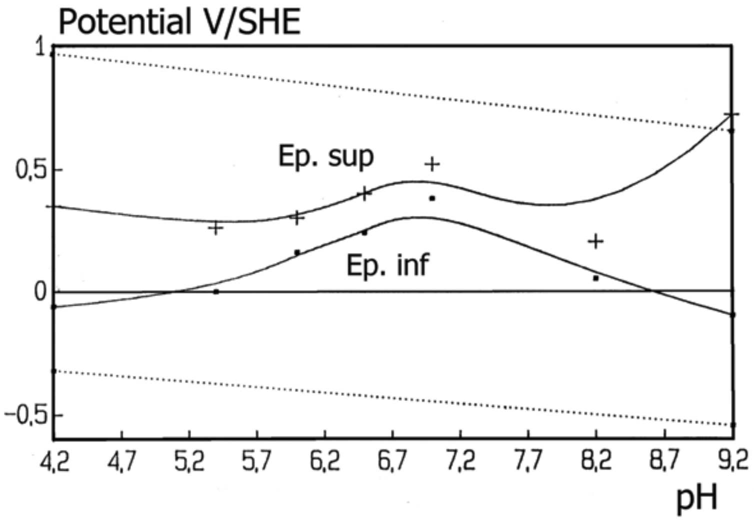

FIGURE 8. Experimental potential-pH diagrams for 6082 alloy between pH 4 and 9 in a buffered solution containing 30 ppm chlorides. Potentials are given versus SHE.

deionized water, pH 5.4) containing 30 ppm chlorides. During the first step corresponding to the slow hydration of the oxide film (see Figure 5a), the current remains low. During the second step corrosion is activated locally around metal inclusions (see Figures 5b and 5c). The more negative the potential applied, the faster the corrosion is.

It is recognized that cathodic corrosion increases with pH. Eventually a modified potential-pH diagram integrating the risks of pitting and cathodic corrosion for 6082 alloy is obtained (Figure 10).

Due to the difficulty of producing localized alkalinization (and therefore cathodic corrosion) in a slightly acidic buffered

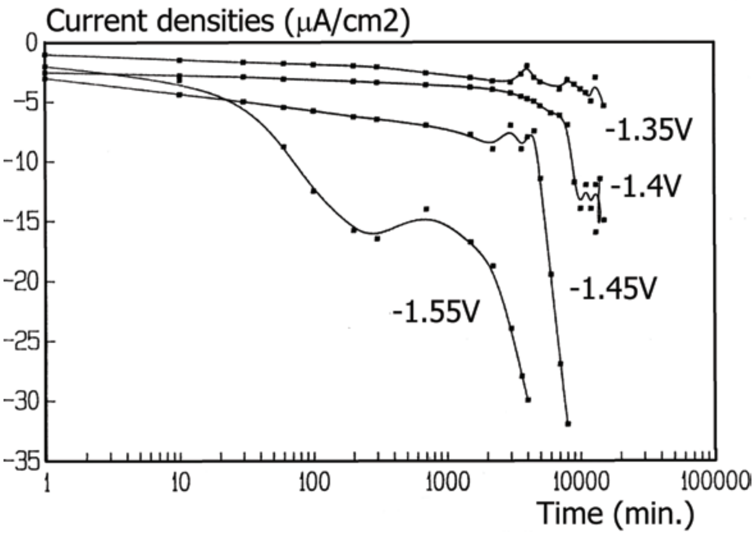

FIGURE 9. Effect of the cathodic potential (versus MSE) on chrono-amperometric plots of alloy 6062 in a buffered unstirred and de-aerated sodium citrate solution (pH 5.4) containing 30 ppm chlorides.

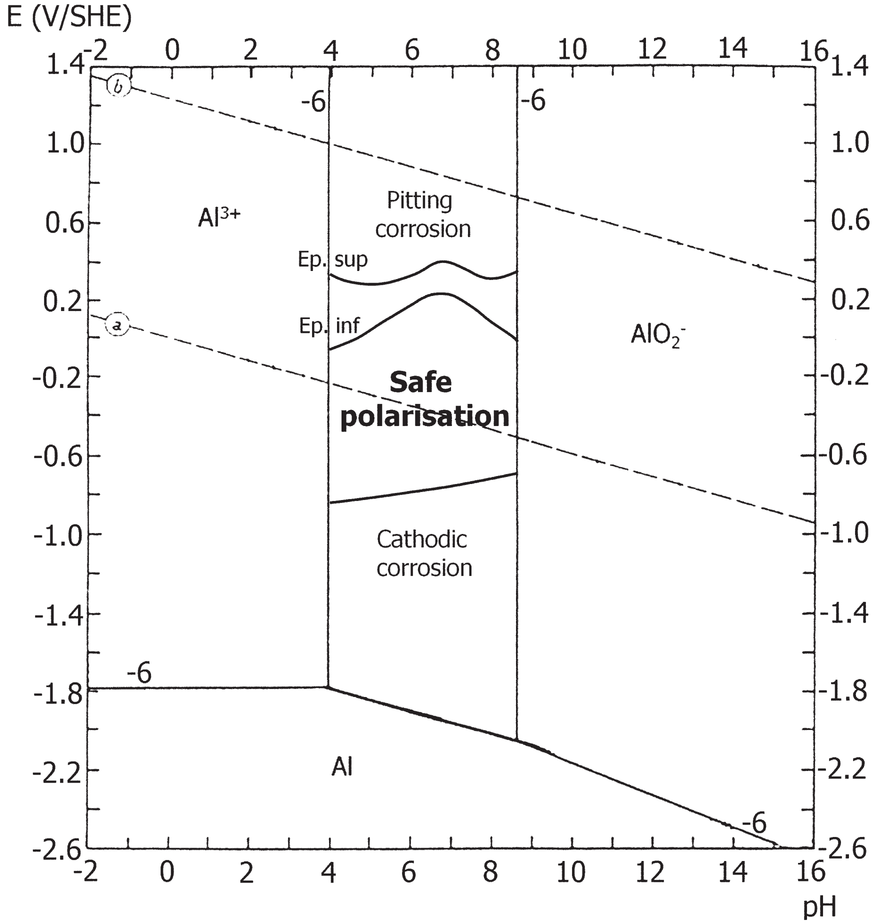

FIGURE 10. Modified potential-pH diagram for the system Al (6082)-H_2O at 25°C and Al species < 10^{-6}M, showing the risks of pitting and cathodic corrosion in solutions containing 30 ppm chlorides. Potentials are indicated versus SHE.

solution, many chlorinated aluminum artefacts have been treated in the 1990s using cathodic polarization at a potential between −0.7 and −0.8 V/SHE in a buffered sodium citrate solution (pH 5.4). Figure 10 indicates that in such conditions, extraction of chlorides should be effective and safe for the artefact. The protocol of treatment has been continuously optimized to adapt to different objects under consideration.

For heavily corroded Al-Cu artefacts found in proximity to iron alloys and covered with corrosion products containing copper or iron species, pre-treatment by immersion in chelating agents (disodium EDTA or sodium citrate) is often done to remove metal cations that would otherwise redeposit on the metal surface. This pre-treatment eliminates most chlorides but must be used with care when paint is present, as it is likely to dissolve any traces of paint. Remaining chlorides can only be extracted using cathodic polarization in a buffered sodium citrate solution. The artefact must be rinsed in deionized water between each step, and the whole process lasts a few weeks (Degrigny, 1991).

Crusts on composite artefacts containing iron alloys can be eliminated electrolytically in a 0.04M sodium metasilicate solution between −0.4 and −0.8 V/SHE without any risk to aluminum-based components (Degrigny, 1995). At such low concentration sodium metasilicate behaves like a corrosion inhibitor. Figure 11 shows the FW 190 BMW 801 D2 radial engine illustrated in figure 3 just before electrolytic cleaning in the sodium metasilicate solution.

In the 2000s, Bailey stabilized large components of a crashed Japanese Army Air Force Nakajima Ki 43 II "Oscar" fighter aircraft from Papua New Guinea recovered in 1984 using a similar protocol (Bailey, 2004; see also Bailey, this volume). After its crash in 1944, the aircraft had corroded and suffered extensive deterioration while sitting on swampy ground. Due to the large volume of solution required, the treatment was not preceded by pre-treatment or combined with iron crust removal. Side effects that occurred during the treatment included fungal growth, decrease in the clarity of the solution, production of offensive odors.

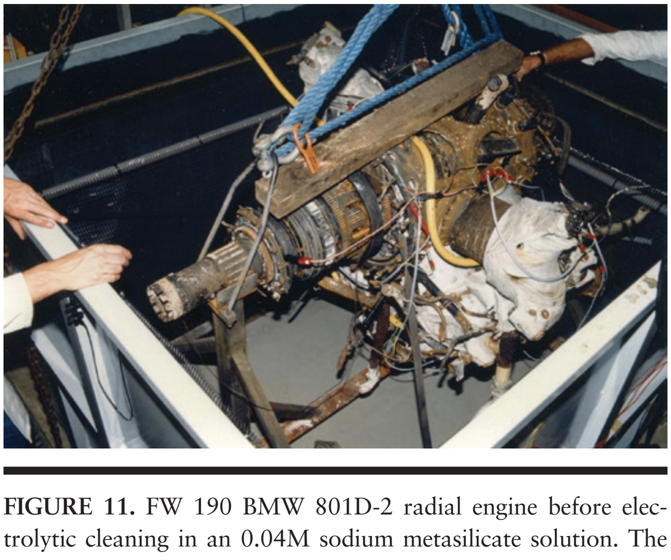

FIGURE 11. FW 190 BMW 801D-2 radial engine before electrolytic cleaning in an 0.04M sodium metasilicate solution. The engine is positioned on a steel frame, which can be attached to the hook of a travelling crane and lifted for close examination during treatment and when the solution has to be changed.

More recently, the sodium citrate solution was selected to clean and stabilize the components of a Dornier Do17 recovered from the Channel in June 2013. This time the solution was sprayed three times an hour on the metal components placed in two hydration tunnels at the Royal Air Force Museum in Cosford (Priday, 2013).

CONCLUSION

Stabilization of remaining materials and replacement and re-polishing of damaged components to produce new surfaces are the two conservation approaches commonly applied on historical aluminum artefacts. The choice of one approach over another or both depends on the conservation philosophy of the owner. Safety issues may also influence the final conservation strategy if the artefacts are exhibited to the public, as well as the level of expertise of the conservation team.

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The Preservation of a Marine Archaeological DC-3 Aircraft

Christina H. Tengnér

ABSTRACT. The single most well-known object at The Swedish Air Force Museum is the wreck of a DC-3 aircraft. It functioned as a flying radio surveillance station when it disappeared in 1952 on a mission over the Baltic Sea. Fifty years later it was located and salvaged. After forensic investigation, it was turned into a museum object. The process of preservation began immediately to make the rapidly corroding wreck stable and exhibitable. The wreck consists of many different materials, of which aluminum is the most prevalent. It is presented in the museum in the same position as it was found on the sea bed, and the preservation of the aluminum body and wings was done with this display in mind. The preservation work was a collaboration between museum experts, corrosion engineers, and an industrial producer of corrosion treatment products.

Keywords: DC-3 aircraft, Cold War, marine archeology, aluminum-copper alloy, corrosion, cleaning, chlorides, coatings

HISTORICAL BACKGROUND

On Friday the 13th of June 1952, a Swedish military DC-3 along with its eight crew members disappeared during a flight somewhere over the Baltic Sea. The aircraft was on a radio surveillance mission aiming its attention at Soviet radio stations located along the west coast of the Baltic states. The search that followed revealed the probable destiny of the DC-3, although it remained missing for another 50 years. A Catalina aircraft that participated in the search was shot down by a Soviet MIG fighter, with the crew surviving the crash. The events surrounding the missing and downed DC-3, dubbed "The Catalina Affair", masked the fact that Sweden was performing advanced radio surveillance on the Soviet Union with USA-supplied electronic equipment. This fact was treated with discretion for the Swedish general public but was hardly a secret to the Soviet Union. All eight crew members of the missing DC-3 disappeared along with the aircraft (Älmeberg, 2007).

In 2003, the DC-3 was found by a privately funded search team named Deep Sea Productions. The group was scanning the sea bed off the Swedish island of Gotland using sonar equipment to look for sunken ships in general and the missing DC-3 in particular. The DC-3 was found in international waters 57 km from the Swedish island Gotska Sandön, resting 125 meters below the surface (Figure 1) (Försvarsmakten, 2007).

Since it was a military aircraft, the military took responsibility for the salvage and forensic investigation. The wreck was placed in the marine base of Muskö on the coast south of Stockholm, where the majority of the preservation work on the body and wings of the aircraft would take place (Figure 2).

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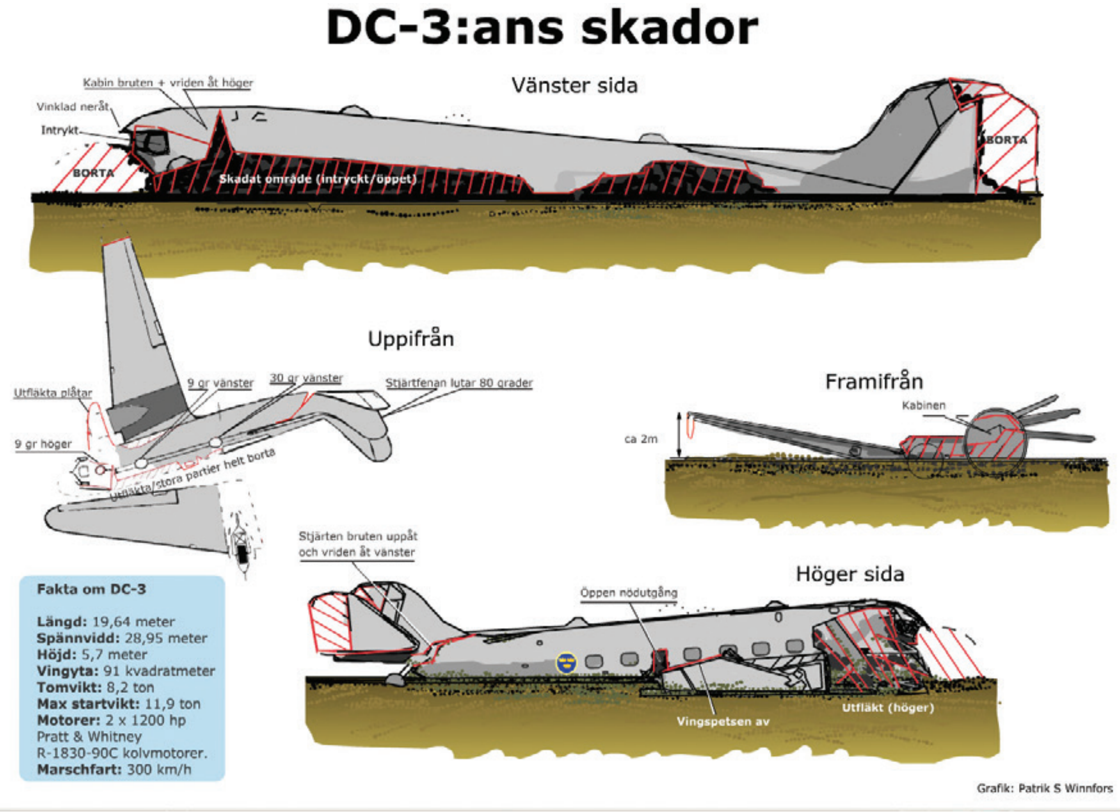

Fakta om DC-3

Längd: 19,64 meter
Spännvidd: 28,95 meter
Höjd: 5,7 meter
Vingyta: 91 kvadratmeter
Tomvikt: 8,2 ton
Max startvikt: 11,9 ton
Motorer: 2 x 1200 hp
Pratt & Whitney
R-1830-90C kolvmotorer.
Marschfart: 300 km/h

FIGURE 1. Graphic representation of the wrecked DC-3 as it lay on the sea bed. Clockwise from top: left side, front view, right side and view from above. © Patrik S. Winnfors.

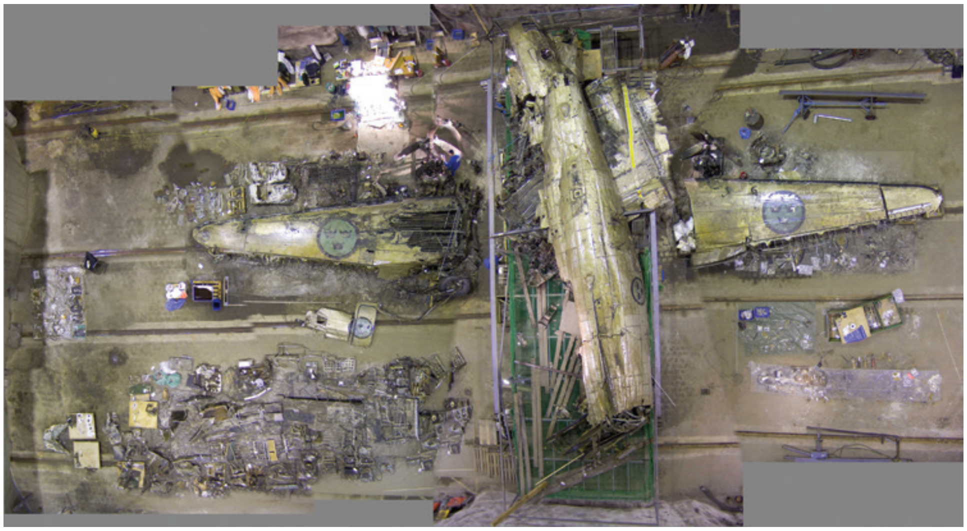

FIGURE 2. Panorama of wreck in pieces during forensic work at Muskö Marine Base. Photo/montage: Air Force Museum Linköping/Forensic investigator Christer Magnusson.

RECOVERY PROCESS

The recovery of the DC-3 was done by lifting the fuselage to the surface and onto a ship using slings and metal baskets. To attach the slings at the depth of 125 meters, a small manned submarine known as a "sea owl" was used. The left wing was disconnected from the body by the impact of the crash and resting on the sea bed next to the body. The right wing was still in its original place attached to the body but had to be taken off in order to lift the body. When lifting the larger parts, many small pieces and loose items fell out of the wreck, while others were already buried in the sea bed before recovery. To prevent any of these items from being lost, a freezing method was used to bring them to the surface. Large freezing blocks or plates with surface areas about the size of a standard freight container were placed on the sea bed, where they froze the mud down to a depth of about 20–30 cm. The sediment was frozen at a temperature of between –20°C to –30°C by a cooling liquid in the blocks. The frozen mud was lifted to the surface and allowed to thaw so that an excavation could be undertaken. Many small but important items like wallets and even remains of crew members were recovered in this way (Försvarsmakten, 2007).

Soon after recovery it was decided that the wreck was to become a museum object, as this story plays an important role in the history of the Cold War in Sweden. Normally after forensic investigation a wreck is discarded, but as this was not going to be the case much work had to be done to stabilize the materials and prevent further degradation. The wreck had to be put into a condition where it could be preserved in a controlled museum environment. Today it is on display at The Swedish Air Force Museum in Linköping. The fuselage, wings and hundreds of loose parts, varying in size from engines and propellers to a gold wedding ring, are presented so as to resemble their locations at the bottom of the Baltic Sea.

Organizing the Preservation

An object of this size and complexity required a number of experts, some of whom could not be found within the organization of the National Swedish Museums of Military History. Corrosion treatment experts with experience in aviation and the transport industry were engaged to identify and develop a system for cleaning and treating the wreck. The body and wings were treated by technicians, including cleaning, chloride measurements, and surface treatments. Larger parts like propellers and engines were treated simultaneously using the same methods. Smaller items like electronics, parts of the cabin interior, and other loose objects that required more careful treatment were moved to the conservation department at The Swedish Army Museum.

AN ALUMINUM WRECK

The most common material in a DC-3 is the 2024 T aluminum alloy (or 24 ST alclad). A prominent feature of this alloy from a marine archaeological or preservation perspective is the relatively high amount of copper: 3.8–4.9% by weight. The problem of intergranular corrosion, caused by the presence of copper, is a feature of this material (Davies, 1999). The surface of the sheet metal was clad with pure aluminum for increased corrosion resistance and often coated with a lacquer. The core metal gave the sheet mechanical strength making it suitable for aircraft construction. The cladding and top coat, however, did not prevent corrosion of the aluminum-copper base metal during its immersion in the brackish water of the Baltic Sea. Naturally, for an alloy with properties suited for an aircraft, there was no need for the aerospace industry to consider how the alloy would act when immersed in sea water, since it would be literally out of its element.

ORIGINAL SURFACE FINISHES AND COATINGS

The original surface of the DC-3 aluminum alclad 2024 was first anodized with chromic acid to thicken the passive oxide layer, then primed and painted. Evidence of the primer was found in the many hidden compartments where the aluminum surface was covered with a primer where the active component is zinc chromate in an alkyd paint (the Swedish military standard for a similar product is MIL-P-6889a). In areas like the inside of the wings, the primer is evidently original, as these parts are made from riveted aluminum sheets not meant to be opened. In some damaged parts where the construction is now visible, the primer can be seen as a thin, transparent, yellow-tinted coating. Other chromate-coated parts that were not exposed to water or sediment look as though they are fresh from the factory. Even delicate details like pencil markings from the time of the construction of the aircraft have been preserved on these surfaces. Thus, the overall condition of the aluminum varies from completely degraded to as good as new.

Surfaces of the outer shell, body, and wings bear remains of lacquer coatings. It is very likely that this DC-3 was renovated and the coating renewed several times during its working life. This aircraft had been bought on the second-hand market after the Second World War, during which it had served as a troop carrier in North Africa and Southern Europe amongst other things. It was brought to Sweden along with a sister aircraft that for a few years served as a replacement after the first DC-3 disappeared. The second surveillance DC-3 is now part of a privately owned aircraft collection in Sweden.

CORROSION

The aluminum sheet metal has been subject to several types of corrosion. Even though this aircraft is modern from a museum perspective, its condition is that of a marine archeological find. The construction of the body with metal sheets riveted together facilitated crevice corrosion. Other materials such as rubber and acrylics mounted on the aluminum also provided areas under which the corrosion was more active. The increased volume of the aluminum corrosion products in the crevices caused parts to break and sheets riveted together to become separated. Because of the presence of chlorides in the seawater, pitting corrosion can be found on most surfaces, eating its way through the metal and leaving a characteristic pattern of growing round-shaped lacunae. Green edges of aluminum sheets indicate the presence of copper ions and demonstrate the galvanic corrosion problems of this alloy (Figure 3).

Galvanic corrosion is also evident in parts of the wreck where aluminum parts come in contact with other metals, most commonly iron/steel; in these cases, the aluminum suffered severe damage. Iron parts also display corrosion, which is not surprising in a saline environment, and the large quantity of copper ions likely accelerated degradation.

A general observation is that the parts of the wreck resting face down in the sediment layers suffered more degradation/corrosion than the parts facing up into the water, quite the opposite of a wooden ship wreck. One hypothesis is that corrosion is more severe in the mud because lower oxygen levels turn the buried metal into an anode, while part of the same metal piece exposed to flowing water and oxygen becomes a cathode. But that is still just a hypothesis on the conservator's part and needs to be investigated further. Oxygen levels at the bottom of the Baltic Sea are very low today, and measurements do not go so far back as to the time of the incident.

FIGURE 3. Detail of corroded sheet metal exhibiting visible copper corrosion of the core aluminum metal.

CLEANING AND TREATMENT

The treatment of the wreck and loose parts was completed in steps, the first step taking place when it was not yet a museum object but a wreck undergoing forensic investigation. The aim of the very first treatment was to stabilize the degrading metals for the duration of the investigation. Since such investigations need the wreck to be as untouched as possible, it was sprayed with an anti-corrosion coating almost without any prior cleaning. The product (Dinitrol 708) used was a petroleum-based coating that forms a drying layer. It has a distinctive yellow tint and forms hard puddles where it collects in holes and crevices.

When the wreck was turned from a wreck into a museum object, the view of its stability naturally changed. It was clear that all materials would need to be treated more thoroughly to last not for a few months but for many years to come. The initial Dinitrol coating was removed, although not all areas where it had penetrated could be reached without causing unnecessary damage to the wreck. The removal of Dinitrol 708 was done with high-pressure tap water; in some areas, pre-treatment with a degreaser based on mineral spirits was necessary to dissolve the coating. Tap water in Sweden is not as chlorinated as in many other countries, but is not completely chloride-free. Sensitive parts like painted areas were covered to keep them protected when cleaning.

As the Baltic Sea is brackish water with less than 0.5% saline level, the chloride levels were assumed to be much lower than in wrecks found in sea water, for instance off Sweden's west coast. In the case of the DC-3, it was impossible to clean all surfaces with the high-pressure nozzle, even though holes were made to gain access, so that contaminants still remain in some parts. Many parts had to be rinsed only by pouring water through the structure.

During cleaning the level of dissolved salts was measured with an ISO-standardized Bresle test (ISO 8502-6, collecting sample with patch; ISO 8502-9, ion contaminants measurement), a field method used when cleaning ships or other large structures prior to recoating (Figure 4). The Bresle test detects chlorides and other water-soluble contaminants, most commonly sulfates in this environment, by measuring the conductivity of water that has been in contact with the metal surface.

After water cleaning, coatings that will prevent further corrosion were once again applied, this time in two steps with two different petroleum-based products (Dinitrol 25B followed by Dinitrol 708). The first product has lower viscosity, penetrates the structure, and helps displace residual water. However, it does not dry but stays oily and slightly sticky. The second product is then applied to work as a drying top coat. After these surface treatments, the parts were placed in tents ventilated with dry air to accelerate the drying process.

As noted earlier, the Dinitrol 708 has a slightly yellow tint, which unfortunately gives the aluminum surface a brass-like appearance. The manufacturer noted that it should be applied in a layer so thin that the tint would not be visible, which perhaps serves as an example of where industry and the museum field

FIGURE 4. Bresle-test of chloride levels on the metal surface. Distilled water is injected under a patch attached to the metal surface, then removed with the syringe and measured for conductivity. © Göran Lundholm, Exova AB.

sometimes see things from different angles, and our priorities differ. The practical solution in the exhibition environment was to use a blue light on the displayed wreck to neutralize the yellow color (Figure 5). It is unlikely that the average visitor notices the yellow surface, but the yellow tint is visible when the service lights are on.

More detailed and diversified treatments adapted to each material were performed on smaller parts and objects in the conservation studio. More complicated objects were electronic devices like transmitters or parts from the cockpit dashboard, since they are composite objects made of a number of materials, including aluminum and other metals, glass, ceramics, polymers, paper, and even wood. The metals had corroded, and the objects were often filled with hardened mud blended with corrosion product. They were delivered to conservation in a dry state, as were all smaller objects. To rehydrate them to a degree where chlorides could be removed was not an option, because it would have done too much damage to organic materials that remained. In addition, since the gel-like aluminum corrosion products had dried, it was almost impossible to dissolve them again. Instead treatment resembled more an excavation or a fine-mechanical disassembly and reassembly of parts than anything else. Some electronic parts could have their hoods removed, but where this was not possible, sediment and loose parts were removed as far as possible through corrosion holes or other gaps formed through impact damage. Aluminum parts were mechanically cleaned but not treated with any products. They have now been on display in a controlled environment (below 35% RH) and show no signs of active corrosion despite the lack of corrosion preventive coatings or desalination. But surely their future well-being is dependent on a low and stable moisture level.

Many parts of the aircraft's aluminum body were painted with green or grey color tones. These paints partly remain in varying stages of deterioration on places like the inside of the hull and interior surfaces of windows and doors. Very little has been done to consolidate or stabilize flaking paints, because this is a part of the wreck that should remain in that condition. Parts that were painted to act as markers or symbols are an exception, however, like the red handles on the emergency exit door and window, and of course the Swedish national symbols with the three yellow crowns on a blue field in a yellow ring on the sides of the hull and on the wings. They have been treated by painting conservators to ensure that the paint will remain (Figure 6).

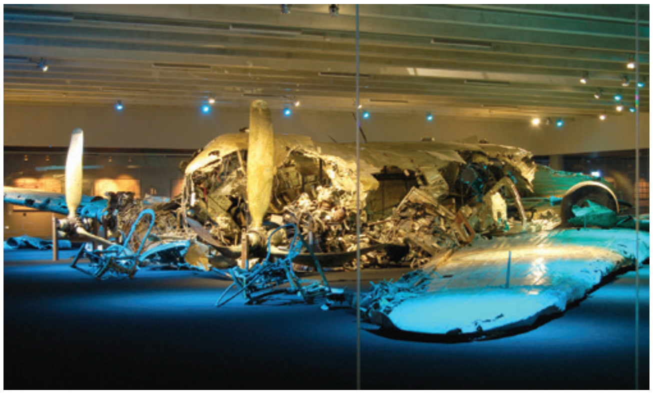

FIGURE 5. The wreck as it is shown today, in its purpose built display area. The display case, or glass room rather, is easy to access, but as the wreck was lifted in place through the roof and another floor of exhibitions was built on top, it would be a demanding task to have it moved for retreatment.

FIGURE 6. Emergency exit door after cleaning in conservation studio. Not all holes are caused by corrosion but instead by the grenade shrapnel of the attacking MIG-fighter. These holes are distinguished by metal edges bent outward showing that the shrapnel penetrated the door as the grenades hitting their target exploded inside the cabin.

MONITORING AND FOLLOW-UP

The DC-3 rests in a controlled environment of below 35% RH and undergoes regular inspections for changes. The “sea bed” in the display area is black so any aluminum corrosion falling onto it is easily noticed. The preservation process was completed with a 50-year perspective on the lifespan of the wreck in mind, an unusually short time frame for a museum object of this type. The wreck appears to be stable, but should it show signs of continuous degradation in the future, retreatment with anything but dry methods in its current location would be very difficult.

A RARE BIRD

The wreck of the DC-3 is a rare bird in the collections of the Swedish Air Force Museum, not just because of its dramatic history. The state of the materials is unusual for a museum with a technical focus. Even more of a challenge is maintenance of the wreck in its degraded condition. Most older aircraft in museums and other collections have been repainted and renovated for pedagogical reasons to resemble their original condition, as is customary for most technical museums. The DC-3 will remain a wreck with the aluminum in a corroded state and the paint layers just barely sticking to the surface, just as it was found at the bottom at the Baltic Sea. The installation at the Swedish Air Force Museum aims to showing this with the wreck of the DC-3 in the large purpose-built display, dramatically located underground. History framed, not polished.

CONCLUSION

During the years of working with the DC-3 wreck, many new experiences have been made that will prove themselves useful when encountering similar objects in the future, for there will be more such objects as museums and marine archeology takes on the period of the Cold War. The most basic measures in the preservation process, such as cleaning and coating, have been those that have made the most difference in the appearance of the final result.

The most striking object among the exhibitions of the Swedish Air Force Museum is not one of their shiny, renovated aircrafts, but this broken-down wreck. Perhaps the most important lesson learned is to take great care to preserve the appearance of such wrecks, since it is often not their type or model that make them unique but their individual history. In this case it was not possible to plan ahead, since the DC-3 had already been recovered when it was turned into a museum piece. Had it been possible not to let parts dry before starting the preservation process, a lot of time and effort could have been saved. It is crucial that from the very first steps of planning the preservation process, all involved experts have a good understanding of the ethical principles and goals of the project. What is the reason for preserving the object in the first place, given that these large items consume both time and funding, and what story do we want it to tell in the future?

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A Critical Review of the 1996 Conservation Treatment of a World War II Aircraft Carried Out at the Australian War Memorial

George T. Bailey

ABSTRACT. In 1984 the Australian War Memorial, Royal Australian Air Force and Royal Australian Navy recovered a crashed Second World War Japanese Army Air Force Nakajima Ki 43 II Hayabusa fighter aircraft (allied code name "Oscar") from Papua New Guinea. The aircraft had crashed at the end of an airfield in 1944, had been sitting in swampy ground for the next 40 years, and had consequently corroded and suffered the ravages of time. In 1996 an electrolytic treatment of the aircraft was carried out. Since 2001 the tail section of the aircraft has been on display, whilst the main plane and cockpit section were kept in storage. In 2013 the treatment process was reviewed, and the aircraft was examined for evidence of further corrosion and coating failure to determine the long-term effectiveness of the treatment.

Keywords: aluminium, corrosion, aircraft, electrochemical treatment, conservation

INTRODUCTION

A concerted effort in the development of conservation techniques for corroded aluminium composite objects at the Australian War Memorial (AWM) began in 1991 with a partnership between the AWM, Electricité de France and the Research School of Chemistry at the Australian National University (RSC), based on the doctoral dissertation of Christian Degrigny (1990). Conservation Scientist Christopher Adams at the AWM further developed the technique through a French Government Scientific Fellowship in Paris in 1992 (Adams, 1992). Further research work was carried out by the AWM and RSC and subsequently published (Hallam et al. 1995). During this period a number of corroded aluminium objects were treated, including two engines from a Lockheed Hudson and the first Royal Australian Air Force aircraft to be shot down by the Japanese during the Second World War. By 1996 development of the treatment process had reached the stage where it was feasible to treat very large aluminium composite objects, and the treatment of components of a 1943 Japanese Army Air Force Nakajima Ki 43 II "Oscar" fighter was attempted.

TREATMENT OF THE NAKAJIMA KI 43 II FIGHTER

The treatment of the "Oscar" components has been described in detail elsewhere (Bailey, 2004), but basically the rear fuselage, wing section, and engine were subjected to the following treatment:

1. Mechanical cleaning to remove loose corrosion, accretions, and vegetation
2. Masking of paint and pencil inscriptions to protect them from the chemical processes

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3. Polarization in a citric acid/sodium hydroxide solution to remove corrosion
4. Polarization in fresh water to remove the previous chemicals (rinse stage)
5. Dehumidification to dry the structure
6. Application of tannic acid to ferrous components that had flash rusted
7. Application of a protective coating to reduce the risk of future corrosion.

Figure 1 shows the rear fuselage undergoing polarization treatment.

For a number of years after treatment, small particles of corrosion products had continually dropped off the rear fuselage of the "Oscar" and Lockheed Hudson engines. All three objects had been on display since treatment in the 1990s, as shown in figures 2, 3 and 4. Careful examination and visual monitoring of the objects had not revealed the incidence of renewed or new corrosion occurring on the engines. It was therefore concluded that the corrosion products falling off the engines could be attributed to corrosion products loosened during the treatment process that subsequently became dislodged by vibrations to which these objects were subjected whilst on display.

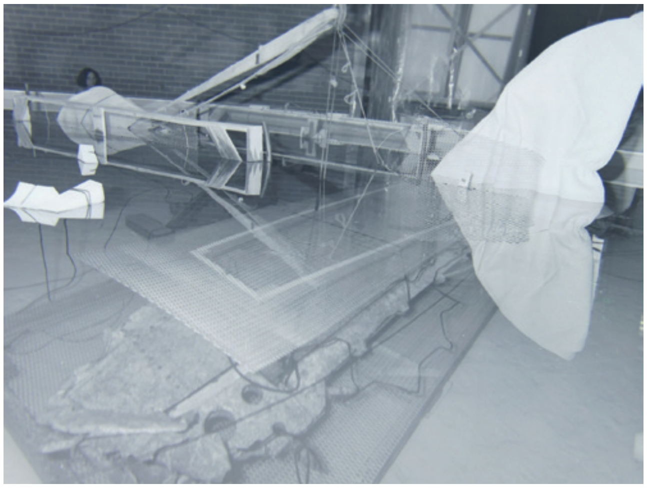

FIGURE 1. Rear Fuselage in Solution During Polarization Treatment. Copyright Australian War Memorial. Source: Australian War Memorial.

FIGURE 2. Hudson Engine 1 on Display in 2014. Copyright Australian War Memorial. Source: Australian War Memorial.

FIGURE 3. Hudson Engine 2 on Display in 2014. Copyright Australian War Memorial. Source: Australian War Memorial.

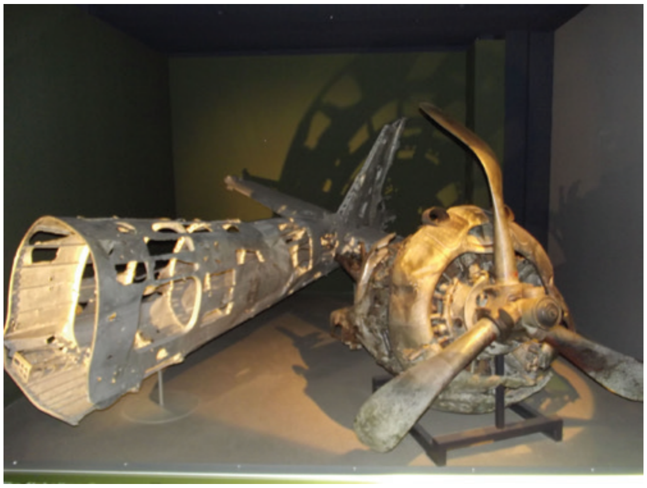

FIGURE 4. "Oscar" Rear Fuselage and Engine on Display in 2014. Copyright Australian War Memorial. Source: Australian War Memorial.

FIGURE 5. Active Corrosion on Upper Part of "Oscar" Rear Fuselage in 2014. Copyright Australian War Memorial. Source: Australian War Memorial.

FIGURE 6. Treatment Chemical Precipitates Under the Cockpit. Copyright Australian War Memorial. Source: Australian War Memorial.

Examination of the rear fuselage revealed some corrosion occurring on the upper part, as shown in figure 5. This area was above the waterline during treatment, and an attempt was made to saturate it by periodic spraying with the solution but proved to be inadequate. It had not been feasible to increase the depth of the treatment bath, because it would have exponentially increased the amount of treatment solution, thus significantly increasing treatment costs, as well as complicating the logistics of getting the objects in and out of the solution. In retrospect, the rear fuselage should have been inverted to allow proper treatment of the upper parts of the fuselage. The rear fuselage is robust enough for this to have been done; however, due to time constraints the decision was taken to forego this option and take the risk of insufficiently treating its upper parts. In this case, the risk did not pay off. When time permits, treatment of the corroding area of the rear fuselage will be attempted in situ using a polarization treatment of the buffered citric acid solution in a gel form.

The wing section has been in storage since treatment, and no incidence of corrosion products falling off has been noted, nor any signs of corrosion recurring in the upper parts that were above the waterline during treatment. The upper areas were sprayed during treatment in a similar fashion to the rear fuselage, but in this case the treatment seems to have been effective.

Under the cockpit the formation of precipitates has been observed along a panel joint shown in figure 6. Initially thought to be corrosion products, tests have determined the white crystals to be a mix of sodium hydroxide and citric acid. This is indicative of insufficient rinsing to remove treatment chemicals. The nature of the wing and fuselage construction is such that there are many voids where treatment chemicals were able to penetrate. Removing the structure from the solution and allowing it to drain before the rinsing stage was not sufficient to remove the trapped chemicals, particularly if the chemicals penetrated from above. Effective removal of these trapped chemicals relies on osmosis, and a longer rinse stage or repeated drain/rinse cycles should have been applied to ensure complete removal of treatment chemicals.

COATINGS

During the treatment of the rear fuselage and wing section a number of areas were coated to protect original paint and pencil inscriptions. Tests prior to treatment determined that the paint was soluble in polar solvents, which ruled out protection with acrylics resistant to the treatment chemicals, and wax applied in a non-polar solvent was not sufficiently resistant to the treatment chemicals to provide adequate protection. The solution was to first apply wax to protect the paint and then apply Wattyl Incralac (basically, B48 acrylic with benzotriazole corrosion inhibitor) to protect the wax. This treatment was very effective, and no paint or pencil inscriptions were lost during treatment.

After the treatment had been carried out, the objects were spray coated with Dinol AV5 to provide protection. At the time of writing, these coatings appear to be intact except where the corrosion has recurred in the rear fuselage and where the formation of precipitates under the cockpit has physically disrupted the film. The coating has not noticeably yellowed in the 17 years since it was applied.

EQUIPMENT FAILURES

One of the ongoing problems experienced in treating both the engines and the aircraft parts was the failure of springs in alligator clips that were attached to the anodes and the objects. This failure is attributed to stress corrosion, because the springs are under tension in a corrosive medium. The clips attached to the anodes were replaced with stainless steel tabs bolted to the anodes with stainless steel bolts. The electrical wire/tab interface was encased in epoxy resin. This effectively solved the failures with respect to the anodes.

Replacement of the alligator clips with tabs for attachment to the objects was not a viable option, because it would have meant drilling holes in the objects. With about 500 alligator clips attached to the wing section, drilling that many holes in the object was deemed highly unethical. The solution was to dip the alligator clips in molten petroleum jelly prior to attaching to the object. This significantly reduced the number of clip failures, but it did make the alligator clips very difficult to manipulate. An alternative might have been to dip the clips in latex rubber to coat the springs and electrical wire/clip attachment points, leaving the teeth uncoated. This has yet to be tested.

CONCLUSION

It has been seventeen years since the treatments of the Nakajima Ki 43 II Hayabusa Fighter "Oscar" parts were carried out. Critical review has shown that the treatment principle developed by Degrigny and further refined by Adams *et al.* is effective when applied correctly. With hindsight, the practicalities of applying the principle to the "Oscar" could have improved the treatment outcome. The rear fuselage should have been inverted to treat the upper parts, and the wing section should have been subjected to either a longer stage or multiple rinse/drain/rinse stages to effectively remove treatment chemicals. Despite these shortcomings, active corrosion of the aircraft has been significantly reduced and the treatment can therefore be regarded as successful.

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The Stabilization of Malton's CF-100 All-Weather Jet: A Case Study

Susan L. Maltby

ABSTRACT. In 1974, the Royal Canadian Legion mounted a decommissioned CF-100 on a concrete pylon in Mississauga, Ontario, as an historical monument. In 2011, the City of Mississauga commissioned a full condition assessment of the jet. The resulting report outlined the condition issues and made recommendations for the long-term preservation and stabilization of the jet.

The condition of the jet had declined considerably in the almost four decades it had been on display. Issues included: faded paint; degrading decals; failing sealants; cracked and delaminating windscreen; weathered Plexiglas canopy; and corroding fasteners. Overall, the Alclad aluminum skin was corroded, leaving the surface grey and chalky in appearance. Lamellar corrosion was evident in localized areas. Removing the landing gear to facilitate mounting the jet left a large gap in the belly of the jet. Attempts had been made to seal the opening with sheet metal patches and screening. However, starlings and pigeons resided in the jet, leading to a large buildup of nesting material and droppings causing corrosion and loss of metal in selected areas.

This paper describes the conservation approach and treatment used to stabilize the jet in its current location while addressing conservation concerns. Eliminating the birds, repairing their damage, and sealing the large belly opening were essential. Aluminum sheet metal installed with pop rivets was used for all repairs. All were fabricated to be sympathetic to the jet's the original assembly.

This was not a restoration project. Repairs were carried out, under the supervision of the project conservator, by a highly skilled sheet metal worker with decades of experience repairing and restoring historic sheet metal. The combination of a conservation approach with work by skilled trades has yielded a satisfactory solution with minimal intervention and loss of surviving original materials.

Keywords: Stabilization, conservation CF-100, jet, aluminum, corrosion, pest

INTRODUCTION

The Cold War era CF-100 all-weather fighter jet, or "Canuck," was the first all-Canadian fighter interceptor. Designed and fabricated by Avro Canada at its Malton (now part of the City of Mississauga, Ontario, Canada) facility, the Canuck was engineered to fly and be combat-ready in all weather conditions, from the extreme heat of the desert to the subzero conditions of the arctic. The CF-100 responded to the Royal Canadian Air Force's post-war commitment to home defense, NORAD and NATO. The jets were produced from 1951–1958; the last was retired from active service in 1981.

In 1974, the local branch of the Royal Canadian Legion mounted a decommissioned CF-100 Mark 5 on a concrete pylon in Wildwood Park, Mississauga, as an "historical memento" commemorating both Avro and the CF-100 (Figure 1). The jet sat with seemingly little-to-no maintenance until 2011, when a call from a concerned citizen to the mayor's office prompted the City of Mississauga to commission a full condition assessment of the jet. The resulting report outlined the condition issues and made recommendations for the long-term preservation and stabilization of the jet.

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FIGURE 1. Malton's Avro CF-100 jet fighter, before treatment. Photo by author.

FIGURE 2. Lamellar corrosion at the base of the Plexiglas canopy. Photo by author.

This paper describes the conservation approach and treatment that strived to stabilize the jet in its current location while addressing the obvious conservation concerns.

DESCRIPTION

The CF-100 was not intact. Both engines had been removed and the openings sealed. Ferrous blanking plates covered the intake cowlings at the front of the engine and plywood plugs sealed the openings at the aft. The landing gear had been removed to facilitate mounting and the resulting gap sealed with sheet metal patches. Most of the equipment had been removed from the interior of the jet when it was decommissioned. The pilot and navigator's seats were extant and two flight helmets – complete with goggles, headphones and respirators – were wired in place to simulate the flight crew.

CONDITION

The condition assessment was undertaken with the aid of a Teupen articulated lift. The flexibility of the lift, combined with the skill of the operator, gave full access to the jet and allowed the conservator to examine and document all of the exterior components. At that time, the interior was not accessible.

Exposure to the elements for close to 40 years had corroded the outer layer of the jet's Alclad aluminum skin, leaving the surface looking dull grey and chalky. Exposure of the core metal had led to localized areas of pitting and cracking. The aluminum at the base of the Plexiglas canopy was severely corroded with lamellar corrosion (Figure 2) evident in localized areas. Most of the ferrous fasteners, originally protected from the elements with zinc or cadmium plating, had corroded due to loss of the plating. Except for the areas where the skin had been lost to corrosion and those removed to mount the jet, the jet's skin appeared to be reasonably intact. Matching deformations on the port and starboard sides of the fuselage likely dated from when the jet was slung into place.

The red and the black anti-glare paint on the fuel tanks had faded and failed in a number of areas. The paint surrounding the windscreen and canopy was severely weathered, faded and failing in a number of locations. The decals on the top of the wings were almost completely lost. What did remain was faded and heavily degraded. The decals that made up the lettering, roundels, registration numbers, rudder stripes and squadron insignia had survived somewhat better. Although in better condition, they were peeling and lifting in some areas.

The neoprene de-icing boots on the wings and the tail were degraded and faded.

The plywood engine plugs were weathered, and paint on the engine plugs had faded and failed in a number of areas. Water staining and organic growth on the port plug indicated water had been collecting there and eventually draining out of the jet. There was a considerable buildup of debris (including empty water and liquor bottles), organic matter and soil in both of the intake cowlings. The organic matter clearly held moisture creating a localized corrosive environment that also supported the growth of moss. The ferrous blanking plates – originally painted silver to match the jet – were corroded, particularly where they were in contact with the buildup of soil and debris.

Both the Plexiglas canopy and laminated glass windscreen were in poor condition. The windscreen glass was cracked in several places and the laminating adhesive failing. The Plexiglas canopy was scratched, weathered and covered with bird droppings. The cockpit was clearly no longer weather tight with much of the original weather stripping and sealant lost and/or degraded.

The interior of the cockpit was in quite a sorry state. Mounds of bird droppings indicated that the resident birds had been roosting in the cockpit. The flight helmets were severely

FIGURE 3. The large opening in the belly of the jet made it easily accessible to the resident bird population. Photo by author.

FIGURE 4. Many of the aluminum patches originally used to block the opening left by the removal of the landing gear were lost and/or severely corroded. Photo by author.

degraded. The "navigator's" helmet had fallen out of alignment leaving his head facing aft rather than forward.

By far, the biggest conservation concern was the birds that had been using the interior of the jet as a nesting site for a considerable length of time. Mounds of droppings in the jet, cockpit and on the ground were a clear indication of their long-term presence. By 2011, a large opening in the belly of the jet (Figure 3) allowed birds easy access. Unfortunately, we had no documentation related to the acquisition and installation of the CF-100. At best, we could only hypothesize as to what interventions had been made and when. It appears that, from the beginning, an attempt was made to keep birds out by sealing the jet. Unfortunately, the aluminum sheet metal patches were not well executed and proved to be ineffective. It is likely that the first avian inhabitants were smaller birds such as starlings. As the patches failed over time, the jet would have become increasingly accessible to larger birds, eventually leading to the resident pigeon population. The screening around the belly of the jet was likely installed at a later date in response to the pigeons. Acidic mounds of nesting material and bird droppings took their toll. A number of the patches had been lost in the interim and those that remained were severely corroded (Figure 4). The nesting material and droppings had also accelerated the rate at which the jet's Alclad skin and ferrous fasteners corroded. Components were missing and others were well on their way to being lost (Figure 5). Live and dead pigeons were present during the condition assessment. Unfortunately, the screening appeared to be more effective at trapping pigeons than keeping them out.

In addition to nesting in the jet, the pigeons found the top of the concrete pylon a convenient and desirable perch giving them a good view of the park below. Pigeons, by their nature, like to perch at a height so that they can look down at the surrounding area.

FIGURE 5. Corrosive bird droppings and nesting material led to the loss of original material. Photo by author.

MOVING THE CF-100

City staff initially discussed moving the jet indoors for its preservation. Clearly, objects survive better indoors than out, particularly in Canada's harsh climate. There are curatorial and conservation concerns regarding this notion. First, the jet memorializes an important part of Malton's history and is listed on the City's Heritage Register for its cultural significance. Its commemorative value would be lost by moving it out of the park. Second, the jet is a fragile object and needs to be treated accordingly. Moving any object puts it at risk of damage. The jet's age, condition and size would make moving it even more difficult and risky. Finally, there is the issue of cost. Moving the jet into long term storage would be an expensive undertaking. As a result, discussions about moving the jet were short lived.

TREATMENT APPROACH

A conservation rather than restoration approach was taken. Despite the many condition issues, the decision was made to stabilize the jet in its current location and to address the most pressing conservation concern: the birds. We needed to get the birds out of the jet and keep them out. Evicting the birds, removing their nesting debris and excrement where possible, repairing their damage, and sealing the large belly opening were all essential. There was no appetite, or budget, for a full restoration.

TREATMENT

Aluminum sheet metal fastened with pop rivets was used for all repairs. Only holes large enough to allow birds access were patched. Smaller losses were left, essentially acting as weep holes. All were fabricated to be sympathetic to the jet's the original assembly. To further discourage the birds, an aluminum shroud, or skirt, was installed around the perimeter of the concrete base. The shroud ran from the top of the concrete mount to the jet's fuselage, essentially eliminating the birds' perch.

All work was carried out under the supervision of the project conservator. Work began in the fall of 2012. At that time, live birds were evicted and the netting, bird debris (i.e., nesting material and excrement) and bird carcasses removed where accessible. A thick layer of debris had formed on top of the concrete mount, held in place by the netting. The debris on top of the concrete and from the interior of the jet was shoveled and pulled out by hand. The debris from the intake cowlings of both engines was also removed. Once the debris had been removed, the areas were rinsed with water. Finally, the jet was temporarily sealed with Fiberglass insulation (Figure 6). The insulation was an effective and easily reversible means to keep the birds out of the jet and off the concrete mount until the remainder of the work could take place. The cleaning was undertaken by a local industrial cleaning contractor. The bird removal and installation of the temporary barrier were also handled by a local specialist.

FIGURE 6. Fiberglass insulation was used to seal the jet after the initial cleaning. Compare with Figure 8. Photo by author.

The success of this project depended on hiring the right people for the job. The initial cleaning and sealing of the jet could easily be handled by City maintenance staff or outside contractors. The sheet metal repairs and fabrication and installation of the shroud were tasks best carried out by skilled sheet metal workers with considerable experience repairing historic sheet metal. This project required someone who was detail-oriented, sensitive to working on what is essentially a museum object, and able to take direction. It was important that the City viewed this work as a conservation treatment rather than sheet metal work. The budget cost for this part of the project far surpassed the City's limit for sole sourcing. Thankfully, the City's project manager was able to persuade the City's purchasing department that the preservation of Malton's CF-100 was a special case. This allowed us to retain a firm specializing in repair and restoration of historic sheet metal.

There are safety concerns related to treating a jet. Active jet fighters have a number of potentially dangerous components that need to be removed and/or deactivated when a jet is decommissioned. The conservator was advised to consult the Department of National Defense (DND) to check and confirm that at the time of decommissioning the following tasks were undertaken: a) both ejection seats and the canopy explosives were de-activated and tagged as inert; b) the fire extinguishing system (methyl bromide bottles with explosive squibs) was removed and/or drained, tagged and marked inert; c) the oxygen system has been drained and tagged inert; and d) all accumulators were drained of pressure. DND assured City staff the jet was fully decommissioned prior to being transferred to the municipality and there were no outstanding issues. Asbestos, found on hoses, heat ducts and sealing strips, was another concern. Birds have been known to use asbestos for nesting material. The potential for asbestos combined with the toxicity of the bird droppings necessitated that all work be undertaken wearing appropriate protective clothing and equipment. Proper disposal protocols were also followed.

The remainder of the work began in February 2013 and was carried out solely by sheet metal worker Scott Faragher, Field Superintendent, Heather & Little Ltd. Initially, the port plywood engine plug was removed so that we could see the interior of the jet. About 15–20 cm of bird debris covered the aft end of the engine port. Further exploration proved that much of the interior, wings and fuselage – tip to tail – were filled with this material (Figure 7). It was clear that this corrosive material had to be removed. As a result, the scope of Heather & Little's involvement expanded to removing all of the bird debris. This was painstaking work. All was removed by hand using specially fabricated tools to reach as far into the jet as possible. All was disposed of properly.

Although the birds had been excluded in the fall, once the repair work began both pigeons and starlings quickly tried to re-inhabit the interior of the jet. Open areas were plugged at the end of each work day to try and limit the number of birds inside.

As noted, the existing sheet metal patches were unattractive and poorly fabricated. The metal had not been rolled to conform to the profile of the jet, which made some of the patches appear "puckered" at the edges. The fact that the patches did not follow the existing seams made them more obvious. The patches were larger than necessary, in one case covering striping on the jet's belly. All of these patches were carefully removed by drilling out the pop rivets so the repairs could be done properly.

The order in which the work was carried out was important. Clearly, the repairs to the belly of the jet had to be done in advance of installing the shroud. New patches were fabricated from .032 gauge aluminum sheet and installed using 1/8" × 7/16" pop rivets (Figure 8). The sheet metal was rolled to match the profile of the jet. For strength, large spans were covered using two pieces supported by a bridging strip of sheet metal. Severely corroded areas in need of repair had to be removed in order that an effective repair could be made. This was the exception rather than the rule. Removal also facilitated cleaning out bird droppings and debris as these areas were not easily and/or safely accessible. A missing navigational light cover on the port fuel tank was also patched as it was large enough to allow access to the interior. Thankfully, most of the air intakes and/or vents retained their original screening.

The shroud was fabricated from the same sheet metal as the patches. The shroud was attached to a starter strip that was fastened to the fuselage and concrete pylon. The shroud closely followed the profile of the jet. The joint between the shroud and the fuselage was sealed with polyurethane sealant. The ends of the steel support were a major point of access for the birds (Figure 9). These too were boxed in to prevent access. The birds remained persistent to the end. Fire crackers were used to clear the jet of birds before it was finally sealed. Figures 6 and 8 show the jet before and after repair. Figures 8–10 show the jet after the repairs

FIGURE 7. Nesting material and droppings in the fuselage. Photo by Scott Faragher.

FIGURE 9. After treatment. Note that the steel support has been completely encased in sheet metal. Photo by author.

FIGURE 8. After repair and installation of the bird shroud. Compare with Figure 6. Photo by author.

FIGURE 10. After treatment. Note replacement plywood engine plugs. Photo by author.

were made and the shroud installed. The plywood engine plugs (Figure 10) were replaced in kind and a weep hole drilled in each.

RECOMMENDATIONS FOR THE FUTURE

The conservator made three basic recommendations: annual inspection, maintenance and review of the jet's condition.

INSPECTION

Birds, like many animals, habitually return each year to an established nesting site. The jet should be inspected every spring to ensure that birds are unable to gain access and resume their nesting. If they do find a new access point, it should be sealed up. This will require careful inspection and long-term monitoring.

MAINTENANCE

A commitment to annual maintenance is key. Maintenance tasks include cleaning out the weep holes in the engine plugs and removing debris and organic matter from the engine intake cowling. These are tasks City's maintenance staff are equipped to carry out.

CONDITION REVIEW

The condition of the jet should be reviewed on an annual basis. The conservator provided the City with a CD of images documenting the condition of the jet in the fall 2011 when the initial assessment took place and after the work was completed. These images can act as a benchmark allowing the condition of the jet to be monitored over time. Dramatic changes in condition should be noted and steps taken to respond accordingly.

CONCLUSION

This was not a restoration project. Repairs were carried out, under the supervision of the project conservator, by a highly skilled sheet metal worker with decades of experience repairing and restoring historic sheet metal. The combination of a conservation approach with work by skilled trades has yielded a satisfactory solution with minimal intervention and loss of surviving original materials. All interventions were completely reversible allowing restoration to occur in the future if desired.

ACKNOWLEDGEMENTS

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The Ultimate Modern Material: Aluminum in Contemporary Art

Rosa Lowinger

ABSTRACT. Aluminum begins to be commonly used in artistic practice in the United States in the 1960s, when monumental abstract sculpture became the norm for public work. Such works were typically anodized, powder coated, painted, shot blasted or pattern-sanded to achieve a desired appearance. The most unique and difficult-to-maintain works are those that employ the material's raw, milled finish for its industrial, yet soft aesthetic, such as Donald Judd's *100 Untitled Works in Milled Aluminum*. In all cases, such finishes are produced by industrial fabricators, and their maintenance and conservation frequently requires collaboration with industry, which ranges from a completely hands-off approach to total resurfacing. Because aluminum is known to be relatively inert, it is often erroneously considered a "no-maintenance material" that can be employed outdoors, especially in marine and tropical locations, with little regard for long term care. This paper is based on original interviews with fabricators and conservators who made and conserved some of the 20th century's most important aluminum sculptures.

Keywords: aluminum, milled finish, anodizing, Donald Judd, Ellsworth Kelly, Alfred Lippincott, Ron McPherson, Jonathan Borofsky, Tony Smith.

INTRODUCTION

Aluminum can be said to be the ultimate modern and contemporary art material. Lightweight, reflective, malleable, relatively resistant to corrosion, and capable of being shaped, polished, cut, suspended, and colored with ease, it has been used prodigiously by contemporary sculptors since the 1960s. For many artists, this material's value rests in its being a substrate for color that is three times lighter than steel and can be painted, powder coated, and anodized to produce different effects. Others are drawn, instead, to the aesthetic of uncoated aluminum itself. In both cases, the surface of these contemporary aluminum artworks tends to be industrially produced. As such, their care and treatment frequently calls for the close collaboration between conservators and fabricators and solutions that are invasive and can rest outside the parameters traditionally employed in art conservation.

RECENT HISTORY AS AN ART MATERIAL

Aluminum was a rare material in artwork prior to the late 1950s. Marcel Duchamp included sheet aluminum in his 1946 *Étant donnés: 1° la chute d'eau, 2° le gaz d'éclairage* and aluminum framing in the 1927 *Bride Stripped Bare by her Bachelors, Even*. Cast and anodized aluminum figures make up the chess pieces in Man Ray's 1947 *Aluminum Chess Set*, and the cannon of mid-twentieth century art contains other

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examples of the limited use of aluminum in conjunction with other materials. But despite these intermittent uses, aluminum's prominence as an artistic material does not occur until the advent of minimalism and geometric abstraction, when works of pure shape and color and massive scale began to take advantage of its physical properties as artistic content as well as a means to a structural end. Artists like Billy Al Bengston and Frank Stella used aluminum as the structural support for works that were shaped, cut, and dented, and they employed automotive painting techniques to create aesthetics that had not been seen before in art making.

This early 1960s aesthetic coincides with the founding of national public art initiatives, like the General Service Administration's (GSA) Art in Architecture Program and the National Endowment for the Arts (NEA), programs that mandated that a percent of construction for new buildings (usually between .5 and 1%) be set aside for art commissions by living artists.[1] By the mid-1970s, most states and many municipalities began to institute programs that mimicked the national initiative, resulting in widespread construction of public artworks in a style that was unique to the modern period and promoted the minimalist aesthetic of the era's contemporary artists. The result was a period of government spending for public art that rapidly changed the landscape of America's public places with monumental abstract works by artists like Claes Oldenburg, Tony Smith, and Alexander Liberman. The call for large-scale works in materials that could express contemporary ideals while being easily maintainable spearheaded an interest in the use of aluminum that continued for decades and continues into the present day.

Large-Scale Aluminum Painted Sculptures

One of the earliest artworks to employ aluminum's aesthetic properties on a large scale was *Sculpture for a Large Wall*, a site-specific public art installation by Ellsworth Kelly. Designed for the lobby of architect Vincent Kling's 1956-7 Transportation Building at Penn Center in Philadelphia, *Sculpture for a Large Wall* is a 65' long piece comprised of 104 anodized aluminum panels in varying shapes and colors set at different angles. It was Philadelphia's first abstract work of public art, intended by Kelly to serve as a color-rich counterpoint to the austerity of the modern building—("*The monochrome buildings demand color, and the spaces demand an image on a large scale*"[2]). The aesthetic of this piece rests entirely in the choice of anodized aluminum to provide the luminous color that could be seen from the street. Anodizing allowed for deposition of a thin, bright, even, coat of color that remained transparent on the aluminum surface. Used regularly by this time for coloring household objects and treating architectural aluminum,[3] this was the first time the process was used on such a scale for artistic production in the United States.

Within ten years of Kelly's installation, aluminum would be a regular component of the sculpture fabrication cannon. By around 1968, abstract monumentality had become the norm in sculpture production, and aluminum made its way alongside steel and stainless steel as a primary material in the works of Claes Oldenburg, Ellsworth Kelly, Tony Rosenthal, Roy Lichtenstein, Kenneth Snelson, George Sugarman, Ronald Bladen, and Robert Morris, to name but a few masters. Because of the technical rigors and scale of these works, they were produced at art fabrication studios, primarily Lippincott, LLC in North Haven, Connecticut and, after 1971, at Peter Carlson Enterprises in Los Angeles. These art fabricators were entirely new types of businesses, opened expressly to provide artists with "a sympathetic environment and technical expertise that enabled [them] to achieve a scale of which they had only dreamt before."[4] The resulting "quiet collaboration"[5] between artist and fabricator changed the field of sculpture production in the United States and allowed for industrial processes to become the norm rather than the exception in the creation of monumental work.

According to Alfred Lippincott, brother of Lippincott's founder Donald Lippincott and a partner in the firm since the 1980s, aluminum was used at their studio since they opened in 1968. First employed as a base for painted sculptures, it was preferred because its lightness—at 1/3 the weight of steel—allowed for complex pieces that could be suspended overhead and forms that could be easily manipulated and shaped. Another valued feature of aluminum was its ability to "be rolled out much flatter than a plate of steel or stainless steel . . . . which allow[ed] for flatness in different shapes, like in George Sugarman's work."[6]

Apart from being lightweight and able to be rolled out to be strikingly flat, aluminum is also much easier to weld, grind, and polish than stainless steel. Ron McPherson, a Los Angeles-based fabricator responsible for the aluminum structure of Charles Ray's iconic *Firetruck* (1993), the aluminum framing and supports for Ed Ruscha's shaped rotunda murals in the Miami Dade Public Library (1985), and Jonathan Borofsky's colossal aluminum *Molecule Man* (1977–1995) sculptures, explains the process thusly: "When we're grinding aluminum the air is full of aluminum dust. When we grind steel, the air's full of grit."[7] In other words, aluminum's softness relative to stainless steel dramatically reduces labor time and therefore fabrication costs. Moreover, because sculptural metal is priced by the pound, aluminum automatically comes in at 1/3 the material cost of stainless steel. The result is a product that is overwhelmingly more economical to fabricate as well as easy to manipulate to achieve desired artistic effects.

The ability to control corrosion from the inside with hollow fabricated works is another advantage to aluminum. "For pieces like that, if you don't use aluminum you could have the whole sculpture corroding from the inside and not know about it until it's too late,"[8] explained Lippincott, in reference to painted hollow pieces situated outdoors. This fact is clearly seen in Ron Bladen's *X,* a monumental 1968 work fabricated by Lippincott located at the downtown campus of Miami Dade College. Though the paint surface of this sculpture was in need of conservation, there is no internal corrosion disrupting welds and connections, despite the fact that the sculpture has been situated in a tropical environment within a mile of a saline body of water for nearly fifty years.

Highly complex structures like the Tony Smith *Space Lattice* series—which Lippincott fabricated posthumously for the Smith estate in 2005-7—would be nearly impossible to fabricate in any material other than aluminum. Consisting of polyhedrons connected to each other across expanses of space, these works use cast aluminum ends and fabricated sides in a system of complex interchangeable parts. Lippincott described the process of fabricating *Smoke* for the Los Angeles County Museum of Art, which at 47' × 33' × 24' is one of the largest of this series:

> *Tony's geometry tells you exactly where you have to be. The sculpture is an extended octahedron, built in sections, with its longest section 8' long. We cast aluminum bulkhead ends that are machined very accurately to form the precise geometry to fit against its neighbors. The sections are bolted from the inside and they are interchangeable. We held the tolerance closely and there is just enough torque in the aluminum to allow the fit. One of the other things we learned along the way was that if you want it to be accurate you bolt it together in a rigid, highly accurate fixture, then you weld it. We lost a lot of sleep before putting the first of these together because there was no room for error.*[9]

The technique of combining cast aluminum forms in conjunction with fabricated elements was employed again by Lippincott in Claes Oldenburg and Coosje Van Bruggen's 96' high *Batcolumn* (1977) for the Harold Washington Social Security Center in Chicago. One of the largest pieces ever built by the firm, it consists of a fabricated steel lattice top with a column base shaped with compound curves that were more accurately and smoothly achieved by casting in aluminum. Notes Lippincott: "We did fabrications of compound curves in the past, like for [Louise] Nevelson, but those were more sharply articulated . . . If you want it to be smooth, as a compound shape you have to cast it."[10]

Present-day American public art programs—which currently number in the hundreds—aim to commission works of art that are easily maintainable. Because of this, painted and unpainted aluminum artworks are ubiquitous in these collections. Yet the maintainability of such works is not always as simple as it appears to those who select aluminum primarily for its corrosion resistance. Alfred Lippincott explains that fabricated works that employ excessively thin panels, for example 1/8–3/16" in thickness, can result in pillowing at the welds.[11] Another concern is that aluminum welds are not as strong as welds in stainless or mild steel, and when one makes a piece where the welds are not left in place but ground down to produce a flat surface, weld cracking can be an issue, "especially for pieces that have been out in the world for a while."[12] Still another vexing contemporary phenomenon is the substitution of powder coating for paint in colored surfaces. Powder coating is a process in which a free-flowing, dry powder—which can be either a thermoplastic or thermosetting resin—is substituted for liquid paint and distributed across a metal surface by means of an electrostatic charge and curing under heated conditions. The intent is to create a finish that is tougher and harder than conventional paint. Ron McPherson notes that he tends to prefer paint for sculptural surfaces because the powder coating palette allows for many fewer color choices. He also adds that the type of even heating that is required for powder coating is not feasible with larger forms.[13] For conservators, the main problem with powder coating lies in the fact that once breached—by scratching, a ding that cracks the coating, or other impact—it is almost impossible to match the sheen and flatness of powder coating with a paint system. Local repairs are therefore unfeasible, and pieces must be dismantled and recoated. This renders powder coating impractical in a public setting, especially where public interaction with a sculpture cannot be avoided. Public outdoor aluminum sculptures are highly susceptible to scratching and denting, or nicking by gardening equipment. Cast aluminum works in tropical and marine climates are also subject to corrosion and to deformation from strong wind loads. The treatment of these types of damage can be straightforward, but because of aluminum's high malleability often it is impossible to fully erase the visual imprint of these events. Conservators of public outdoor aluminum sculptures frequently are tasked with educating stakeholders as well as artists about the potential risks of working with aluminum, even while it is touted as the most corrosion-resistant and outdoor-friendly material.

UNPAINTED ALUMINUM FINISHES

In the early 1980s, Lippincott, LLC undertook the fabrication of Donald Judd's *100 Untitled Works in Mill Aluminum*, a site-specific installation that is likely the most ambitious work ever produced in uncoated aluminum. Made to be sited in two former artillery sheds that comprise the center of the Chinati Foundation's buildings in Marfa, Texas,[14] *100 Untitled Works* consisted of 100 rectangular aluminum boxes with identical outer dimensions (41 × 51 × 72 inches) and unique interiors. One of the foremost American artists of the postwar era and a major figure in the Minimal Art movement (though he vigorously eschewed the term), Judd frequently used aluminum to create works characterized by "open, somewhat weightless volumes. . . . [and] explorations of space, scale and materials could be ends in themselves."[15] The surface of these works included brush, mill and mirror finishes, anodizing, painted finishes, and powder coating.[16]

As with all of Judd's work, extraordinary precision went into the fabrication of *100 Untitled Works*. Alfred Lippincott explains:

> *The aesthetic was governed by Don Judd's desire to get as pristine a material as possible without signs of processing and human interaction. We start with*

> *[aluminum] in 16" thick [blocks], shaped the size of two king-sized mattresses. The metal is heated and rolled to get it thinner and thinner down to ½". The rollers [are] three stories high and it's done at a mill that's 75 acres under one roof. At first we keyed in on the alloy 6061, but the people at Reynolds– we got them involved because it was such a big order– suggested 3003 F because of its surface quality and flatness. You have to understand that this is 90,000 pounds of aluminum. You want to know that the first plate is going to look like the last one and that the front and the back will match. That problem had to be solved by the fabricator by understand[ing] how this is done in the industry. One of the things they typically do with this material is stress or stretch alleviate it. The material is pulled and when they let it go again, it's flat. We went through the entire process of what this material would undergo at every single step and were able to evaluate this and make changes as needed. We made sure the rollers were all clean. We did not have them cut the edges, we had them ship it and we cut them off ourselves.*
>
> *In July '83, at the halfway point, there was a letter from Don [Lippincott] to Don Judd. He states that the 3003 F which was selected for its surface quality and flatness presents a disadvantage in softness. It's easy to scratch or mark, and the screws or pins don't hold as well. But we had made a decision about the alloy . . . it had a lustrous bright reflective quality and the flatness made sense when you assemble the boxes. We traded softness for flatness and relative uniformity.*
>
> *The whole idea was not to touch it. That was the finish. Even with all the efforts that were made, there were still issues that you had to try to minimize and work around and place in a situation where they weren't at a primary viewing angle. It's acreage of material. It's one thing to show Judd a square foot panel in Italy and have him say yes I want everything to be like that but it's impossible to make it happen* (Lippincott, Alfred- personal communication 2014).

The rigors of Judd's surface requirements, the softness of the aluminum alloy, and the milling imperfections that became a part of the work itself combine to make *100 Untitled Works* one of the most challenging of all contemporary artworks to maintain. Eleonora Nagy, a consultant to the Chinati Foundation and the author of the Foundation's guidelines for caring for Judd artworks, notes that the rigor of such works practically defies any regular attempts at conservation. Moreover, because the works themselves are located in a site specific non-climate controlled location that is subject to extremes of temperature—from blazing summers to freezing winter temperatures—structural deformation of the works is an ongoing problem without a clear remedy.

Donna Williams, a Los Angeles-based conservator who has collaborated in conservation treatments with Lippincott, describes how these factors require conservators to make decisions that fall outside the norms of usual conservation:

> *Works of this type fall into a category where you can either do nothing, or you have to refinish them completely. You can't treat the problems locally. While I don't have a problem with refinishing a piece, this can't happen without the proper approvals* [from the artist].[17]

In other words, while some unpainted aluminum sculptures can be successfully treated with traditional methods, most will need to be addressed with one of two diametrically opposed approaches: either a nearly hands-off method for highly fetishized surfaces like those seen in Judd's *100 Untitled Works,* or complete resurfacing. In all cases, guidance from the artist and his/ her fabricator is recommended in order to properly interpret the intended the aesthetic.

CONCLUSION

The use of aluminum in the production of late 20th century artwork allowed for the large-scale, complex forms, and surface finishes that have embodied the contemporary aesthetic of the era more than any other material. Because so many of these works are produced industrially, their conservation requires not only a continued collaboration with fabricators and living artists, but a careful understanding of the artist's intent. There is no single approach to these works and two works that appear the same in terms of their material choice—for example a machine finished surface on a 1980s Judd sculpture and one on a 1990s Jonathan Borofsky—might well be conserved differently[18]. Prudence and restraint are the keys to making informed decisions for aluminum contemporary artworks. Though it is always possible to refinish a work, it is never possible to retrieve a surface that has been recklessly altered because it has been improperly understood.

NOTES

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14. Donald Judd spent much of the latter part of his life in Marfa, Texas, on a 340 acre tract of desert land that included the abandoned buildings of the former U.S. Army Fort D.A. Russell. Judd meticulously restored many of these buildings for the purpose of displaying his work and that of his friends. After Judd's untimely death in 1994, these buildings and their site specific installations would become the non-profit art Chinati and Donald Judd Foundations. For more information see http://www.chinati.org/ and http://www.juddfoundation.org/.
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16. Industrial metals are so important in the production of works by Judd that the Judd Foundation website includes a list of guidelines for their care and conservation. http://www.juddfoundation.org/guidelines/Metals.htm.
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18. The treatment by Silverlake Conservation, LLC, of Jonathan Borofsky's Molecule Man at the Los Angeles Federal Building was one that achieved a compromise between these two approaches. The conservators in this case were advised by Ron McPherson to grind the surface down to achieve the bright finish preferred by Borofsky. In a personal communication with the author, Silverlake partner Amy Green noted that while this was a reasonable approach while the artist was alive, removing the surface every few years was not a long-term solution to a work of this monumentality. In the end, Ms. Green worked out a compromise approach with McPherson that reinstated the brightness of the metal without removing original surface.

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Conservation Treatment of *Les Nageurs* (1973): A Monumental Aluminum Sculpture

Virginie Ternisien

ABSTRACT. This paper describes conservation treatment carried out on the monumental aluminum sculpture *Les Nageurs* (*The Swimmers*) by French artist Françoise Salmon (1919–). In 1973 the sculpture was attached to the exterior façade of a sports complex located in La Courneuve, a suburb of Paris. After a building fire, the sculpture fell from its original location, causing severe impact damage and surface alteration, which disfigured it. In order to reestablish the original appearance of *Les Nageurs*, treatment included cleaning, disassembly, reshaping, reassembly, and surface finishing. A multidisciplinary team of metal conservators and craftsmen faced and met many challenges generated by the extensive damage and sculpture's monumental size.

Keywords: Aluminum, stainless steel, monumental contemporary sculpture, impact damage, surface alterations, conservation, repair, multidisciplinary

INTRODUCTION

In 1973, the monumental aluminum *Les Nageurs* (*The Swimmers*) was attached to the façade of a swimming pool at the sports complex Langevin-Wallon (renamed Béatrice-Hess in 2009) in La Courneuve, a suburb of Paris (Figure 1). The sculpture was made by Françoise Salmon (born 1919), a French artist of the post–World War II period who survived a Nazi concentration camp. During her career from 1949 to 1993, she largely produced war memorials, busts, portraits, and nudes, but also popular and humorous figures, which are exhibited in museums, public, and private collections in France and worldwide, notably in Japan and Germany. Wood, stone, and bronze were her primary materials of choice (Taillade, 2008), and *Les Nageurs* is unique in her production because of its theme, monumentality, and use of aluminum.

The sculpture presents the backs of a group of three parallel swimmers: the upper two are partially superimposed, while the third figure is centered between them below. Their slender bodies are abstract and devoid of human details (Figure 1a,b). The sculpture measures 800 cm in length, 120 cm in height, and 65 cm in depth; it weighs 130 kilograms. To make the sculpture, aluminum panels about two millimeters thick were shaped, hammered, and joined together by welding (Viseux, 2008). The sculpture was attached near the entrance to the building at a height of about eight meters by bolting its armature to a wall bracket. The sculpture's armature consisted of a pair of L-shaped aluminum angles welded to the upper swimmers and riveted to an aluminum bar. During installation, the bar was bolted to the wall bracket's steel beam, which had been bolted to four threaded steel bars coated with aluminum and inserted in the wall.

In 2006, a fire devastated the sports complex's steel-frame and wood structure, covered with plastic panels (Figure 1c). After the fire, the attachment of *Les Nageurs* to the

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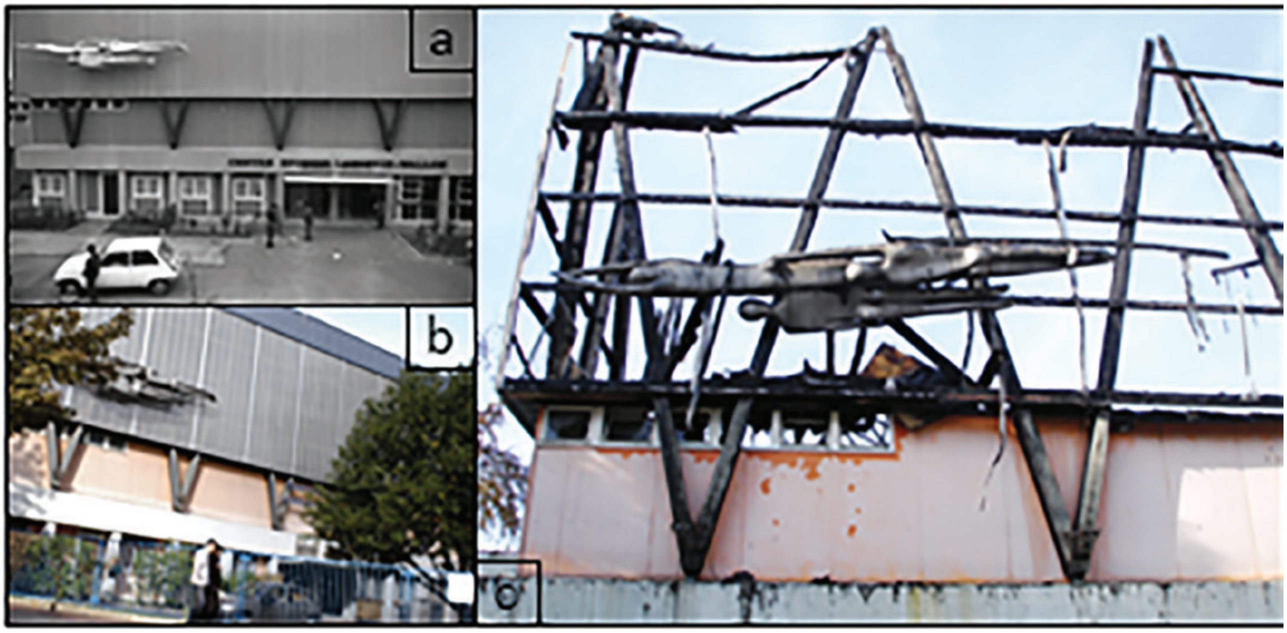

FIGURE 1. *Les Nageurs.* (a) On the façade of the sports complex after installation in 1973. (b) In the 1990s. (c) After the fire in 2006. © Archives de La Courneuve.

building was fragile, with a potential for collapse. Improper and insufficient equipment for dismantling the sculpture caused it to crash to the ground, taking the attachment system with it; and the sculpture was transported for storage to a sport warehouse in La Courneuve. A year later, rehabilitation of the building led the local city council to seek conservation treatment of the sculpture, which was historically and symbolically associated with the site. At that time, however, the council's search for the artist failed.

CONDITION ASSESSMENT

In 2008, condition assessment in the warehouse compared damage to archival black-and-white photographs taken at the time of installation in 1973, two color photographs from the 1990s, and images taken after the fire (Figure 1). Major mechanical and surface alterations were revealed (Figures 2 and 3). The lowermost swimmer, previously in the same plane as the upper swimmers, was bent 90° with respect to them. The legs of one upper swimmer were distorted so that they were above the line of its body. Scratches and indentations were observed on about 75% of the surface, with deepest dents located on buttocks, backs, and arms. Components of the attachment system were bent, rendering them unusable for reinstallation.

The surface was covered by deposits from the burning of the building and its immediate surroundings. Thick porous layers of melted plastic (brown, reddish and yellowish) from the building's plastic panels covered top surfaces of swimmers close to the façade and followed the curvature of the sculpture in long drips (Figure 3). Greasy black deposits of soot stemmed from the wood frame of the building (Figure 3). Drips of greyish metal in hollows of the sculpture, especially on parts of the attachment system, corresponded to solders or metal alloys with low melting points, such as lead or tin. The lowest regions of the sculpture in close proximity to the façade were affected by pitting corrosion in a pattern of parallel drips along the length of the sculpture, probably intensified by the release of chlorine from the swimming pool through the wall. Soot was retained in the pits, increasing corrosion. After the fire, debris of dead leaves and dirt adhered to the metal. Original finishing was thought to have been executed only on surfaces exposed to display, while surfaces facing the building that were invisible from the ground remained unpolished, which contributed to their corrosion (Viseux, 2008). More or less deep scratches on the surface crossed deposits from the fire, providing evidence that they resulted from poor handling after the fire.

CONSERVATION OBJECTIVES AND PROJECT

The two successive events, the fire and the fall of the sculpture, deeply damaged the sculpture, leaving it a ruin, but the local city council sought conservation treatment to retrieve its original appearance. The building's design was altered so that the

FIGURE 2. Structural damage and surface alterations as found at the warehouse. © R. Larsonnier; A.-C. Viseux.

FIGURE 3. Examples of surface alterations found at the warehouse. © R. Larsonnier; A.-C. Viseux.

sculpture would face a busy artery of La Courneuve, attached to a concrete wall with a platform underneath. The new design would provide access to the sculpture for periodic monitoring of its fastenings and condition as well as safety for pedestrians below. The conservation project aimed to retain as much original material as possible; if additions were necessary, the same type of material would be used. Four hundred hours were programmed to complete the conservation treatment under the supervision of a metal conservator. The conservation team included two metal conservators, an auto-body mechanic, and a metal artisan. Their skills and knowledge of aluminum and the tools to work it were essential. For convenience, the work was performed in several locations. The sculpture was cleaned in the warehouse, while disassembly, re-shaping, reassembly, and surface finishing were mostly performed at a conservation workshop. The re-shaping of some aluminum portions was conducted at the autobody mechanic's workshop. Proper ventilation and personal protective equipment were enforced for health and safety purposes. A semi-trailer truck provided transportation of the sculpture when necessary.

CONSERVATION TREATMENT

Cleaning

The surface of the sculpture was discolored by various adherent deposits from the fire. After testing, mineral spirits were used to remove black greasy deposits. Solvent-soaked paper towels were wrapped around the swimmers, sealed with plastic film, and left on the sculpture from several hours to overnight (Figure 4).

This allowed deep penetration of the solvent into the thickness of the deposits, which could then be reduced mechanically with soft plastic spatulas and light duty scrubbing pads. This method proved inefficient for eliminating remains of melted plastic, which was harder, more adherent, and largely removed using tools that included scalpels and air abrasion with Archifine®, a fine aluminum silicate powder. A thin brown layer that remained on the surface was partially diluted using the very reactive polar solvent, dimethylformamide (DMF), applied to the surface using the paper towel method or, for the most adherent layers, on scrubbing pads.

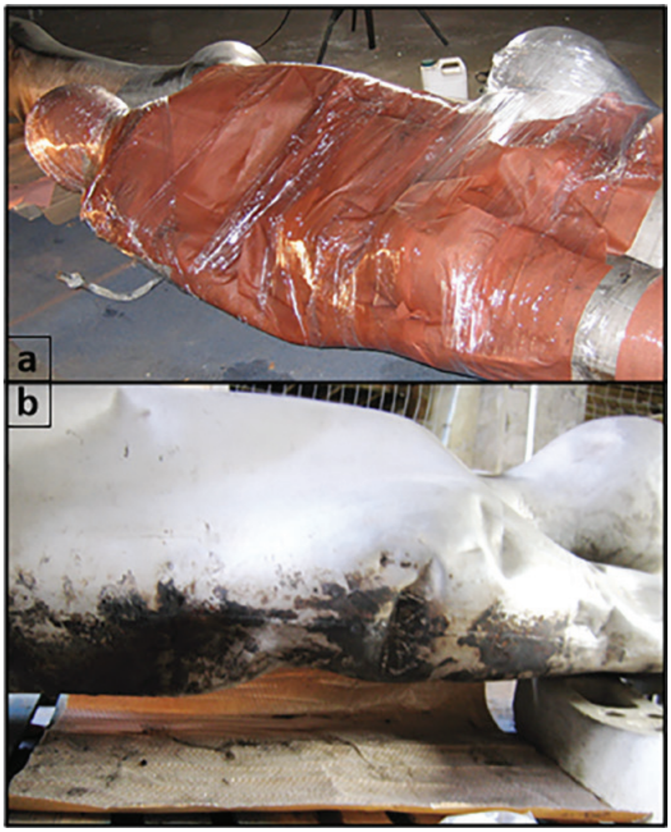

FIGURE 4. Removal of black, greasy deposits: (a) The sculpture wrapped with solvent-soaked paper towels and covered in plastic. (b) Upper area after cleaning. © A.-C. Viseux.

Disassembly

Disassembly involved two procedures. First of all, bolts were unfastened between the sculpture's armature and the threaded steel bars, which were replaced by new ones made of stainless steel coated with aluminum like the originals. Secondly, access panels were cut in the aluminum to access deformed areas for reshaping; when feasible, this was done along the original weld lines and in areas that would face the wall.

Three areas were considered for separation: the lower swimmer, the aluminum angles used for attachment of the aluminum bar, and dented aluminum areas on the figures. Initially, aluminum was drilled in a line and cut with an electric saw. Thereafter, plasma cutting (a melting process) was used, because it was more suitable for cutting the thick aluminum on account of its cutting speed, cut quality, and flexibility. Dry plasma cutting was utilized with 80% of argon and 20% of hydrogen. It resulted in a large heat-affected zones but created smooth sections with very little dross formation that facilitated welding during reassembly (AGA, 2014). The critical separation of the lowermost swimmer at contact points with the other two figures was accomplished beginning with the removal of two large areas on the figure's chest and upper legs (Figure 5a).

Access to the interior of the sculpture revealed organic materials such as leaves, branches, nests, and dead birds, which had entered through two original trap doors that faced the wall (Figure 5b). Since the materials were unburned, they provided evidence that the sculpture had been little affected by the fire.

FIGURE 5. (a) The lower swimmer partially cut away from the upper swimmers. (b) Unburned organic materials found inside the lower swimmer. (c) Pitting of the aluminum. © A.-C. Viseux.

The lower side of the lower figure's arm revealed a decrease in thickness, with evidence of corrosion from stagnation-flushing cycles of moisture (Figure 5c).

An attempt was made to weld the original aluminum angles back in place on the sculpture's back so that they would be parallel to the steel beam of the wall bracket. After it failed, the conservators opted for complete removal and replacement of the angles.

Reshaping

Reshaping aluminum portions was performed by hammering with the aid of traditional tools of metal artisans, such as forming dollies, beak irons, and wooden shapes. Weights of hundreds of kilograms were also attached to deformed regions to move them back into their original positions while the sculpture was lifted. This technique was unsuccessful on the lowermost swimmer, and the process was halted when micro cracks were observed.

Reassembly

After aluminum sections separated from the sculpture were reshaped, they were reattached in their original locations by welding (Figure 6). Gaps remained at the connection of the lower swimmer to the rest of the group. New aluminum sections were added and shaped to correct these defects (Figure 7).

Three-mm-thick sheets of Aluminum AG 3 (or aluminum alloy 5754) were selected for replacement sections (Ternisien, 2009). As the major alloying element, magnesium improves mechanical properties and resistance of the aluminum to corrosion (Hegmann, 1993; Vargel, 1999). Aluminum parts were welded using gas tungsten arc welding (GTAW) technology. A gas shield of argon fed through the GTAW torch protected the electrode and weld area while providing the required electrical arc characteristics. The widely used ER 4043 was the aluminum alloy filler; silicon, its major alloying element, lowers the melting point of the aluminum (AWS, 2014). Temporary joins made by bolting stainless steel hinges to the sculpture maintained the alignment of the aluminum sections during the welding process (Figure 7b). After removing the hinges, the bolt holes were plugged with aluminum solders. New aluminum angles were held in position parallel to the beam by the insertion of aluminum sheets bent to form a triangular section (Figure 7c).

The weakened portion of the arm of the lower swimmer was reinforced by the adhesion of a new aluminum piece on the

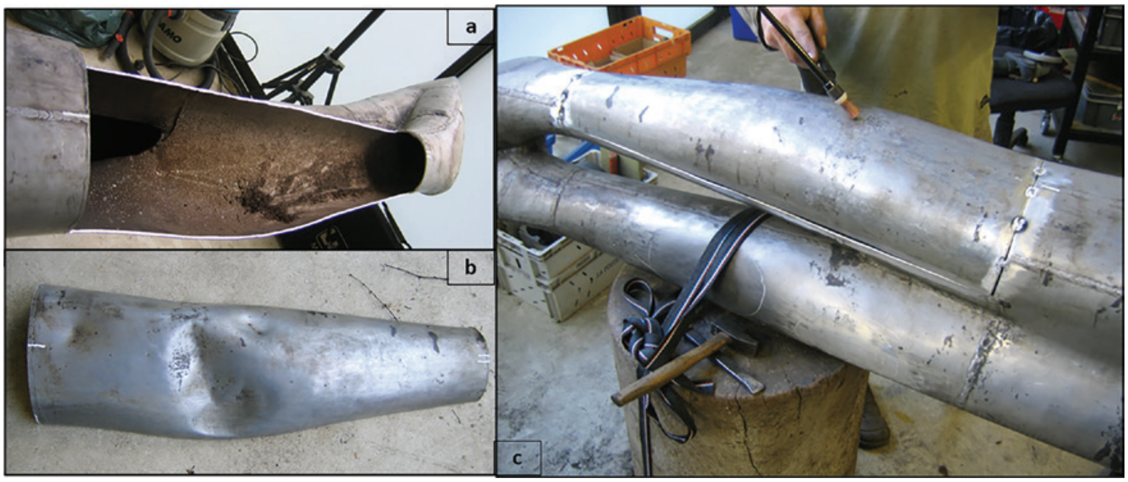

FIGURE 6. Repair of a dented leg: (a) After removal of a dented section by cutting. (b) The dented section. (c) After reshaping and re-assembly. © A.-C. Viseux.

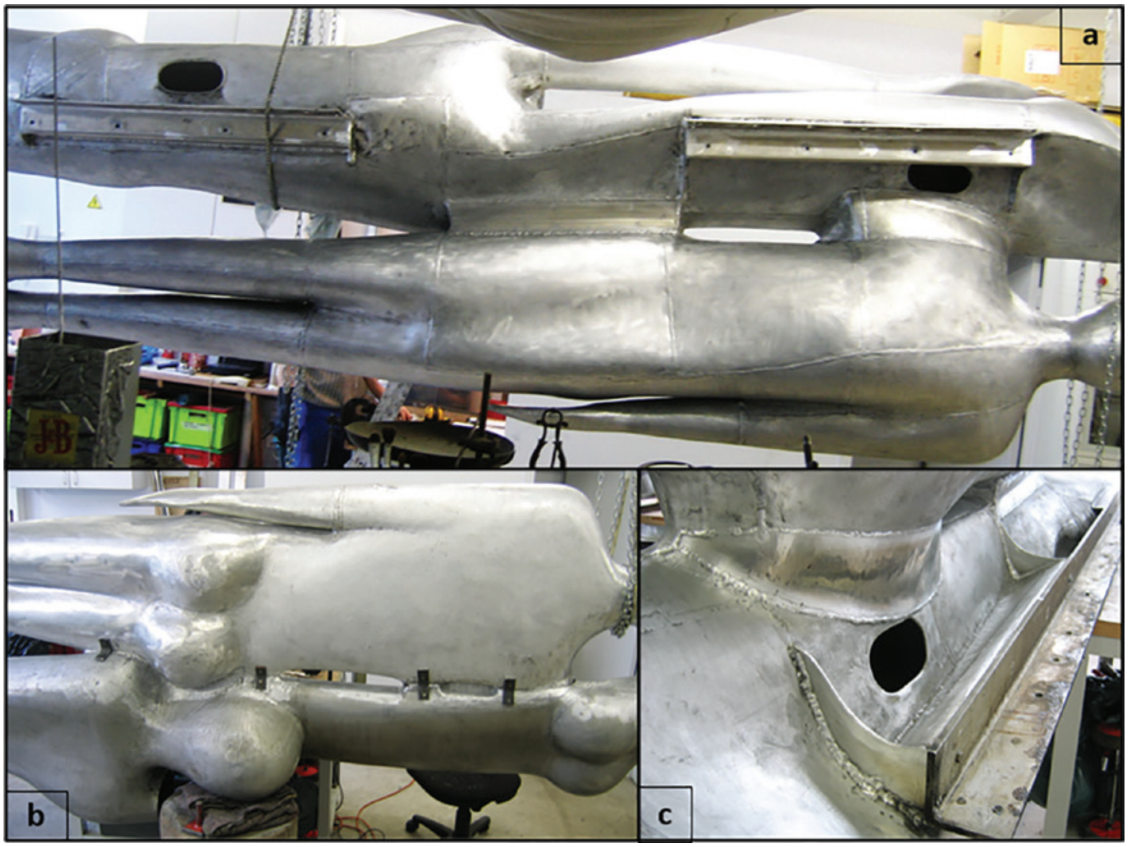

FIGURE 7. (a) The back of the sculpture that faces the wall after reassembly, showing the aluminum angles used for riveting on the aluminum bar. (b) Front of the sculpture upside down, showing temporary hinge joins made between the lower swimmer and two upper swimmers to maintain alignment during reassembly. (c) Detail of new aluminum sheets added to fill missing areas adjacent to the new aluminum angles. © A.-C. Viseux.

inner surface with the polyester mastic in common use in autobody mechanic workshops. Replacement was not done, because the arm does not support any other features of the sculpture (Ternisien, 2009). During inspection, fine steel mesh covering two trap doors that face the wall at the extremities of the upper swimmers was found loosely attached, and it was replaced with new fine polyethylene mesh. Figure 8 shows the full extent of cutting and reshaping of the figures.

FINISHING SURFACE TREATMENT

The surface of the sculpture had a heterogeneous appearance as a result of the fire, the sculpture's fall from the building, and the various conservation treatments. The surface generally had dark grey coloration with a dull aspect. Three consecutive abrasive techniques were used to achieve the satin finish observed in the archival photographs. The aluminum surface was brushed with successive abrasive grades from coarse to extra fine. First, a hand sanding machine with abrasive Scotch-Brite® pads eliminated any imperfections on the surface in terms of roughness and coloration. Then, the surface was worked by hand with non-woven polyester pads. Finally, calcium carbonate was applied with soft brushes. No surface protection was considered necessary, since aluminum is known to spontaneously create a layer of aluminum oxide (alumina) in contact with the oxygen. This physical barrier would be efficient in resisting atmospheric corrosion (Vargel, 1999; Viseux, 2008). It is expected that the sculpture will gain homogeneity over time while exposed to atmospheric conditions. Since weld marks and new sections largely face the building and remain invisible to observers, they were not resurfaced (Figures 7 and 8).

DISCUSSION

When observed from the significant distance to the sculpture on the wall (Figure 9), no one can guess that the sculpture was a ruin before conservation treatment. Nonetheless, damage prevented perfect realignment of the lower swimmer in its original plane with the other figures, and new sections had to be welded

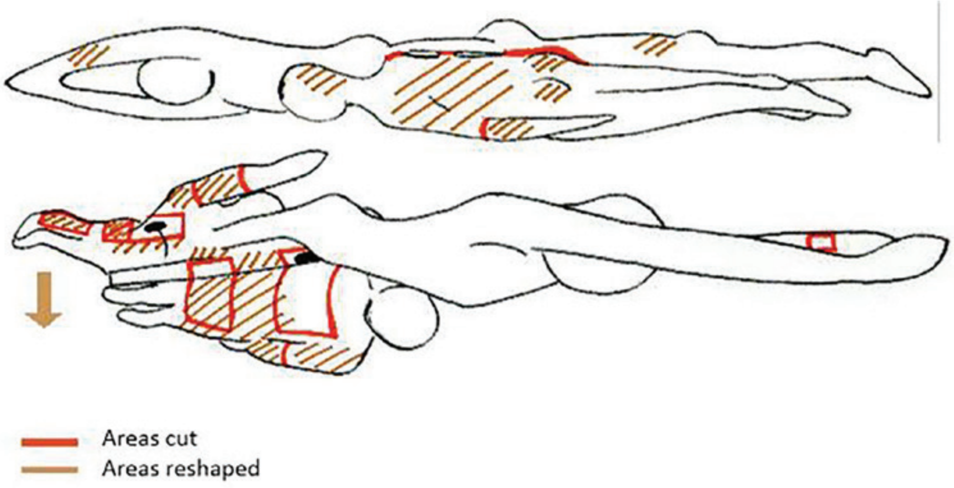

FIGURE 8. Drawing showing cut and reshaped parts: above, profile view from below; below, back of the sculpture that faces the wall of the building after falling. © A.-C. Viseux.

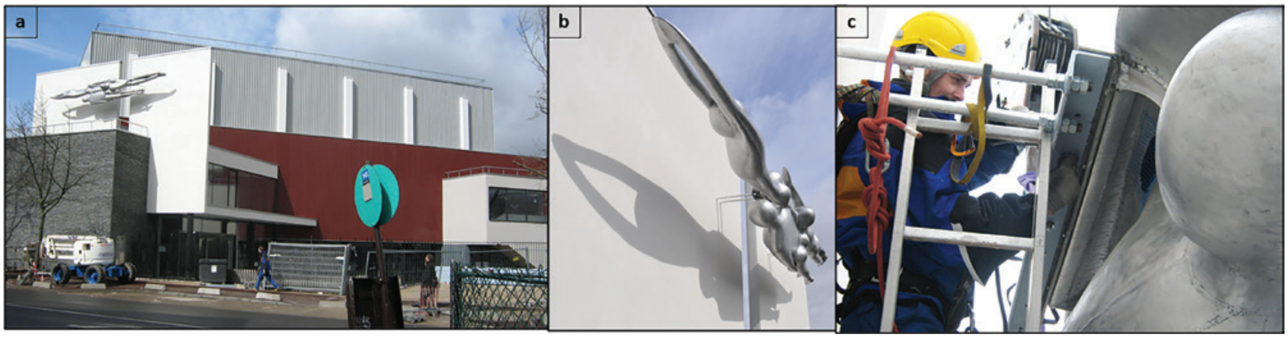

FIGURE 9. *Les Nageurs* after conservation treatment. (a) Installed on the building. (b) Profile view from below. (c) Detail of the attachment system during installation. © V. Ternisien; A.-C. Viseux; V. Evrard.

onto the lower swimmer and areas near the aluminum angles (Figure 8). Removal of a crease between the lower and upper swimmers would have required additional cutting and reshaping without any guarantee of better reassembly, and it was decided that the change was acceptable.

If the appearance of the sculpture after conservation treatment achieved the conservation objectives, the procedures chosen were inevitably invasive and led to questions regarding the sculpture's authenticity. After conservation treatment had been completed, the artist Françoise Salmon was finally located by the author. If the meeting was very moving, memory loss inhibited her recall of information about the sculpture. However, she expressed the wish to re-establish the original appearance of *Les Nageurs* even if damage occurred. For the artist, the authenticity of the sculpture lies in the image of the creation rather than the materials and techniques used; a replica would not have bothered her (personal communication, 2009).

It is hoped that galvanic corrosion will not occur between the stainless-steel beam and the aluminum angles of the attachment system because of aluminum's capacity for self-passivation in contact with oxygen (Vargel, 1999). Finally, the sculpture was installed further away from the concrete wall to avoid moisture and air stagnation.

CONCLUSION

This study exposes the conservation treatment of *Les Nageurs*. Attached near the entrance to a sports complex, the monumental aluminum sculpture was part of the daily lives of the community of La Courneuve since its installation in 1973. In 2006, a fire of the building and the subsequent fall of the sculpture from its original position ruined its appearance, including severe and extensive structural damage and surface alteration. A collaborative team of metal conservators and craftsmen met the challenge of re-establishing the original appearance of the sculpture expressed by the local city council. Fortunately, it conformed to the artist's intention. The treatment was accomplished through a combination of expertise, knowledge of the aluminum properties, and appropriate tools. The amount of mechanical damage caused by the fall and the monumentality of the sculpture created difficulties in the cutting, reshaping, and reassembly of the aluminum.

Nonetheless, the treatment provides an excellent demonstration of the use of different aspects of the conservation sphere (both remedial conservation and restoration) with necessary repairs to save the significance of this shattered heritage and ensure its future accessibility to present and future generations.

ACKNOWLEDGEMENTS

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Materials, Deterioration, and Conservation of Aluminum Foil on James Hampton's *Throne of the Third Heaven*: All That Glitters is not Gold

Helen Ingalls

ABSTRACT. *The Throne of the Third Heaven of the Nations' Millennium General Assembly*, produced in virtual secrecy between 1950 and 1964, was the life's work of self-taught artist James Hampton. The 180-piece installation owes its visual impact to aluminum foil. The plain, colored, and textured foils derive not only from store-bought rolls of kitchen foil but also from liquor store displays, wine bottles, and cigarette packs. The aluminum components were augmented with paint, glue, colored papers, and toned varnish coatings. The installation was created in an unheated garage often opened to a dusty alleyway to provide light and air to the claustrophobic space. Dust was problematic enough for the artist that many of the elements were covered over again during his lifetime, apparently to refresh dust-embedded parts of the large ensemble. Extremes of temperature and humidity were also endemic to the artist's workspace and almost certainly contributed to the deterioration of the poor quality components and the aluminum films.

Maintenance and treatment of the *Throne* over the decades since its acquisition in 1970 by the museum has been impeded by difficult access due to the close packing of the elements when on view, the sheer scale of the installation, and the nearly constant display of much of the iconic ensemble. Travelling exhibitions for large portions of the *Throne* increased incidence of handling, and long-term exposure to light has damaged the colored elements of the *Throne* and hastened deterioration of adhesives and coatings. Some corrosion is present on the foil, and some of the paints and glues have caused severe deterioration. The artist's use of foils, their deterioration, and maintenance strategies will be discussed in this look at the creation, history and conservation of an icon of American self-taught art.

Keywords: Self-taught art, aluminum foil, cellulose acetate, cellulose nitrate, filiform corrosion, hide glue, FTIR (Fourier Transform Infra-Red spectroscopy)

INTRODUCTION

The Throne of the Third Heaven of the Nations' Millennium General Assembly (hereafter *Throne*), produced between 1950 and 1964, was the life's work of self-taught artist James Hampton (Figure 1). The 180-piece installation appears to be made of aluminum foil, though in fact that metal forms only the skin covering wood, cardboard, and other elements such as light bulbs, dowels, and jelly jars. These materials were scavenged from discarded office supplies, bought second hand or found on the streets of Washington DC. The plain foil derives from store-bought rolls of kitchen foil; colored and

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FIGURE 1. James Hampton, *The Throne of the Third Heaven of the Nations' Millennium General Assembly*, ca. 1950–1964, Gold and silver aluminum foil, Kraft paper, and plastic over wood furniture, paperboard, and glass. Smithsonian American Art Museum, Gift of anonymous donors.

textured versions were also gleaned from liquor store displays, wine bottles, and cigarette packs. The foils were secured in place by means of crimping, pressing, gluing, and nailing. The components were adorned with paint, glue, colored papers, toned varnish coatings, and cryptic writings. Various forms of deterioration are present on the foil, and some of the paints and glues have caused severe degradation. The innovative use of materials, their inevitable deterioration, and maintenance strategies for the large installation will be discussed in a look at the conservation of unique, powerful, and vision-driven icon of American art.

Since the *Throne* came to public notice only after the death of James Hampton, study of its fabrication has relied heavily on research done in the early 1970s by Lynda Roscoe Hartigan, then an intern (Registrar's Office, 1973, National Collection of Fine Arts, now the Smithsonian American Art Museum, SAAM) and later a SAAM curator. Hartigan's primary sources include interviews with an elderly relative of Hampton and a small number of people who visited the *Throne* during Hampton's lifetime. She combed employment, military and area high school records for sparse documentary evidence of the reclusive artist. We are indebted to her for her thorough and provocative research, since knowledge of the circumstances of the *Throne*'s creation is critical to the understanding of its material composition and current condition. Aside from this contextual groundwork, most of our understanding of this large environmental work is based on physical evidence gathered over decades of caring for the *Throne*.

THE ARTIST AND HIS WORK

James Hampton was born in 1909 in Elloree, South Carolina; his father was a self-ordained Baptist minister and gospel singer (Livingston 1989). He moved to Washington, DC in 1931 at age 22 to live with an older brother. His employment history is mostly unknown, although it appears that he worked as a cook in local restaurants from 1939–1942. In 1942 he was inducted into the military and served in many posts, including some exotic locations: Texas, Seattle, Saipan, Honolulu, and Guam. It is conceivable that he may have been exposed during his travels to handmade indigenous art; one small object, possibly the first of the ensemble, is labeled *Made on Guam/Apirl* (sic) *1945*. Honorably discharged in 1945 after the war, he returned to DC, working odd jobs until landing a position as a laborer at the General Services Administration (GSA). He worked at GSA from 1946 until his death in 1964 at the age of 55. After his late shift from 1950 to 1964, anecdotal evidence suggests that the artist combed the streets for discarded materials on the way to his garage studio rented at 7th Street between M and N Streets in the Shaw neighborhood (Figure 2).

There he would continue working into the night on his project, an ambitious scheme to create an ecclesiastical environment to serve as a staging for the second coming of Christ foretold in the Revelations book of the Bible. According to those who knew him, he spoke of one day setting up a storefront ministry (Konrad and Hartigan, 1974).

FIGURE 2. James Hampton in his garage with *The Throne of the Third Heaven of the Nations'Millennium General Assembly* behind him. Photo from Registrar's Office, Smithsonian American Art Museum.

The garage where Hampton worked was unheated, sparsely furnished, and lit with raw light bulbs. It was accessed by large carriage-house double doors, which were often left open to a dusty alleyway to provide light and air to the claustrophobic space. Components housed in the uncontrolled conditions of the garage during fabrication and after the artist's death would have encountered many agents of deterioration: unstable climate including wide extremes of temperature and relative humidity and light (both UV and visible). If, as seems likely, the uninhabited building envelope was not well sealed, street dust, insects, rodents, and other agents of deterioration could have negatively impacted the materials of the *Throne*. No insect damage has been observed on *Throne* elements, but some paper components show significant water staining and tidelines.

SUBSEQUENT HISTORY AND STORAGE OF THE *THRONE*

In 1970, six years after Hampton died, the National Collection of Fine Arts (now SAAM) acquired the entire work. Human agents intervened to structurally improve but also stress the fragile constructions further through handling, packing, storage, travel, and display. The ensemble was first displayed publicly in 1971 in the National Collection of Fine Arts (NCFA) exhibition, *Hidden Aspects*.

After extensive structural repairs at the museum, a portion of the *Throne* complex (roughly 50 of 180 components) travelled packaged in cardboard boxes and crates to the Abby Aldrich Rockefeller Folk Art Center at Colonial Williamsburg in Williamsburg, VA (1972); The Walker Art Center exhibition *Naïves and Visionaries* (120 objects) in Minneapolis (1974); the Whitney Museum in New York City (1976); the Museum of Fine Arts Boston (1975–76); the Montgomery Museum of Fine Arts in Alabama (1977); and several other venues. It was loaned again to Colonial Williamsburg's Wallace Gallery in 2000, and parts have been loaned since 1982 to at least ten museums. Furthermore, the *Throne* has been moved within the museum at least four times (Personal recollection of the author, employed at SAAM since 1988). The non-archival storage, frequent loans, and movement within the museum were wearing on the fragile *Throne* elements.

THRONE FABRICATION

Materials chosen for construction of the *Throne* by the impecunious and untrained artist were many and varied. They included wooden furniture, sometimes cut in half; drawers were pulled out and inverted to add height to low tables and desks. Homasote®, cellulose-based fiber wall board, acoustic insulation board, poster board, desk blotter paper, and Kraft construction paper were also used as supports. Glass jars and vases were foil-covered for use as vases, light bulbs were employed as supports for decorative balls, and electrical conduit was foil-covered for use as rounded beading. Iron casters were nailed to wooden bases, so that larger parts could be easily moved. Nails, brads, tacks, and pins were used for attachment of supports, and adhesives were used to enable layering of decorative surfaces. The most important decorative material was aluminum foil, either by itself or covered with plastic-cellulose acetate overlay film, inks, tar, paints, dye-based marker, pen, and pencil.

ALUMINUM FOIL

MANUFACTURE

Prior to the early 1900s, tin and tin-clad lead had limited use as food packaging, mostly for tea, tobacco, and cheese (Faymonville, 1953: Sections 1–5), but as early as 1845 the unusual properties of aluminum were recognized as having a promising future. The ability of aluminum to undergo cold-working, its relative resistance to ordinary corrosion, the formation of a protective oxide layer on the surface, and the non-toxic characteristic of aluminum salts made the material ideal for individual packaging (Faymonville, 1953). Production was low, however, until after the invention of a new extraction process by Charles Martin Hall and Paul T. Héroult in 1886, and commercial costs plummeted with the availability of cheap and abundant electrical power in the early twentieth century. Beginning around 1913, aluminum began to be used to contain tobacco, candy, chewing gum, fancy boxes, and greeting cards (Hanlon, 1992) (Faymonville, 1953) and quickly filled the need for an all-purpose sterile food packaging.

Foil is generally defined by manufacturers as having a thickness between 0.1524 mm and .00635 mm (.006 and .00025 inches, commonly designated in the U.S. as 6 mils and .25 mils, or thousandths of an inch). Household foil may be sold in a range of thicknesses. The rolled foil intended for industrial applications is workhardened, but the household product is annealed prior to final inspection, because most foil is used in the full soft condition, which results in the ability of the foil to dead-fold, that is, stay where it is put without springing back or cracking (Angle and Green, 1968). This annealing also burns off any oil lubricants used in the rolling process. Indeed analysis of laboratory aluminum foil showed no traces of oil present (Jennifer Giaccai, Smithsonian Museum Conservation Institute, Suitland, MD, November 2013, personal communication). The purity of most packaging foil is about 99.35–99.55% aluminum; addition of minute parts of other metals strengthens and hardens the aluminum (Angle and Green, 1968). This high purity leads to the conclusion that aluminum foil deterioration on the *Throne* is due primarily not to the foil itself but to laminates, adhesives, and coatings used both on consumer products and added by the artist.

Foils used in the fabrication of Hampton'd *Throne* appear to be of four general types:

- out-of-the-box Reynolds household foil, used and new
- textured foils, mainly silver-colored
- silver-colored foil/paper laminates
- paper-laminated foils with gold-toned coatings

Paper laminates such as sulfite, glassine, Kraft, or parchment paper are used in the industry to reinforce thin foils, permitting less metal to be used and reducing costs while maintaining the moisture impermeability imparted by even the thinnest metal films (Faymonville, 1953: Section 2-1). The foil may be laminated to the carrier (or backing sheet) with aqueous, wax, thermoplastic or asphalt adhesives. The actual paper/foil laminating adhesive generally used for Hampton's paper-backed foils is unknown. However, a uniform adhesive coating on the underside of one paper-laminated sample detached from the *Throne* was analyzed by FTIR (Giaccai, 2013), and its spectrum matched reference spectra for polyvinyl acetate (PVAc) resin; this thermoplastic adhesive is reportedly used to heat-seal laminated foils to another substrate for use as wrapping paper or advertising displays (Aluminum Foil Association, p. 36). When the carrier deteriorates, such thin foils have little physical support and become vulnerable to mechanical wear, resulting in tearing and losses, such as those seen on frequently-handled areas of the *Throne*.

Coatings to provide additional gloss or alter the color of the aluminum metal for decorative purposes are applied to plain or laminated foil products in special and separate operations from other manufacturing processes (Faymonville, 1953) (The Aluminum Foil Association AFF, 1981, p. 36). In addition, decorative embossed patterns could be applied to plain foil. Both types of treated foils were used selectively to good effect by Hampton.

SOURCES OF HAMPTON'S DECORATIVE ALUMINUM FOILS

Hampton's sources of aluminum varied: some came into use pristine, others after being used as display materials or packaging for cigarettes or foodstuffs. Whether Hampton's compulsion for foils would have caused him to select food wrappings from the GSA office trash where he worked is conceivable but not documented. If so, acidic foodstuffs or fatty residues could have made their way into the works and stimulated corrosion, especially on scratched and stressed sheets (Davis, 1999):

> [while] in general, food products . . . are not corrosive to aluminum many hygroscopic products packaged in thin foil may cause some reaction particularly if the product contains salt or salt and some mild organic acid, in the case of cheese or mayonnaise (Alcoa, 1953).

Wrapping papers or liquor store display materials would likely have been less contaminated, but most were manufactured with dyes and coatings as well as adhesives such as glues or waxes (The Aluminum Foil Association, 1981, p. 36).

The most important sources of Hampton's raw material, however, were rolls of household aluminum foil. This usage is signaled by telltale paper tabs at the end of rolls, advising the buyer that "Only 6 feet remain. Buy more Reynolds Wrap," which are present but invisible to the casual viewer at the back of some *Throne* elements (Figure 3).

This store-bought wrap, a modern material carefully cast, rolled, and finished for purity, flexibility, and resistance to corrosion, proved among the more stable materials chosen for *Throne* construction. Clean and flawless, the foil provided a material that the artist could model and sculpt in pursuit of his artistic vision.

HAMPTON'S ADDITIVE FABRICATION METHOD

Although Hartigan's inquiry into Hampton's military history indicated that air-strip maintenance and carpentry may have been among the duties of Hampton's non-combatant military unit, his artistic methods did not utilize traditional carpentry techniques. In most cases his structural attachments were made with insubstantial items, such as thick cardboard straps, tinned-iron tabs from adhesive tape rolls or canned goods, and thin iron brads, which sometimes did not penetrate all intended layers. In his 1974 inventory of the *Throne* component materials, paintings conservator Tony Konrad listed no screws (NCFA-SAAM Conservation files, July 1974); the few screws found on the larger upright elements appear new and were added by museum staff in 1974 to secure taller pieces to withstand travel and loan. (NCFA Conservation files, 1974).

FIGURE 3. "End of roll" tab of Reynolds household wrap, on the reverse side of a large *Throne* element. Photo by Susan Edwards, Lunder Conservation Center, Smithsonian American Art Museum, Washington, DC.

The structural adhesive that Hampton most relied upon was hide glue, identified on four samples taken from detached pieces by FTIR analysis in comparison to the spectrum of a known sample (Giaccai, 2013). The artist may have discovered the utility of this material in discussion with purveyors in the used furniture district he is known to have frequented (Hartigan, 1977:12). This material would have been inexpensive and readily available in bulk to be mixed up in individual batches as needed. The strength of this adhesive served Hampton well to some degree, securing layered papers and foils to wooden substrates and to other decorative layers.

Cellulose nitrate, listed as one of several coatings used as ‘primers’ to ensure good adhesion of ink and other coatings on aluminum foil (Angle and Green, 1968: p. 6), was found on foils of subtly different gold tones (greenish, pinkish, and yellowish). FTIR analysis of all three colorations revealed cellulose nitrate as the toning medium, matching the spectrum of aged cellulose nitrate spectrum more closely than a new cellulose nitrate standard (Giaccai, 2013) (Figure 4).

Continual adjustments were made by the artist to find workable methods and materials based on years-long experience with the inherent vice of his chosen materials. It is suspected that some materials used early on in the artist’s process were subsequently abandoned because they had proven defective. Moreover, because of the failure of materials applied initially, some surfaces were redone by covering them with foil or additional foil-covered cardboard layers, particularly on small plaques.

Deterioration of Hampton’s Aluminum Foil

Early and ongoing significant inherent vice was at work on the *Throne* due to the methods and materials used by Hampton. The contractile forces of hide glue, for example, worked to the artist’s disadvantage because glue applied to paper-backed foils caused shiny surfaces to shrivel and distort, resulting in withered appearances (Figures 5a and 5b). This property of aged hide glue would have been exacerbated by the extremes of temperature and humidity endemic to the artist’s workspace. While aluminum

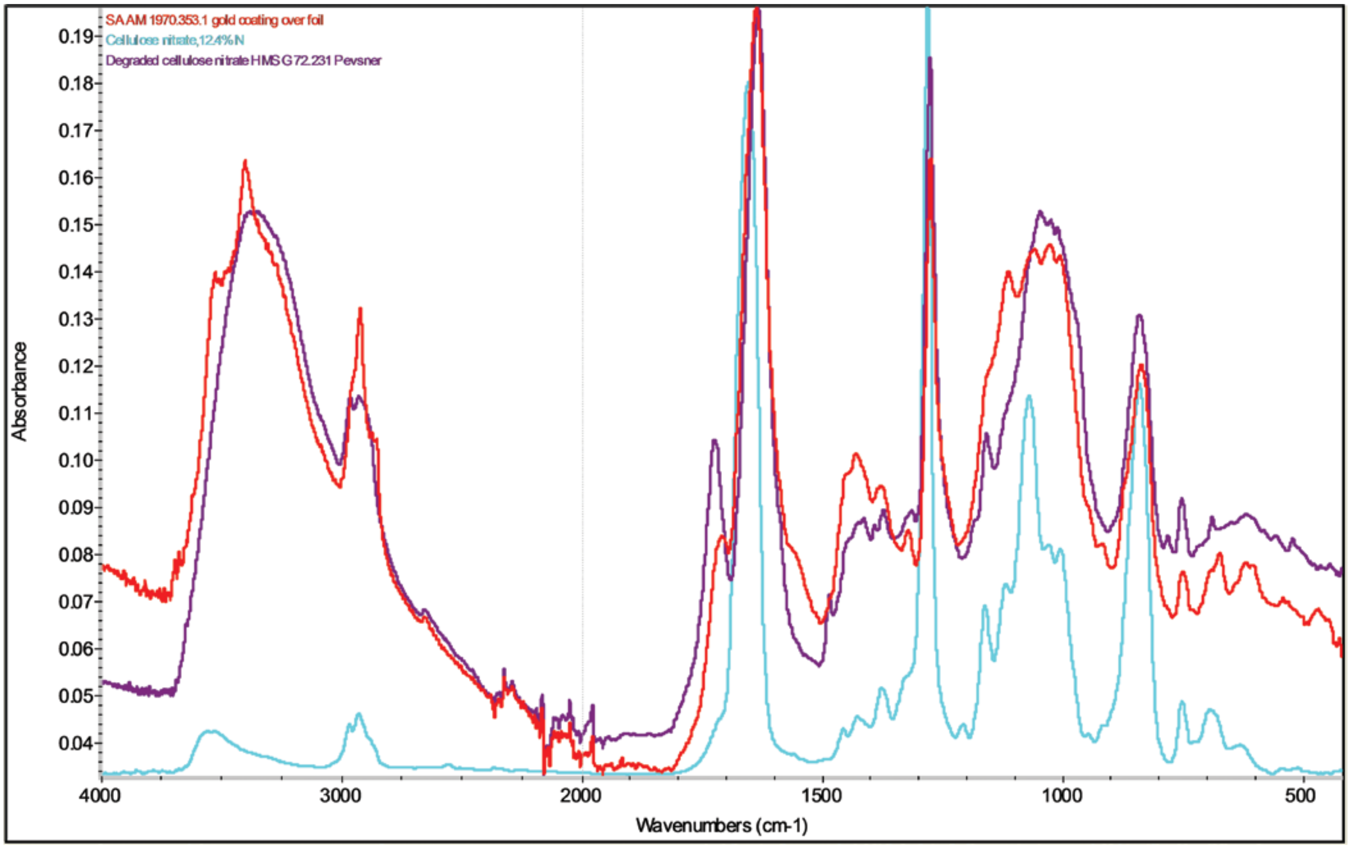

FIGURE 4. A gold-colored coating from a *Throne* foil sample closely matched infrared spectra of known degraded cellulose nitrate and, to a lesser degree, new cellulose nitrate. ATR-FTIR Analysis Report, Jennifer Giaccai, Smithsonian Museum Conservation Institute, Suitland, MD. November 22, 2013.

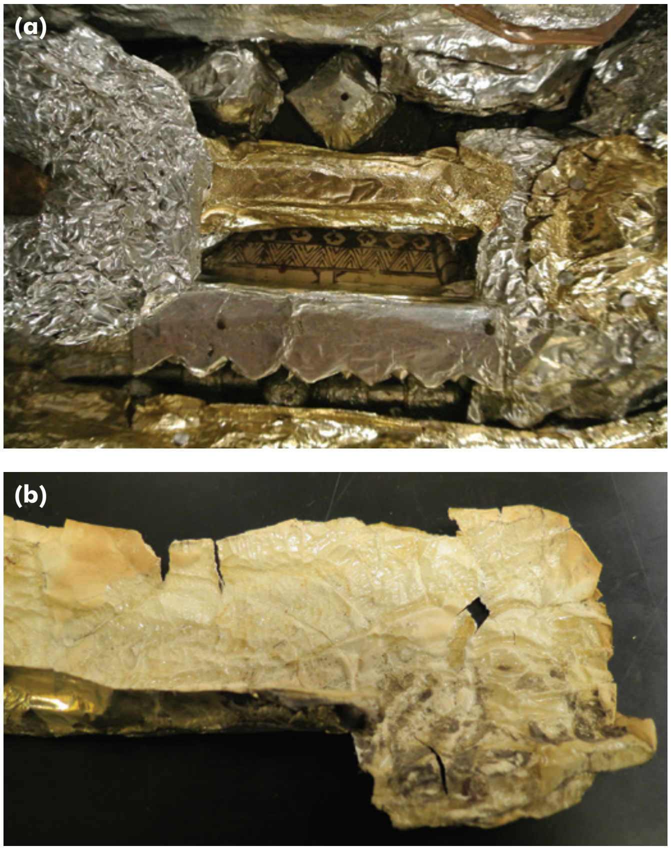

FIGURE 5. (a) Gold-toned foil on paper backing, horizontal bar showing shriveling and distortion. (b) Paper-backed gold foil with crackle pattern in hide glue coating, showing the source of distortion of the front of the foil layer. Photo by Helen Ingalls, Lunder Conservation Center, Washington DC.

FIGURE 6. Detail of *Throne* element showing recovering over time of foil sculptural elements by the artist, which blunted original crisp details such as rows of silver balls or light bulb decorations. This may have been done to combat dulling due to dust deposition. Photo by Susan Edwards, Lunder Conservation Center, Washington, DC. December 2013.

FIGURE 7. Detail of *Dispensation* element with tar, house paint, water staining, rusted tacks, and fading of green desk blotter paper. Photo by Susan Edwards, Lunder Conservation Center, Smithsonian American Art Museum, Washington, DC.

is corrosion-resistant in the presence of neutral glues, acidic or alkaline glues can cause pitting (Aluminum Association, 1981, p. 44), such as that observed on many foils adhered with a sticky black material referred to by Tony Konrad as tar (NCFA Conservation files, July 1974). Several brown-toned paints resembling house paints, have caused distortion and staining of some paper elements as well as attracting dirt (Figure 6). The cellulose nitrate coating used to tint the aluminum is also well-known to have poor aging properties.

Although in general the silver-colored household aluminum foils survived well, the artist appears to have been discontented with dust and dirt embedded in the interstices, because he took steps to stop the alteration of the shiny surfaces by covering some with plastic overlay film and others with new household foil right out of the box. In time, as he covered over dulled surfaces, the relief details lost their crispness and complexity (Figure 7).

Another reason for covering existing foils may have been to hide corrosion. This includes corrosion apparently stimulated by tars and paints. Structural weaknesses caused by repeated folding and manipulation also seems to have rendered the foils vulnerable to corrosion (Davis, 1999: p. 25). Acidic food residues could have attacked weak areas of foil resulting in corrosion. Filiform corrosion, appearing like mole tunnels on the surface of paper-backed aluminum foil, was observed on a few samples

(Figure 8). This type of corrosion, which normally occurs only on aluminum with organic coatings (Selwyn in Vargel 2004: p. 134), such as a gold-toned cellulose nitrate, was perhaps caused by the adhesive used during fabrication to attach the paper backing re-enforcement to the thin foil.

Many paper-laminated sheets have not held up well, some due to mechanical stresses associated with handling in the process of moving rusty-wheeled components (Figure 9).

The poor storage environment at the garage would have played an important role in furthering delamination of paper-laminated sheets by weakening the thin foils and increasing their tendency to tear with pressure. *Throne* laminates with gold-toned coatings perhaps fared the worst because of sensitivity of the coatings to dust, light, and abrasion (Figure 10).

FIGURE 8. Detail of filiform corrosion on uncoated surface of paper-backed aluminum foil revealing paper substrate beneath. Photo by Susan Edwards, Lunder Conservation Center, Smithsonian American Art Museum, Washington, DC. December 2013.

CONSERVATION AND MAINTENANCE

Maintenance and treatment of the *Throne* over the decades since its acquisition in 1970 has been challenging due to the sheer scale of the installation, the nearly constant display of the iconic ensemble, and difficult access due to the close packing of the elements when on display. Travelling exhibitions of large portions of the *Throne* launched after its discovery and acquisition exacerbated damage by multiple campaigns of intensive handling and significant periods of exposure to light. The artist's use of cheap construction papers led to fading early on of colored elements of many *Throne* components. While readying large components for travel to early loan venues, Hartigan and Konrad discovered bright purple and rose-colored papers hidden beneath layers added by the artist; the colors had not been evident at the time of accession, having already begun to fade during the artist's lifetime (Hartigan, 1977: p. 13). Beginning in 1988 with the hiring of a full-time objects conservator, regular maintenance was begun, with a program of dusting. In-depth cleaning and repair campaigns have occurred periodically in 1992, 2002 and 2012.

Various dust-preventive concepts have been considered over time, including constructing a Plexiglas® barrier to protect the Throne from dust and visitor interaction, a practice utilized in historic rooms during the 1970s and 1980s. Prior to the re-opening of the renovated Patent Office Building (renamed the Donald W. Reynolds Center in 2006), a positive pressure system was conceived to prevent dust from entering the *Throne*

FIGURE 9. Delamination of paper-backed gold foils on the base of a large *Throne* element due to handling. Photo by Susan Edwards, Lunder Conservation Center, Smithsonian American Art Museum, November 15, 2013.

FIGURE 10. Abrasion, darkening, and loss of degraded gold-toned coating on silver aluminum foil. Photo by Susan Edwards, Lunder Conservation Center, Smithsonian American Art Museum, November 15, 2013.

enclosure and depositing on the foil elements, but financing did not materialize for this engineered solution. Display in a carpeted gallery exacerbated the common problem of dust influx in the museum exhibition space. Currently the *Throne* is maintained by dusting as staff availability allows. Recent construction of the nearby MacMillan Education Center allowed for readjustment of the gallery airflow into vents at the front of the raised platform to intercept dust and reduce deposition.

In order to reduce light-induced deterioration, advances in museum lighting have also been considered, including motion detectors calibrated to respond to human presence in the *Throne* gallery area (Herskovitz and Rummel, 2007); however, a dark gallery waiting to be motion-activated was deemed uninviting to visitors. Laser emitting diode (LED) lighting is being utilized to augment incandescent light sources in an effort to save energy and reduce the need for access to bulbs for replacement in areas with difficult access (Scott Rosenfeld, Smithsonian American Art Museum May 14, 2013, personal communication).

CONCLUSION

In spite of poor-quality materials, experimental methods, non-standard joinery, constant revision, poor storage, frequent loans, and long-term display, the *Throne* has endured since its inception in a garage workshop in 1950 until the present. The artist was a poor man and could only use what he could scavenge or purchase second hand, with the exception of one material: abundantly available, high quality, yet inexpensive household aluminum foil whose inherent stability under deleterious conditions is perhaps the element most responsible for preserving the earthly incarnation of James Hampton's spiritual and artistic vision.

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The Use and Characterization of Aluminum-Based Metallic Paints in Australian Paintings of the First Half of the Twentieth Century

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ABSTRACT. This paper presents the results of research into the composition and use of metallic aluminum paints in three paintings by Australian artists from the first half of the twentieth century as well as a contemporary can of aluminum stove paint. A brief history of the development of aluminum paint and its uses is presented. The material characteristics of aluminum powders and binders used with them are described, as well as the effects variations of components have on resulting paint films. Analyses found leafing aluminum flakes and nitrocellulose binder on two paintings and identified coumarone as the binder for the stove paint.

Keywords: aluminum paint, metallic paint, binder analysis, SEM, μ-FTIR

INTRODUCTION

Silver-colored metallic paints are typically made from flakes of aluminum suspended in a quick-drying, transparent media. Although available from the mid-nineteenth century, they became extremely popular paints from the 1920s to the 1940s for household and decorative purposes. Artists adopted sign-writing, coach and craftwork paints during this period, since metallic aluminum paints were not marketed as artist's colors. The composition of aluminum metallic paints used by artists in the first half of the twentieth century has not previously been investigated in Australia, and this study offers a number of considerations regarding the structure of the paint layer and presents some unusual paint binders. Findings may have implications for future care and conservation treatments of paintings containing aluminum paints.

Aluminum metallic paints have been identified in several paintings in the collection of the Art Gallery of New South Wales dating from the 1930s to 1940s. The earliest example is *Magnolia and Path* by Roy de Maistre (1894–1968), one of a group of six wall paintings on canvas painted for a London apartment in the early 1930s (Figure 1a). The canvases were ready-prepared with an overall silver-colored aluminum layer covering all the walls in the room, which would have created a rich decorative scheme. *Abstract*

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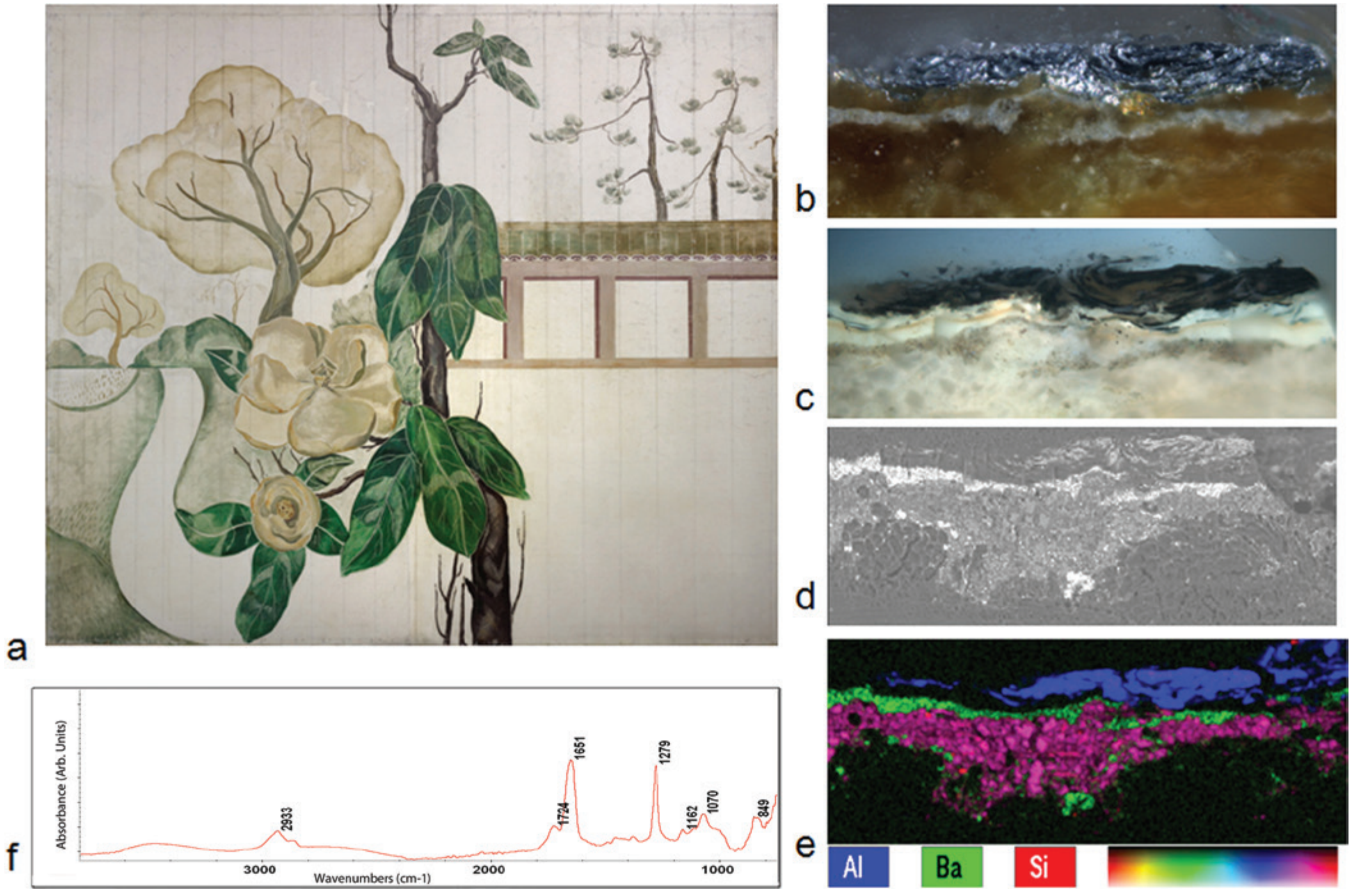


FIGURE 1. (a) Roy de Maistre, *Magnolias and Path*, early 1930s, oil, gold and silver-colored aluminum paint on linen, Art Gallery of New South Wales, © Caroline de Mestre Walker; (b–f) Cross-section taken from upper right edge; (b) In incident light, (c) Ultraviolet fluorescence, (d) SEM, in backscatter mode, (e) Pseudo-color EDS image, (f) Extracted spectrum of a synchrotron FTIR map for nitrocelluse.

(Kitchen Stove) was painted by Eric Wilson (1911–1946) in 1943 (Figure 2a), soon after his return to Australia from Europe, where he had been influenced by cubism and collage paintings. Thick, turgid aluminum paint in addition to paper collage, sawdust, sandpaper and alkyd and oil-based enamel paints provide an early example of an artist's use of non-artist grade and synthetic painting materials. An untitled 1941 painting by Ralph Balson (1890–1964) is one of a group of abstract paintings by the artist with brass, copper, aluminum, and bismuth paints used alongside conventional artists' oil paints (Figure 3a). Exhibited in 1941 in the first solo artist's exhibition of purely abstract paintings in Australia, it is now in a private Sydney collection. These three paintings, along with a can of Taubmans' Silvafros™ (1940–1950) (Figure 4b), provide a rich source of information for the study of these unusual paints.

A HISTORY OF ALUMINUM PAINTS

Availability

The first aluminum powders were developed in the mid-nineteenth century, and by 1886 they were available commercially in large quantities (Gettens and Stout, 1942:92). By the beginning of the twentieth century the French Ripolin® Company included a pre-mixed aluminum paint on their color swatch card (Gautier *et al.*, 2009). A 1938 catalogue of the English artists' paint manufacturer Winsor & Newton lists a number of metallic paints in the decorative craft section but not amongst the artists' paints (Winsor & Newton, 1938). In most instances the Winsor & Newton paints were sold in two parts, with an envelope or bottle of powder or paste and a separate

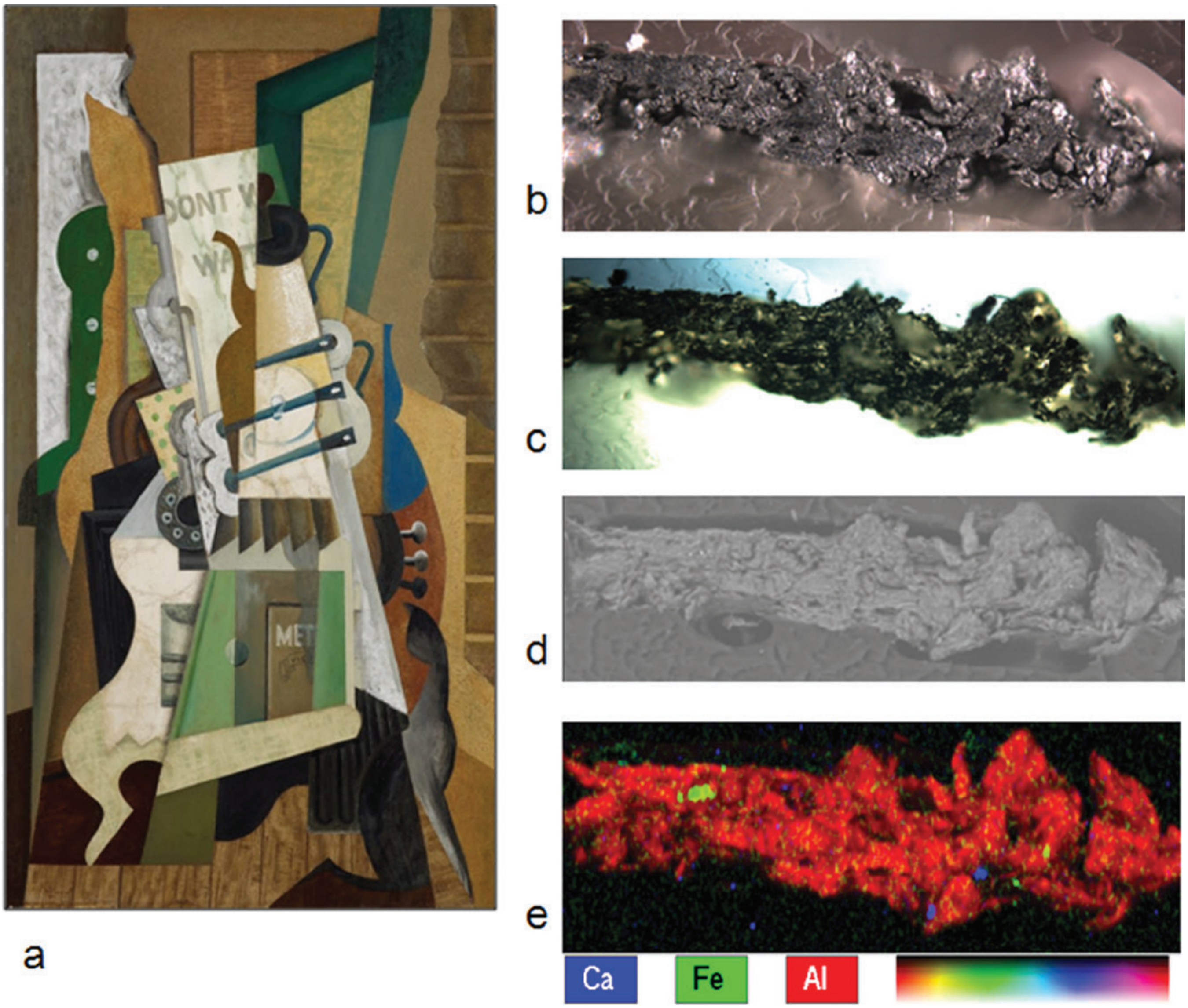


FIGURE 2. (a) Eric Wilson, *Abstract (Kitchen Stove)*, 1943, alkyd, oil, collage, sand, sawdust, and aluminum paint on plywood, Art Gallery of New South Wales. (b–e) Cross-section taken from the center of the painting; (b) In incident light, (c) Ultraviolet fluorescence, (d) SEM, backscatter mode, (e) Pseudo-color EDS image.

bottle of the suggested binder, but they were also supplied premixed in liquid.

Aluminum powders had many beneficial qualities for paints, including protection against weathering and corrosion. The paints also provided excellent insulation and could cover superficial marks and damage (Lewis Berger & Sons. 1923). Taubmans manufactured a silver-colored nitrocellulose paint in Australia called Fascinac™ for repainting shoes and leather goods, which was particularly popular during the Great Depression of the 1930s (Todd, 1990, *Taubmans. The First Century* unpublished). Silvafros™, another premixed silver-colored paint manufactured by Taubmans and available from the 1920s to 1970s, was often promoted for repainting stoves and domestic appliances (Figure 4a). By the 1930s the automobile industry incorporated aluminum powders into car paints (Morvan, 2002:6), and aluminum paints were used widely for protective and anticorrosive coatings.

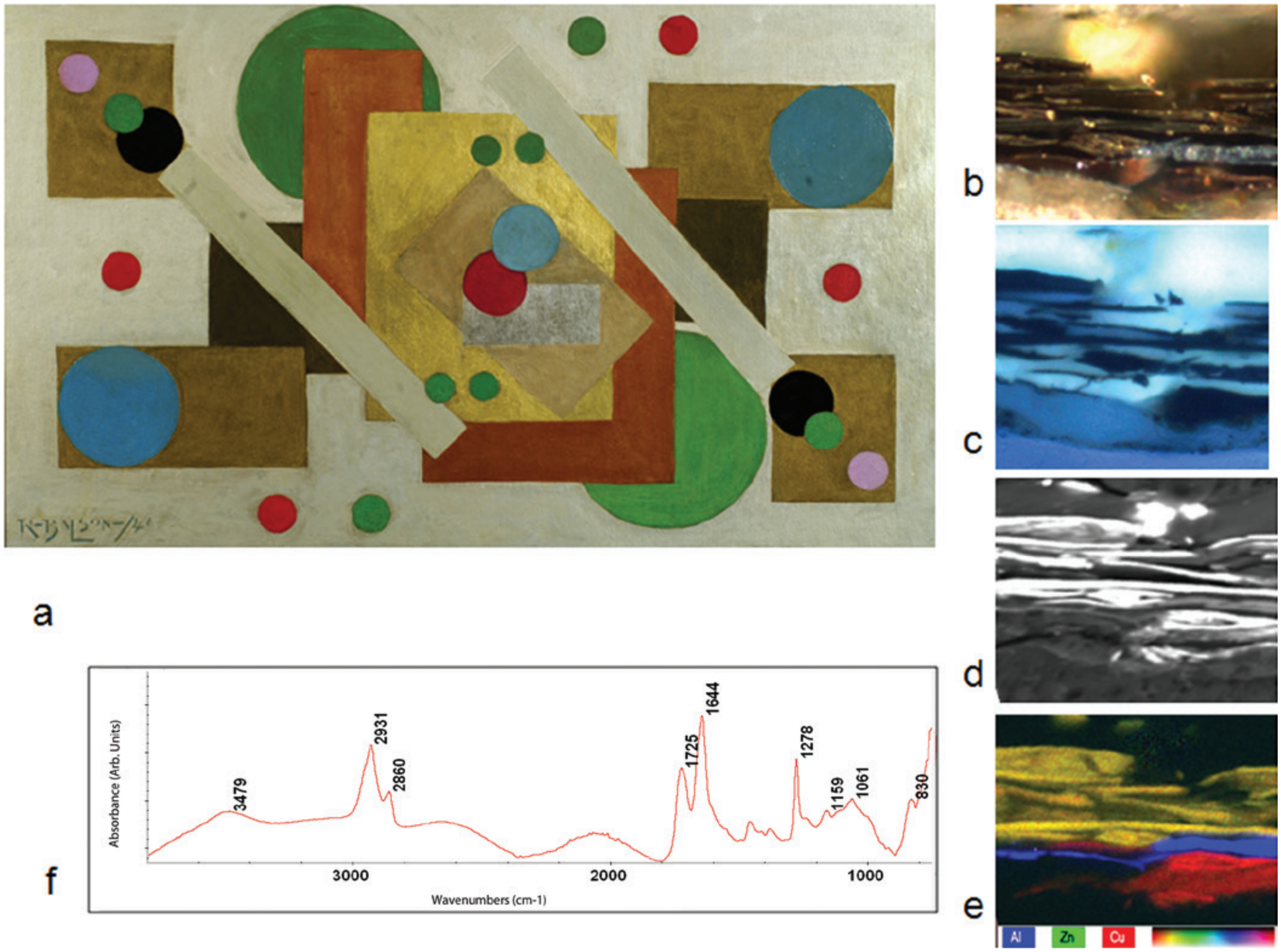
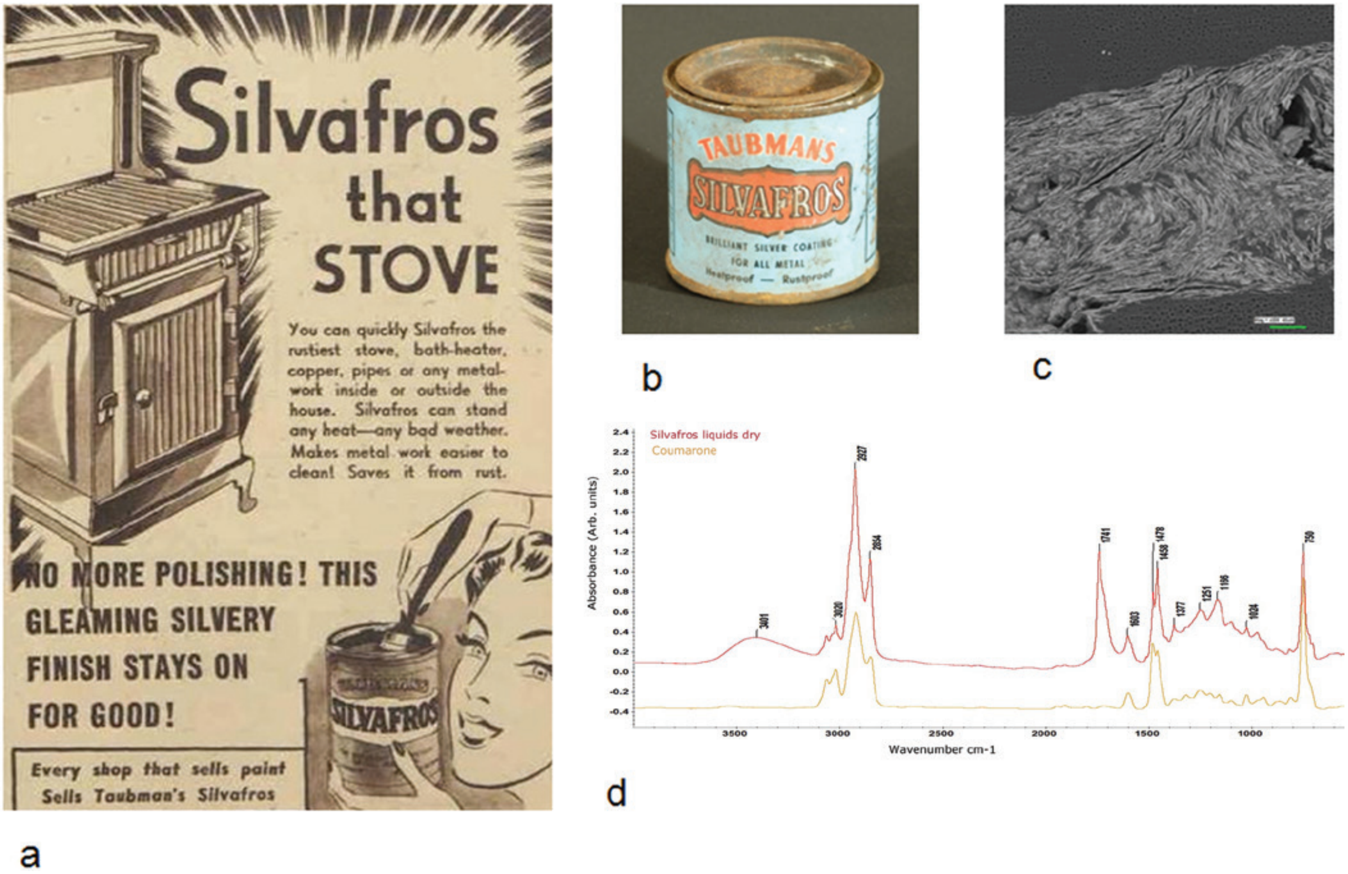


FIGURE 3. (a) Ralph Balson, *Untitled,* 1941, oil and metallic paint on cardboard, © Balson Estate; (b–f) Cross-section taken from the bronze-colored rectangle at lower right; (b) In incident light, (c) Ultraviolet fluorescence, (d) SEM in backscatter mode, (e) Pseudocolor EDS image, (f) Extracted spectrum of a synchrotron FTIR map showing nitrocellulose.

ALUMINUM POWDERS AND THE IMPORTANCE OF LEAFING IN PAINTS

Both the aesthetic and protective qualities of aluminum paints are heavily reliant on the ability of aluminum powders to leaf. Leafing is a term widely used in the literature to describe the behavior of flake-shaped particles to rise quickly to the surface of certain binders and form a continuous metallic layer or leaf (The Decorator & Painter for Australia & New Zealand 1929:31). This leafing behavior provides the highly reflective, anticorrosive and insulating properties of aluminum paints (Bieganska, Zubielewicz and Smieszek, 1988:219). Non-leafing aluminum powders are instead evenly suspended in media and tend to produce dull surfaces, although they retain some protective qualities, particularly against corrosion (Bieganska, Zubielewicz and Smieszek, 1988:225).

Aluminum powders have been manufactured using a number of different methods. In the Hall process, in use from 1886, small pieces of aluminum were stamped in a ball mill with mineral spirits and lubricant to produce leafing pigments (Edwards, 1936: preface). The impact of steel balls moving in a rotating drum hammered the aluminum into flakes. After stamping, the liquid evaporated and further lubricant was introduced to prevent the particles from welding together. A second process used to manufacture leafing pigments involved stamping very thin sheet or foil aluminum to break it into flakes and then polishing the particles in a drum to enhance their surface sheen. On the other hand, spherical



You can quickly Silvafros the rustiest stove, bath-heater, copper, pipes or any metalwork inside or outside the house. Silvafros can stand any heat—any bad weather. Makes metal work easier to clean! Saves it from rust.

FIGURE 4. (a) Taubmans Silvafros™ advertisement, *Australian Women's Weekly*, 8 July 1939: 53, (b) Silvafros™ can, 1940s–1950s, (c) SEM image in backscatter mode of a dried sample from the can, (d) FTIR spectrum of dried liquid from the can shows a match for coumarone resin, also mixed with oil.

or atomized aluminum powders are dark grey and do not leaf (Edwards, 1936:10–16).

Leafing ability is also determined by properties of the lubricant and binder, including surface tension between them, viscosity, acidity and drying conditions (Morvan, 2002:9, Edwards, 1936:22–24, Heaton, 1956). Modern leafing pigments tend to be stamped in saturated fatty acids, particularly stearic acid, while non-leafing pigments are stamped in unsaturated fatty acids, such as oleic acid. The lubricant controls the way the aluminum particles act in a binder and provides a barrier protecting against oxidation of the aluminum. Pre-mixing aluminum paints is also believed to result the flakes not forming a leaf to the same extent (Edwards, 1936:46).

BINDERS FOR ALUMINUM PAINT

In 1929 binders recommended for use in aluminum paints were heat-bodied linseed oil, often combined with tung oil to ensure a harder film and to speed up drying time; and natural resin varnish, particularly long oil spar varnish, which has a high proportion of oil (The Decorator & Painter for Australia & New Zealand, 1929: 33). Shellac could be used, but after the late 1920s, nitrocellulose lacquers became common binders for aluminum paints (Bishop 1941: 16). Nitrocellulose (also called pyroxylin or banana oil) was formulated as a paint medium in the late 1920s by dissolving nitrocellulose solids in amyl acetate solvent and plasticizing them with the addition of naphthalene, oil or alkyds. In the 1930s, it was recommended that aluminum paint binders should be used with solvents with a high degree of surface tension, should have a low acid number (mg of potassium hydroxide required to neutralize one gram of oil), and should not be used with lead driers (Edwards 1936:51).

Other examples of binders described for use with aluminum powder paints include alkyds, gloss oils (solutions of treated rosin or resin in mineral spirits), phenolic resins and coumarone (1-benzofuran). The latter is an unusual synthetic resin derived from coal-tar, which is suitable for aluminum paint because it has acid, alkali and water resistance, zero acid value, and is neutral. It was specifically mentioned as promoting leafing and producing a paint film of a particular brilliance (Martin, 1969:77). In fact, coumarone was used to test various aluminum powders for their ability to leaf because it was such a strong promoter of the effect (Edwards, 1936:31). Although water-based binders are generally not recommended as binders for aluminum paints due to the negative reaction of uncoated aluminum and water, one source did provide a method of using a water-soluble binder of gum, sugar or honey mixed with glycerin (The Decorator & Painter for Australia & New Zealand 1929:315).

The range of potential binders for aluminum paints identified in the literature is diverse and includes a number of semi-synthetic and synthetic types not commonly associated with artist's paints prior to the 1950s. Thus, identification of the binder used in an aluminum paint on an artwork may be critical to understanding deterioration and determining safe conservation methodologies.

CHARACTERIZATION AND EVALUATION OF ALUMINUM-BASED METALLIC PAINTS IN CASE STUDIES

Methodology

Micro-sized samples of paint were taken from damaged areas of the three paintings and embedded in polyester resin. Whilst soft, a microtome was used to cut 5µm thin cross-section suitable for micro-Fourier Transform Infrared Spectroscopy (µ-FTIR) analysis in transmission mode. The remaining embedded unpolished cross-section was examined using optical microscopy under visible and ultraviolet (UV) light to characterize the paint layers and the size, appearance and positioning of metallic flakes within the binder. These cross-sections were further examined under Scanning Electron Microscopy (SEM) and analyzed with Energy Dispersive X-ray Spectroscopy (EDS) to map the inorganic metal flakes in each paint sample. A sample from the can of still liquid Silvafros™ was painted out and sampled when dry. Thin sections were made for µ-FTIR analyses using a synchrotron.

RESULTS OF ANALYSIS

Optical and Scanning Electron Microscopy (SEM)

Optical microscopy of cross-sections under reflected incident and UV light could clearly distinguish aluminum from paint media in samples taken from de Maistre's *Magnolia and Path* (Figure 1b–c) and Balson's painting (Figure 3b–c). Distinct flakes of metal were aligned horizontally and positioned near the top of the binder layer, indicating leafing of the aluminum. In contrast, samples taken from Wilson's *Abstract (Kitchen Stove)* show aluminum dispersed throughout the binding layer in reflected incident light (Figure 2b), although non-uniform orientation of aluminum flakes was distinguished under UV light (Figure 2c), while there is an overall orientation, a proportion of the flakes are seen to have settled at a different angle to the majority (Figure 2c, 2d, 2e). This suggests the use of a non-leafing aluminum paint, a pre-mixed paint that had lost its leafing ability, or modification by the artist that altered the properties of a paint. The presence of discrete masses of calcium and iron, visible in the pseudo-color X-ray fluorescence image (Figure 2e), and the variable color of the aluminum paint on the work indicate that the artist may have mixed ivory black and iron oxide in with the aluminum paint as he worked.

The sample from the can of still liquid Silvafros™ showed flakes of metal powder evenly dispersed through the paint film, indicating a non-leafing paint (Figure 4c). Whether this was the intended effect of the paint, or a result of the long storage in the liquid is unknown.

SEM and EDS identified aluminum as the principal metal powder in all samples with one exception. While a sample from the bronze-colored lower right corner of Balson's painting contained aluminum, a sample taken from a silver-colored rectangle at the center contained bismuth as well. Although incredibly unusual, it appears that Balson may have employed a method of application that involving burnished bismuth powder to achieve a highly reflective silver-colored surface (Gold, 1998:166–178).

Organic results

Characterization of the binders in aluminum paint samples from artworks is challenged by the opacity of the metallic flakes, which prevent analysis with conventional transmission Fourier Transform Infrared Spectroscopy (FTIR). Attenuated total reflectance FTIR of the top surface of paint layers is also unsuccessful as many of these paints have little binder present at the surface. In samples of aluminum paints, synchrotron-sourced FTIR can be a useful technique when thin-sections are made and measured in transmission mode. The high lateral resolution (up to 5 microns) provided by the synchrotron-source ensures that spectra are measured only for the binder layer surrounding the metal flakes. Analysis of thin-sections using synchrotron-sourced FTIR identified nitrocellulose as the principal binder in de Maistre's *Magnolia and Path* (Figure 1f) and Balson's painting (Figure 3f) by distinctive absorption peaks associated with nitrate at 1656 cm^{-1} and 1281, 1060 and 846 cm^{-1} (Learner, 2004:91). Samples from the painting by Eric Wilson could not be successfully analyzed as the interstices between aluminum flakes were too small for effective transmission, even with the synchrotron's highly resolved capability. A sample of the binder taken from the tin of Silvafros™ was identified by conventional µ-FTIR as coumarone resin mixed with oil (Figure 4).

CONSERVATION CONCERNS

The identification of coumarone and nitrocellulose paint binders in this study is an important finding, since these binders may present potential solvent sensitivity and vulnerability to ageing. The literature suggests that coumarone was not used for general paints as it has poor color retention and can change on exposure to light (Martin, 1969:76–77). Nitrocellulose is also considered not to be a light stable material. However, it is interesting to note that both the de Maistre wall paintings and the Balson *Painting* 1941 are in good condition and show no visible signs of the binder breaking down. The ability of the aluminum to rise to the surface and form a continuous opaque film may protect the binder from light, enabling paint makers to use binders that might not otherwise have had good longevity (Decorator & Painter for Australia & New Zealand 1929: xv). The aluminum paint on the works by de Maistre and Balson may therefore be rare examples of 1930s and 1940s nitrocellulose paints in good condition.

When loss compensation is required, issues of leafing and the orientation of the aluminum flakes can present significant problems for matching and retouching in areas of damage. A microscopic examination to determine the size and orientation of the pigment flakes may help with matching the grade of pigment, its reflectivity and method of application to reduce visual differences between original and retouching materials.

Care should be taken when treating these paintings to avoid damaging the thin protective organic coating on the aluminum powders as it could negatively affect the appearance and resistance of the pigments. It is important to be aware of the possibility of oxidation of an uncoated aluminum paint layer and formation of the dull coating of aluminum oxide on exposed particles in damaged areas of the artworks.

CONCLUSION

Despite one source noting that nitrocellulose as a binder for aluminum paints had '*little to recommend it besides its quick drying*' (*The Decorator and Painter for Australia and New Zealand* 1929:33) and comments that aluminum powder did not usually leaf in this binder (Edwards, 1936:62; Gettens and Stout, 1942:92), nitrocellulose was identified in samples taken from two paintings in this study, both of which clearly demonstrated leafing characteristics.

The research into the composition and use of aluminum paint in paintings by a number of Australian artists during the twentieth century is ongoing, and many areas remain to be investigated. A wider range of paintings incorporating metallic pigments could contribute to further research into the range of binder types that might be present. While the literature suggests there were many options for binders other than nitrocellulose for these paints in the first half of the twentieth century, no others have yet been identified on paintings. Synchrotron-sourced µ-FTIR was successfully used to identify the binders in a number of the samples. Further refinement of the methodology of thin-section sample preparation is needed to expand the potential of this technique.

APPENDIX

Cross-sections were examined in the SEM using a JEOL 840 and analyzed with an energy dispersive spectroscopy (EDS) system controlled by a Moran Scientific Microanalysis system. X-ray mapping at 20 kV accelerating voltage of the cross-sections was also used to obtain detailed information of the inorganic components (metal flakes) in each paint sample.

Samples examined with synchrotron-sourced µ-FTIR were characterized in transmission mode using a Bruker Hyperion 2000 FTIR microscope (Bruker Optic GmbH, Ettlingen, Germany) working at 36x magnification at the Australian Synchrotron IRM beamline (Clayton, Victoria, Australia). Thin sample sections were further compressed between diamond windows of a ThermoFisher (Waltham, MA, USA) microcompression cell and areas of 5×5 microns on the sample, either as individual points or as part of a custom-defined grid points were investigated over the 3800–750 cm^{-1} wavenumber range.

Conventional transmission µ-FTIR was performed on paint samples with a Thermo Nicolet Nexus Spectrometer attached to a Continuum IR Microscope and MCT-A Detector with KBr window (11700–600 cm^{-1}). The spectra were recorded in the range 4000–550 cm^{-1} using 16 scans at 4 cm^{-1} resolution. A micro-compression cell with diamond window was used as a sample platform, and samples were rolled flat with an FTIR roller prior to analysis.

ACKNOWLEDGEMENT

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Aluminum's Challenges for the Architectural Conservator

Richard Pieper

ABSTRACT. Despite some very prominent architectural applications at the end of the nineteenth century, significant use of aluminum for the exteriors of buildings began only in the 1920s. The cast aluminum spire and cresting of the German Evangelical Lutheran Church in Pittsburgh (1926), and the cast spandrel panels of the Empire State Building (1931) and Rockefeller Center towers in New York City (1932–39) stand out as early large scale uses. These installations are in remarkably good condition after nearly a century, yet have not received significant repair.

For an anodic metal so low on the galvanic scale, aluminum has fared remarkably well in the urban environment. More than most metals, it seems to benefit from benign neglect. Other "white metals" of the modern period (such as stainless steel and nickel silver) require periodic cleaning or maintenance to retain their appearance in exterior application. Aluminum frequently receives none. Some of this durability is clearly due to the inherent properties of this remarkable material, but some may be attributed to the chemical or electrochemical treatment the metal received prior to installation. Early aluminum treatments such as "deplating" and "Alumilite" finishes are neither widely understood nor appreciated, and yet undoubtedly have contributed significantly to the protection of the metal.

This paper discusses the challenges facing the architectural conservator in establishing programs of treatment for aluminum in the built environment.

Keywords: aluminum, Alcoa, aluminum finishes, architectural

INTRODUCTION

Virtually every book on the use of aluminum in architecture written in the United States includes a reproduction of an 1884 lithograph from *Harper's Weekly* (fig. 1), which shows the setting of the aluminum pyramidion at the top of the Washington Monument on December 6th, 1884 (Figure 1). This pyramidion is often cited as the first use of architectural aluminum in the United States.

The selection of such an anodic metal alloy for the tip of a monument to our nation's founding father seems a bit odd today; why not gold, platinum, or another more "noble" metal? The use of aluminum for this prominent element can undoubtedly be credited to three facts:

1. In 1884, two years before the development of the Hall-Heroult process, aluminum was still a precious metal. The metal was then valued at about a dollar an ounce, the same as silver, and the pyramid weighed about 6¼ pounds, so the metal of the pyramidion was worth about $100 dollars, a significant sum at a time when a laborer earned about a dollar a day.
2. Aluminum is an excellent conductor of electricity, and the metal tip was intended to serve as the tip of a conductor for a lightning protection system.

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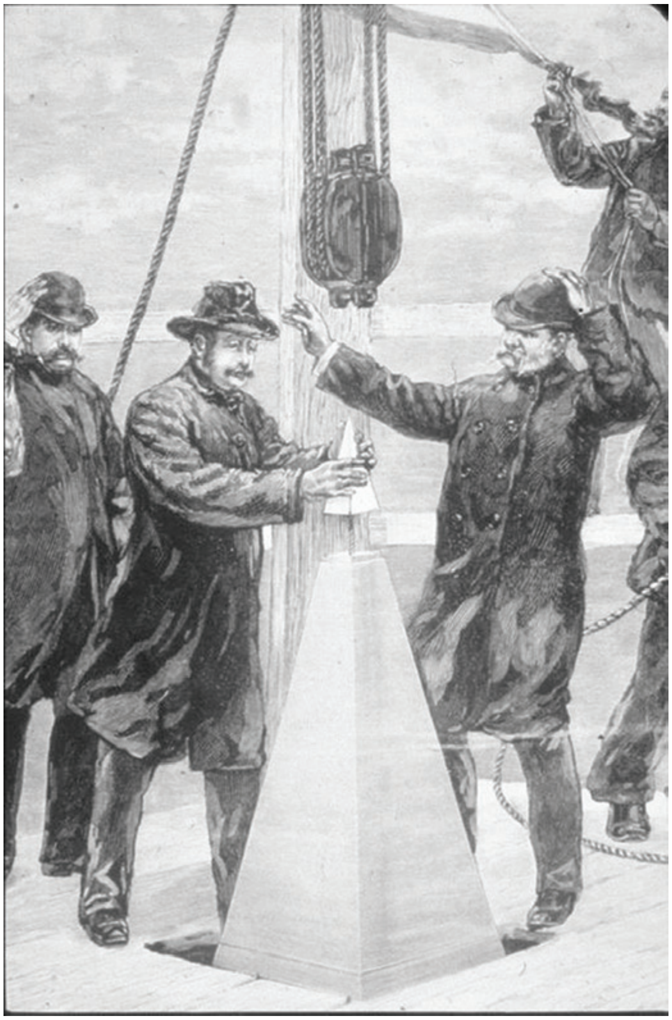

FIGURE 1. Setting of the pyramidion on the top of the Washington Monument, *Harper's Weekly*, December 20, 1884.

3. Like chrome, tin, and titanium, aluminum develops a microscopically thin layer of oxide that resists further corrosion; just as importantly, the corrosion products that do form do not stain the white marble masonry of the obelisk below it.

FIGURE 2. Reinstallation of lightning protection on Washington Monument, ca. 1934. Photo courtesy Judy Jacob, National Park Service.

So, how has the pyramidion fared after 130 years of exposure? The answer is muddied a bit by the addition of a rather large and ungainly lightning protection system, which was added to the monument after a lightning strike only a year after its erection (Figure 2).

This "crown" was made of plated copper, and while it has gone through several incarnations over the years, it is still there, and it has caused areas of pitting where it is in contact with the aluminum. The rest of the pyramidion, a block of polished but otherwise untreated metal, is remarkably intact, so much so that after cleaning the original shallow inscription of dedication at the tip is still legible (Figure 3).

When the monument was shrouded in scaffold and worked on in 1999, conservator Judy Jacob of the National Park Service was asked to inspect and treat the apex, and gave this report of the treatment:

> The apex was cleaned in a two-step process. Surface dirt and some corrosion products were removed with a nonionic detergent and a stiff natural-bristle brush. Two slurries of alumina polishing suspensions (5 microns and .05 microns) were then rubbed over the surface to further reduce the corrosion products. An attempt was made to reduce the corrosion layer beneath the lightning sleeve with a silicon carbide paper but this was not successful. All surfaces were thoroughly rinsed.
>
> Following treatment, the aluminum was considerably lighter in color and the inscribed text that had not been covered by the sleeve was legible. The corrosion layer beneath the sleeve could not be removed nor could that text be made legible.

FIGURE 3. The original inscription on the pyramidion was legible after cleaning. Photo courtesy National Park Service.

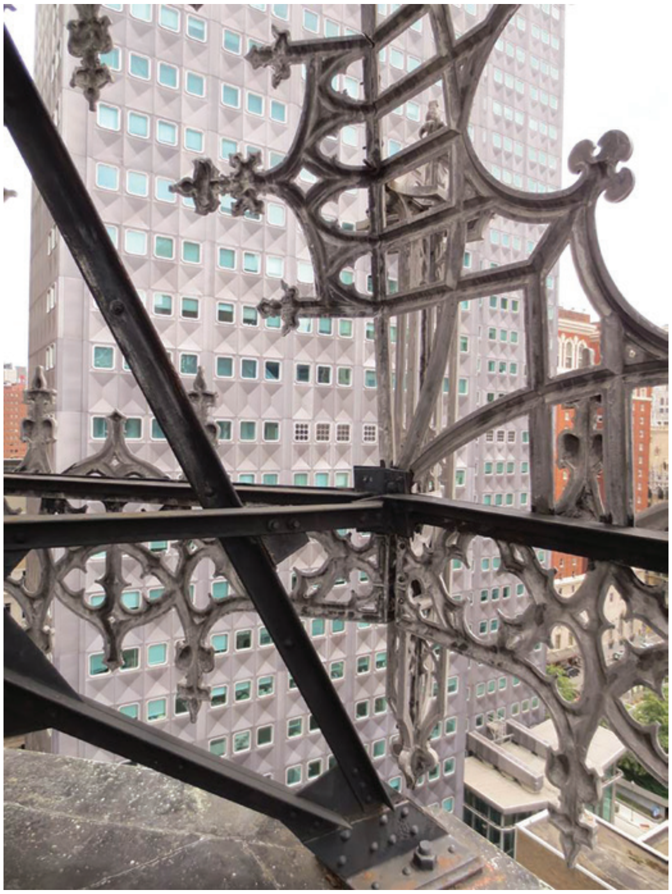

FIGURE 4. Aluminum castings of the spire of the German Evangelical Lutheran Church, Pittsburgh, Pennsylvania, constructed 1926. Aluminum curtain wall of the Alcoa Building in background.

The development and patenting of the Hall-Heroult process initiated the long and inexorable drop in the price of aluminum, which allowed aluminum to take an important place in architecture. With the exception of a few well known interior applications, such as railings in the Rookery in Chicago, aluminum was not to see significant architectural use until the 1920s, however. An important 1929 marketing pamphlet of the Aluminum Company of America ("Architectural Aluminum") pictures seven buildings that made significant use of aluminum for exterior applications. One of the early adopters of the metal was the New York and Pittsburgh architect Henry Hornbostel, who was the designer for three of the seven buildings pictured in the Alcoa publication. This includes the Grant Building, which made early use of cast aluminum spandrel panels, an application that was to become quite popular in the early 1930s. Three of the seven buildings were also located in Alcoa's home town of Pittsburgh, among them Hornbostel's German Evangelical Lutheran Church (now called the Smithfield United Church of Christ), which was constructed with a cast aluminum spire in 1926 (fig. 4). A brief visit to the spire in September 2013 found the castings and supporting steel without significant visible deterioration, even at the sites of steel fasteners and connections to the supporting frame, and after 90 years of exposure to the environment. There are a number of aspects of this installation that would be interesting to investigate further, especially the finishes on the aluminum and steel, and the presence of gaskets at points of contact between the castings and the supporting frame. As it turns out, the church is quite close to another significant use of cast aluminum, the Alcoa Building, which made use of a bolted curtain wall of aluminum castings in 1951 (Figure 4).

About four years after the Smithfield Church was constructed, aluminum castings played an important role in what is often called the first large scale use of aluminum in architecture in the US: the Empire State Building. In his history of Alcoa's "From Monopoly to Competition" (1988), author George Smith states that the Empire State Building utilized 750,000 pounds of aluminum from Alcoa. At that time the company had a monopoly on aluminum smelting operations in the US, and controlled the majority of aluminum fabrication in the country. Several sources say that the spandrel castings of the Empire State Building were finished by "deplating". The meaning of this somewhat confusing term was clarified for me by conservator Xsusha Flandro, who found and forwarded a 1931 specification from the New York City Transit Archives:

> "Deplated" finish shall mean the surfaces of aluminum finished by sand blasting, followed by anodically oxidizing by electrolytic treatment in a sulphuric acid bath of low concentration, to produce a very dark gray color, and then coated with a clear lacquer.[2]

"Deplating" is, in effect, anodizing by another name. The use of the term makes a bit more sense when you read Alcoa's introduction to anodizing in their *Finishes for Aluminum* booklet which was first published in 1938:

> The process differs from electroplating in that the articles to be treated are attached electrically as anode rather than cathode in the electrolyte. In electroplating, a metal is deposited on the article being coated, while in anodic treatment, in effect, oxygen is deposited instead of metal, and combines with the aluminum to form aluminum oxide, integral with the surface of the metal.[3]

The Empire State Building was just being completed when work began on a second significant use of aluminum castings in NYC: the complex of buildings at Rockefeller Center. While the Alcoa history confirms that they provided window sills, it says nothing about window spandrels (Figure 6). Whichever firm was responsible for their fabrication, the 3,000,000 pounds of aluminum used on the project certainly includes Rockefeller Center's spandrel panels. These also appear to have been "deplated," although documentation does not confirm that. In 2005, when work began to reopen the original observation deck at 30 Rockefeller Center, I was asked to survey the conditions of the extraordinarily large spandrel panels and copings which ornament the top of the building, and I found two significant and interesting modes of deterioration.

The center portions of some cast copings, which protect the top of the wall behind the spandrels, exhibited significant corrosion (Figure 5), disaggregating into small grains of metal, presumably because they were bedded in an alkaline mortar.

FIGURE 5. Corrosion had affected some of the copings at the roof of 30 Rockefeller Center, in New York City.

If you ran your hand over the area of failure the metal of the casting rubbed off like grains of sand. Traces of an old gray epoxy repair were present at the perimeter of the failure, but this itself had failed as the metal beneath it continued to disaggregate. These copings were eventually replaced. Alkaline sensitivity is a common mode of failure for aluminum mounted against mortar or concrete, and contemporary specifications generally call for aluminum to be back primed with an asphaltic paint, or an aluminized asphaltic paint. The back of the spandrel panels are similarly unpainted, and displayed superficial deterioration where mortar between bricks contacted the backs of the spandrels. Because water could not pond on this area, however, the panels were not severely affected.

The fronts of the spandrels were generally in excellent condition, although soiled (Figure 6).

FIGURE 6. Spandrel panels at 30 Rockefeller Center and other Rockefeller Center buildings are fabricated of cast aluminum, with a dark gray surface resembling a "deplated" finish.

Where there were problems, they generally occurred primarily at the base of panels in locations where the castings were exposed to runoff from copper roof flashings, resulting in pitting, apparently from galvanic corrosion (Figure 7). This condition was addressed by mild abrasive cleaning by hand, and subsequent cosmetic treatment using patination chemicals, such as the aluminum blackeners made by Birchwood Casey and Jax.

Aluminum is obviously capable of exceptional durability in exterior environments, as the Washington Monument and the Smithfield Church demonstrate. As we have seen at Rockefeller Center, however, it does have a few notable vulnerabilities, such as:

1. Sensitivity to alkaline materials, such as mortars and concrete, from which it must be protected with paints or coatings.
2. Vulnerability to galvanic deterioration with certain metals, especially copper, but also tin, iron, and steel. This vulnerability extends to runoff from copper flashings, and contact with copper bearing materials, such as pressure-treated woods.
3. Sensitivity to chlorides and to certain acids, such as hydrochloric acid, as well as tannic acid in or leached from wood.

These seem like fairly minor problems, certainly ones which can be addressed with careful design. What are the challenges for the conservator? Since the conservation of architectural aluminum is still in its infancy, architectural conservators aren't yet blessed with a set of developed and accepted conservation practices such as those that exist for many other architectural metals. The challenges that follow are the issues that conservators must focus on if they are to develop a methodology for conditions investigation and treatment.

FIGURE 7. Bases of spandrel panels exhibited pitting, apparently from galvanic corrosion, where exposed to runoff from more cathodic metals.

CHALLENGE 1: THE ALLOY

The first challenge is the alloy: it takes just 3½% of carbon to transform iron from a malleable, eminently workable material into rust resistant but brittle gray cast iron. Add less than 1% of magnesium to this and the iron is transformed into a ductile cast iron with significantly altered mechanical properties. Just 2% of molybdenum transforms stainless steel into chloride resistant 316 alloy. Obviously, it takes a very small trace amount of an element added to an alloying material to completely change a metal's properties and durability.

As early as 1908, building upon German experiments, Alcoa was working on the development of a heat treatable aluminum /copper/magnesium alloy (called "Duralumin") which rivalled the strength of steel. This went on to become known as Alloy #2024, and was to play a prominent role in the development of the aircraft industry. Zahner's "*Architectural Metals*" (1995) today lists seven common casting alloys, primarily alloys of aluminum, silicon, copper, and magnesium, but some contain small amounts of iron, nickel, zinc and manganese. For each of them Zahner describes differences in fluidity, surface smoothness, sand casting properties, and the ability to anodize, and indicates significant differences in general durability, as well as durability in marine environments.

Given how significant alloying materials are to other metals, it is interesting that architectural conservators don't stress alloy identification when evaluating conditions or proposing treatment. When faced with an aluminum conservation issue today, many architectural conservators pay little attention to alloy composition and place more importance upon mode of fabrication (cast, rolled, or extruded). This may be due to the fact that there is very little documentation detailing modes of deterioration of the different historic alloys in contemporary architectural conservation literature. Conservators need to correct this lack of information with more research, and to begin to think of historic installations as specific aluminum alloys. Is the installation alloy #43 (aluminum/silicon), alloy #195 (aluminum/copper), or some other alloy? It is obviously important that we begin to identify the alloys that we are treating at the beginning of any evaluation and recognize that some issues (such as the alkaline sensitivity and corrosion of the copings at Rockefeller Center, for instance) are very likely related to the original selection of the alloy and that our recommendations for treatment be tailored accordingly.

CHALLENGE 2: MECHANICAL FINISHES

In 1938, Alcoa published the first edition of its booklet "Finishes for Aluminum," which was reprinted several times over the following decade. This is a wonderfully detailed publication, providing a window onto the burgeoning market for aluminum in the 1930s, and showing just how much experimentation was occurring in the development of both mechanical and chemical treatments for the metal at that time. In the booklet Alcoa defines nearly a dozen types of mechanical finishes, including categories such as scratch brushed, hammered, sandblasted, tumbled, and polished.

One thing that is apparent from the 1938 book is that Alcoa is taking direct aim at the markets that had heretofore been filled by the copper/nickel/zinc alloy market, or "nickel silver".

Bright metals, such as nickel plating, nickel silver, and stainless steel, often pose the added complication of mechanical finishes. Is there any architectural conservator who hasn't received a call about scratches on a brushed stainless steel installation? Replicating damaged mechanical finishes on aluminum presents a significant challenge for the architectural conservator as well.

CHALLENGE 3: CHEMICAL SURFACE TREATMENT

This includes both chemical finishes and electrolytic oxide finishes. Alcoa's 1938 publication also devoted significant sections to what they defined as chemical finishes, essentially chemical conversion finishes, to which they gave names such as "caustic-etched", "diffuse reflector", "frosted", and their proprietary "Alrok" finish, and to electrolytic oxide finishes, what we would today call "anodized" finishes, but which Alcoa at that time called their "Alumilite" finish.

The surface treatments we specify for other architectural metals are different than those we must consider for aluminum. If something is made of exposed wrought iron, cast iron, or steel we assume that it will be painted, and our efforts are devoted to the level of surface preparation that can be achieved, and the nature of the paint system suited for that surface. Exposed historic zinc is also almost always painted. Copper we often leave untreated, or if bronze statuary is involved, we may *patinate* ("chemically finish" to use Alcoa's terminology) and treat using waxes or lacquers. For no other architectural metal do we face the extraordinary range of original chemical finishes that we do with aluminum.

Perhaps the single biggest technical challenge that aluminum poses for the architectural conservator involves original chemical and electrolytic oxide treatments that are both difficult to identify and impossible to reproduce in situ. This is complicated by the fact that Alcoa was then immersed in antitrust negotiations with the Federal government and pressured to allow competition from other fabricators. The finishes book provides extremely detailed recipes for treatment, and was obviously intended to spawn an industry of treatment by outside shops. Absent thorough written specifications, identifying the treatment applied originally may be almost impossible.

As noted above, abrasive cleaning recommended for the spandrel panels of 30 Rockefeller Center was to be followed by application of products to blacken the aluminum, such as those sold by Birchwood Casey or Jax. The Material Safety Data Sheets (MSDS) for those two products reveal different formulations, but most metal blackeners work by producing a sulfide on the surface of the metal. If artfully done this may possibly yield a satisfactory aesthetic match for an original deplated finish. It is not likely to be as durable as the original electrolytic treatment, however. We will need to monitor and identify such treatments to determine their success and requirements for maintenance.

CHALLENGE 4: CLIENT EXPECTATIONS

The Cities Service Building in New York City is located in the financial District of Lower Manhattan. For a brief moment it was the tallest building in Manhattan, until it was surpassed by the construction of the Empire State Building. All of the cast and extruded aluminum of the first floor entries and window surrounds of the building is covered with a silver colored paint. Why would remarkably durable aluminum be painted? Perhaps an original deplated finish looked soiled to the owner, or perhaps the relatively modest maintenance costs of maintaining polished exterior surfaces seemed unacceptable. Educating clients about the appearance of original aluminum finishes and acquainting them with reasonable expectations for maintained appearance, especially if shop treatments are to be replicated in situ, will certainly be one of the architectural conservators' most important responsibilities for any aluminum intervention.

In the end, these challenges for the architectural conservator have much less to do with the vulnerabilities of aluminum than they do with the original methods of its treatment. This is not such a new metal, but ironically, because of its exceptional durability, its conservation in architecture is still in its relative infancy. It is up to us to develop a new lexicon for conditions investigation, and new models for treatment.

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Deconstructing the Dymaxion House: Designing Survival Strategies for an Aluminum Tension Structure

Clara Deck[1]*, *Richard Jeryan*[1], *and James Ashby*[2]

ABSTRACT. The Dymaxion House, a futuristic, mostly aluminum dwelling designed by R. Buckminster Fuller, was acquired by The Henry Ford Museum in 1992, and was conserved and reassembled by 2001. Its history, conservation, preparation for public exhibit, and maintenance are discussed in this paper. Built as two prototypes in the 1940s, it was constructed of components in various alloys with several fabrication and assembly methods. In subsequent decades the parts were subject to the outdoor environment, residential usage and eventual abandonment. Many of the aluminum components suffered varying types and degrees of corrosion.

The paper will address how a multi-disciplinary team of conservators, scientists, architects, engineers, and technicians undertook a three-year conservation program that entailed material testing, finite element analysis, and some innovative treatment methods for the aged and weathered aluminum. The project design included plans for a sustainable permanent exhibit within the museum.

More than simply a narrative of the conservation process, this paper also describes the maintenance and monitoring of the house in the decade following its reassembly. For example, after more than 10 years of active exhibition, cracks in the aluminum floor beams were discovered. The investigation and root cause of the cracks are discussed as well as the preventive steps used to mitigate further crack growth and new cracking. To estimate the expected fatigue life of the floor beams, structural strain measurements and life prediction analyses were undertaken. The measurement strategy, instrumentation, test and analysis results, and the prediction of the expected life of the aluminum beams are presented.

Keywords: Dymaxion House, aluminum, Henry Ford, architectural, Buckminster Fuller, strain

INTRODUCTION

In 1998, The Henry Ford Museum initiated a program to conserve and reconstruct R. Buckminster Fuller's Dymaxion House for a publicly accessible exhibition that opened in October 2001. A multi-disciplinary team including engineers, metallurgists and corrosion scientists identified and characterized the various alloys and corrosion products, modeled structural loading, and restored the house. This paper discusses the treatment of the aluminum components of Dymaxion House by conservators and technicians at The Henry Ford.

After more than ten years of active exhibition, deformation of the roof and fatigue damage to the aluminum deck beams were discovered. The museum initiated an extensive program to reinforce the deck beams and mitigate further fatigue-crack growth. Dimensional monitoring of the roof began. An experimental structural strain measurement program and a fatigue analysis using finite element analysis techniques were conducted to estimate the life of the building deck beams (Deck 2012; Deck 2013).

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BACKGROUND

HISTORY

Buckminster Fuller believed that industrial processes applied to housing could benefit humanity. His design ethos, which developed over decades and employed minimal materials, was inspired by engineered tension structures like suspension bridges and airships. To make the Dymaxion House as lightweight as possible, he decided to use aluminum for structural components.

The house is a suspended cylinder with a domed roof enclosing a single volume, 11 meters in diameter and 6.7 meters high (Figure 1). A central steel tube mast supports a steel-rod ringed cage sheathed in unfinished aluminum. The trussed aluminum deck beams support plywood flooring (Figure 5).

At Beech Aircraft in Wichita, Kansas, Fuller built two prototypes of the Dymaxion House in 1945. Although the house garnered attention, Fuller believed he needed more time to perfect his design for mass production (Baldwin 1996). The project failed, but the parts were saved and were later erected on a concrete foundation, known as the Wichita House, which was lived in until the 1970s. In 1992, after more than twenty years of abandonment, the Wichita House was disassembled and shipped to The Henry Ford.

CONSERVATION/RESTORATION CHALLENGES

Since the Wichita House was made from 3600 pieces of the two prototypes and spare parts by its owner (William Graham), it is not a unified, completed work by Fuller; moreover, the pieces had been displaced several times. In 1998, the exhibit team decided to reconstruct it as a “model home,” just as it had been presented inside the aircraft factory in 1945.

The consulting engineer reviewed structural components and calculated load capabilities using a residential floor loading of 195 kg/m^2, and recommended an occupancy limit of no more than fifteen individuals at one time (Fitzpatrick, comm. 2001). His recommendation was based on finite element analysis using computer modelling that demonstrated susceptibility in the deck beams for over-loading and undue flexing that might lead

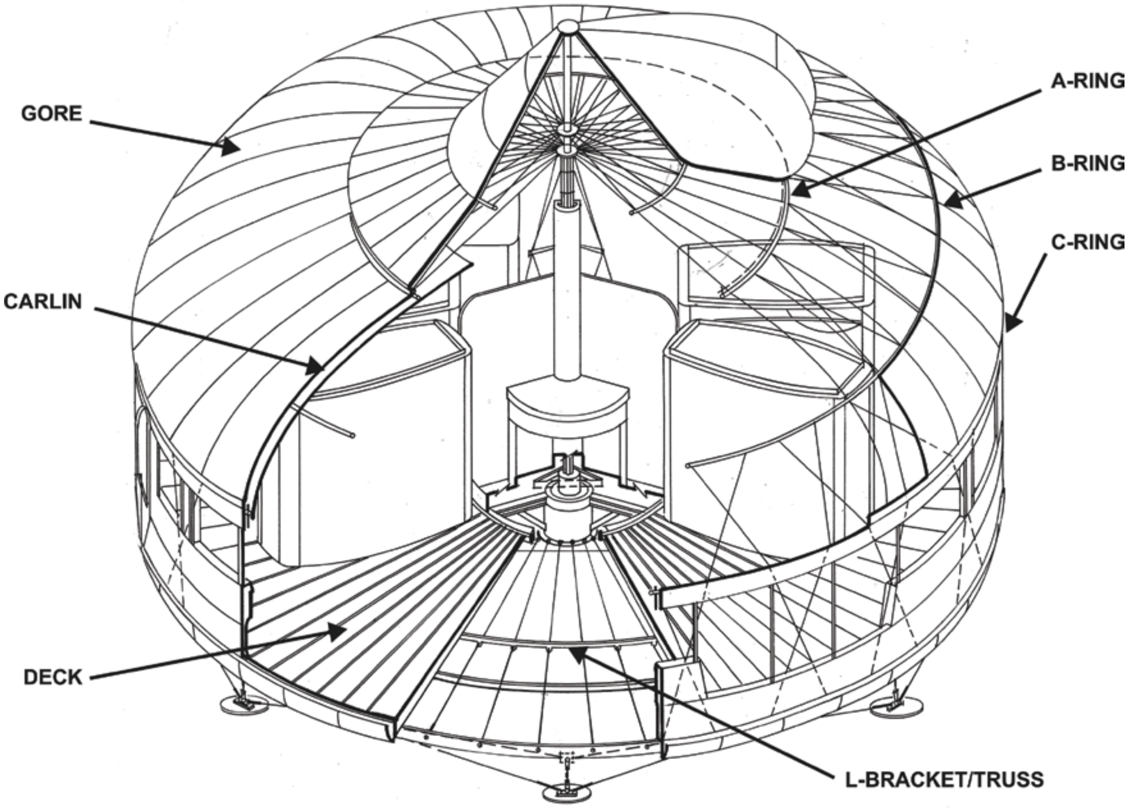

FIGURE 1. Dymaxion House cutaway axonometric showing structural features. From the collections of The Henry Ford.

to structural failure. To add stiffness, he designed a steel ring with I-beam extensions (dubbed the "Fitzpatrick bracket") to add extra support to the inner "Z" ring of the deck, near the central mast. After corrosion-susceptibility testing, the metallurgist strongly recommended heat-treating numerous house components, especially the deck beams, which was done at a facility that specialized in the heat treatment of large parts (Walker 2001). Some original parts could not be adequately reinforced for reuse and were instead newly manufactured. For example, one-third of the original deck beams were replaced after hairline cracks were found at the same location on many of them. Had this cracking been more thoroughly investigated at the time, fatigue problems that developed in the following ten years might have been anticipated.

MATERIALS ANALYSIS

The Dymaxion House prototypes utilized lightweight, non-architectural wrought aluminum-copper aircraft alloys—rolled sheets and extrusions. There were also aluminum castings, and die-stamped pieces. Some components that would have been entirely aluminum in final production, like the outer "Z" ring of the deck, were made up of aluminum and steel combinations for prototyping purposes. The four percent copper in the alloy provides increased strength but at the expense of corrosion resistance (Sicha 1984). On many pieces, the original manufacturer's roll code was still visible. The roof "carlins" (rain-gutter/supports) and many of the deck beams were Pureclad 24S-T equivalent to the modern alloy Alclad 2024-T3. Extruded forms of alloy 2024-T3 were used for the inner and outer deck rings. The outer skin and some of the deck beams were Reynolds R-301-T, equivalent to the modern Alclad 2014-T6 (Lyman 1948 and 1961).

Corrosion ranged from mild surface oxidation and surface pitting on rolled sheet to severe exfoliation corrosion on extruded elements (Figure 2). Regardless of the form of the corrosion, the predominant corrosion product was identified by X-ray diffraction analysis as bayerite (aluminum trihydroxide, $Al(OH)_3$) (Trentelman et al. 2002). Hydroxides are the typical corrosion products of aluminum upon exposure to water and air under ambient conditions (MacLeod 1983; Graedel 1989; Teed 1937; and Hunsicker 1984).

Components exposed to standing water over the years, such as deck beams near damaged windows, exhibited more corrosion than protected ones. Exfoliation corrosion was most severe on the extruded deck rings where they were in contact with steel plates, where they sat on the concrete block foundations, and where parts had been cut or drilled, exposing the transverse surfaces. Steel fasteners caused galvanic corrosion, further contributing to the loss of structural integrity. Similar levels of corrosion were observed on deck beams constructed of Alclad 2024-T3 and 2014-T6. As noted above, many parts were so damaged that they could not be used in the reconstruction.

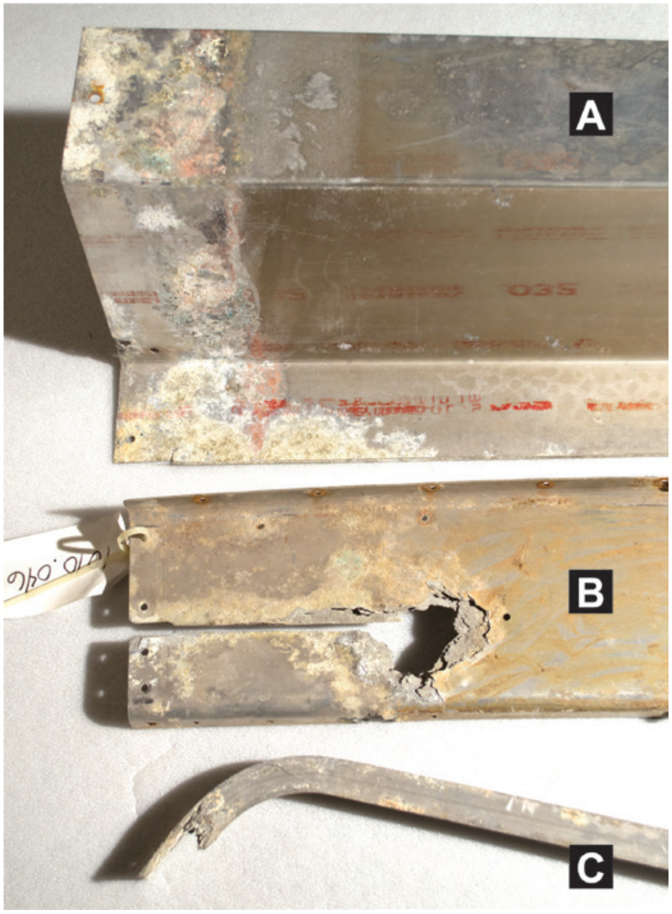

FIGURE 2. Types of corrosion found on the aluminum components. A) Surface oxidation on beam; B) galvanic corrosion from ferrous fasteners on windowsill; and C) severe exfoliation corrosion. From the collections of The Henry Ford.

TREATMENT

REMOVAL OF SURFACE SOILING AND COATINGS

After initial cleaning, non-original paint was removed using proprietary stripper Airstrip®. A layer of asbestos-laden bitumen on the interior of the walls and the roof was removed with mineral spirits using plastic scrapers and nylon 3M white Scotch-Brite™ pads.

CHEMICAL REMOVAL OF CORROSION PRODUCTS

Based on a consultant's recommendation, Cortec VCI-427, an inhibited sodium hydroxide gel was tested (Burleigh 1995). This technique was rejected, because it did not remove all the encrustations, was difficult to clear from crevices, and was difficult to control. Other proprietary alkaline and acidic removers also were tested, but none met the safety criteria, in part because of the large size of many components. In addition, these techniques were not pursued because they are effectively industrial processes.

Mechanical Removal of Corrosion Products

Abrasive Cleaning

Low pressure abrasive cleaning effectively removes porous oxide corrosion products from aluminum (Adams et al. 1991). For this project, 120 grit aluminum oxide at no greater than 172 kPa was most effective. Microscopic examination revealed that the corrosion products were removed with little disturbance to the underlying metal. However, the treated surface was matte gray, differing significantly from the original shiny finish. Abrasive cleaning could also over-heat while dwelling on severely corroded areas, which might change the metal's temper. As a result, it was used only for components with uniform surface corrosion and that would not be visible like the deck beams. It was during the abrasive cleaning that hair-line cracking was discovered at about the half-way point on many beams. All cracked beams were rejected and are retained in storage.

Surface Conditioning

Surface conditioning products tested on the aluminum include polymer pads, wheels, and discs, some with embedded abrasives like silicon carbide or aluminum oxide. Manufacturers 3M and Dynabrade assisted in testing a variety of such tools and products to determine the extent to which they might cause loss of original aluminum or introduce unacceptable stresses. Tensile stresses are a key factor in the formation of stress corrosion, which may lead to cracking and structural failure (Godard et al. 1967; Binger et al. 1984). Proto Manufacturing Ltd. (www.protoxrd.com) used X-ray diffraction to measure changes in the aluminum lattice and to determine the amount of residual stress introduced to the surface. Some products introduced either tensile or compressive stress depending on the amount of pressure or the duration of application. Careful training for the project technicians ensued.

Surface corrosion products were precisely removed using 2.5-cm-diameter bristle discs. Large grit sizes (50 and 80), although effective, caused scratches and were used only on non-visible parts. For smaller parts requiring a shiny finish and for those with minimal damage, flexible shaft tools and wand tools with 120 grit and finer radial jeweler's bristle discs worked well. For treating large areas, 3M Scotch-Brite™ non-woven nylon pads were used on 20-cm-diameter buffing tools with a mineral spirits lubricant. Graduating from coarse to finer pads, this removed the surface corrosion products as well as any abrasion introduced by the other techniques.

Finishing

Hail dents were retained as important evidence of the house's history, and the exterior was restored to the level of shine seen in archival photographs. Three grades of Rolite® aircraft polishes applied with 20-cm rotary cotton pads of varying coarseness imparted a shiny but oily finish (Figure 3).

CORROSION PROTECTION

Incralac® adhered well to toothed particle-blasted parts and was used to coat the deck beams. On highly polished surfaces, it adhered poorly and had a "plastic" appearance. Cellulose nitrate lacquers, which are relatively stable indoors and good barriers to atmospheric pollutants, were successfully applied on the shiny exterior panels (Reedy et al. 1999). A base coat of Agateen® #2 was followed by two more spray-applied coats of Agateen® 8 A (an acrylic/polyester/nitrocellulose resin mixture). Meticulous solvent

FIGURE 3. Polishing a large roof gore with aircraft polishes on cotton buffing pads. From the collections of The Henry Ford.

FIGURE 4. The conserved and restored Dymaxion House in Henry Ford Museum. From the collections of The Henry Ford.

wiping was particularly critical in preparation for the coating application to ensure good adhesion. New replacement parts were not coated unless they were part of a single visual field, such as the roof panels called "gores" (Figure 4), all of which were lacquered. Renaissance® brand microcrystalline wax was applied as renewable protection for wear surfaces, such as door frames and windowsills.

ASSEMBLY

New aluminum rivets were used as in the original construction where practical. Stainless steel nuts, bolts, and turnbuckles were used for structural connections that required greater load capacity. Barely noticeable synthetic polymer Delrin® washers were used to separate aluminum from steel nuts or bolts. Many components required riveted sheet-metal patches to reinforce corroded-away areas. Eight of the 46 triangular roof "gores" were newly laser-cut, and the original ones were patched at lower extremities to replace lost metal. Thirty-one of 96 deck beams were newly fabricated in 2001.

EXHIBITION AND USAGE

Approximately fifty percent of the over 600,000 visitors to the Henry Ford Museum each year pass through the Dymaxion House. After more than ten years in exhibition service, the building showed clear evidence of movement in the wooden floor segments. Buckling of the exterior aluminum walls also implied a possible shifting of the roof and its support rings (Figure 1). Further examination of the structure uncovered cracks in many of the aluminum deck beams.

PRESERVATION PLAN

A plan to ensure the long-term structural integrity of the Dymaxion House was established to:

- measure and monitor dimensional changes in the building,
- modify the structure to mitigate further crack initiation or growth,
- monitor the structure to detect future cracks,
- measure the strain in the deck beams under live load and estimate the time to the initiation of future cracks.

Roof Shape and Dimensional Changes

A circular laser level was used to establish a horizontal plane against which to measure the height position of the A-ring and C-ring. The measurements showed that the C-ring was fairly flat but tipped approximately 12 mm down towards Bedroom 1. This position will be used as a baseline for subsequent measurement to determine if there is any continuing change in the roof position.

Deck Beam Cracks

Floor Design

The 96 radial beams supporting the floor deck of the Dymaxion House (Figure 1) are made of 0.81-mm-thick 2024 and 2014 aluminum sheet formed into a U-shape. They are supported at inner and outer ends and have a cable truss with a central king-post loading an L-bracket underneath (Figure 5).

FIGURE 5. Deck beams and L-bracket with king-post and cable truss. The steel "Fitzpatrick bracket" (designed by structural engineer T. Fitzpatrick) supports the inner "Z" ring. From the collections of The Henry Ford.

Root Cause of Cracking

The deck beam cracks were found to originate at the point of contact and localized loading of the supporting L-bracket with the deck beams. As originally designed, the L-bracket featured a relatively sharp external corner that created a concentrated load on the deck beam (Figure 6).

The cyclic loading of the aluminum beams by the repeated live load from about 300,000 house visitors per year led to the fatigue failures of the aluminum beams at the point of concentrated load. Fatigue is permanent structural damage that occurs when a structure is subjected to cyclic stresses that have maximum values less than the static yield strength of the material. Original deck beams from the Wichita House that had not been used in the restoration and had only experienced residential loading were subsequently examined. They also exhibited fatigue cracks that initiated at the L-bracket contact site, indicating that the structural issue existed in the original design of the building.

Treatment and Remedial Actions

All 96 beams were examined and the ends of each crack were drilled and polished to blunt the cracks and slow future crack growth (Figure 7).

The sharp corner of the L-bracket was given a radius to reduce the localized loading and the attendant stress concentration on the deck beam. U-shaped deck beam reinforcement channels were fabricated from 1.52 mm thick 2024 aluminum and bonded (using 3M Automix® 8115 panel adhesive) and riveted around the building deck beams at the point of L-bracket loading (Figure 8). These reinforcements further reduced the concentrated loads and strengthened the deck beams in their most highly stressed areas.

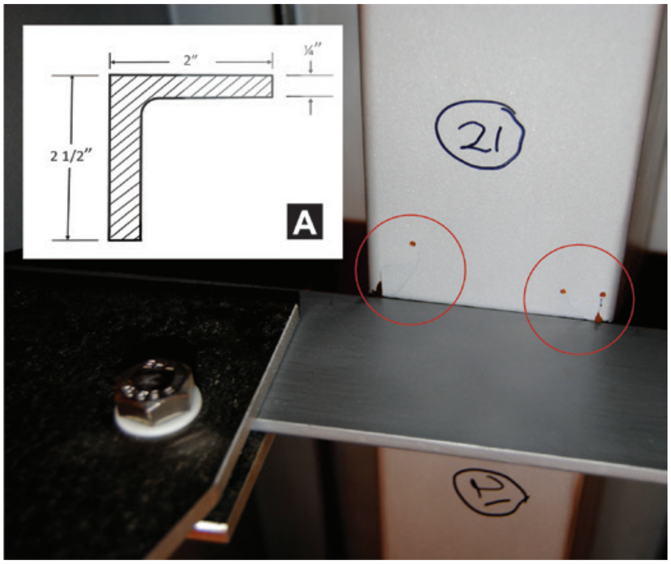

FIGURE 6. Fatigue damage at point of load concentration, indicated by red circles; red dots indicate ends of cracks to be drilled to ease stress, and (A) detail of L-bracket. From the collections of The Henry Ford.

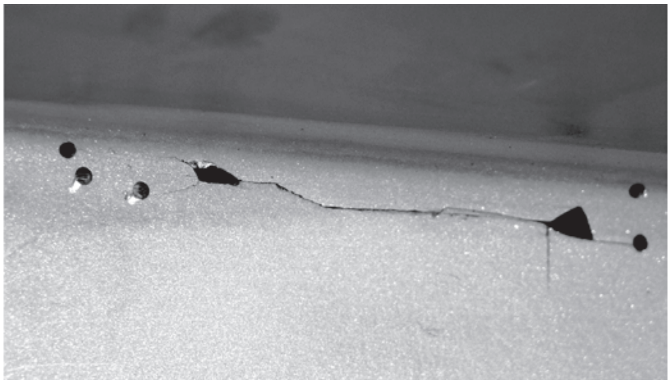

FIGURE 7. Ends of fatigue cracks drilled to inhibit further propagation. From the collections of The Henry Ford.

FIGURE 8. Reinforcement saddles bonded and riveted to the deck beam. From the collections of The Henry Ford.

Instrumentation

The level of strain in the beams while under occupancy loads was measured to predict their expected fatigue life. Two types of strain gages were installed on beams in Bedroom 1, Bedroom 2, and the Kitchen, arranged as seen in Figure 9.

Residual stress strain gage rosettes (Micro-Measurements EA-13-125RE-120/SE) were installed on the beams. With the building unoccupied, a hole was carefully drilled into the center of each rosette according to ASTM Standard E837-08 (Figure 9) (Vishay 2014; ASTM 2013). The strain measured indicated the level of strain in the deck beam without anyone in the building. The measured values serve as the baseline strain value for fatigue life calculations. Four linear strain gages were also installed on each beam. These gages measured the strain in the beam under live occupancy loads and provide the data for the fatigue life estimation. Crack detection and propagation gages were also installed on selected cracks. A routine inspection program was instituted to regularly check the detection gage for signs of crack growth.

Experimental Results

The experimental results presented here were taken from Bedroom 1 (deck beam #20). They are representative of all the data taken and resulted in the shortest estimated time to the initiation of future cracks. The measured strains of the residual stress strain gages were used in the fatigue analysis. Linear strain gage measurements taken over a four-day test period from strain gage 3 (Figure 9) are shown in Figure 10. The fatigue life estimates are based on these data.

Fatigue Data Analysis and Life Projection

The mechanisms and prediction of fatigue failures were not well understood at the time the Dymaxion House was designed. The structural fatigue analyses used here are empirical methods based on subsequent years of testing and numerical data analysis. The material data including strengths, moduli, and fatigue data for 2024-T3 aluminum were taken from U.S. Department of Defense MIL-HDBK-5 J (U.S. Dept. of Defense 2003).

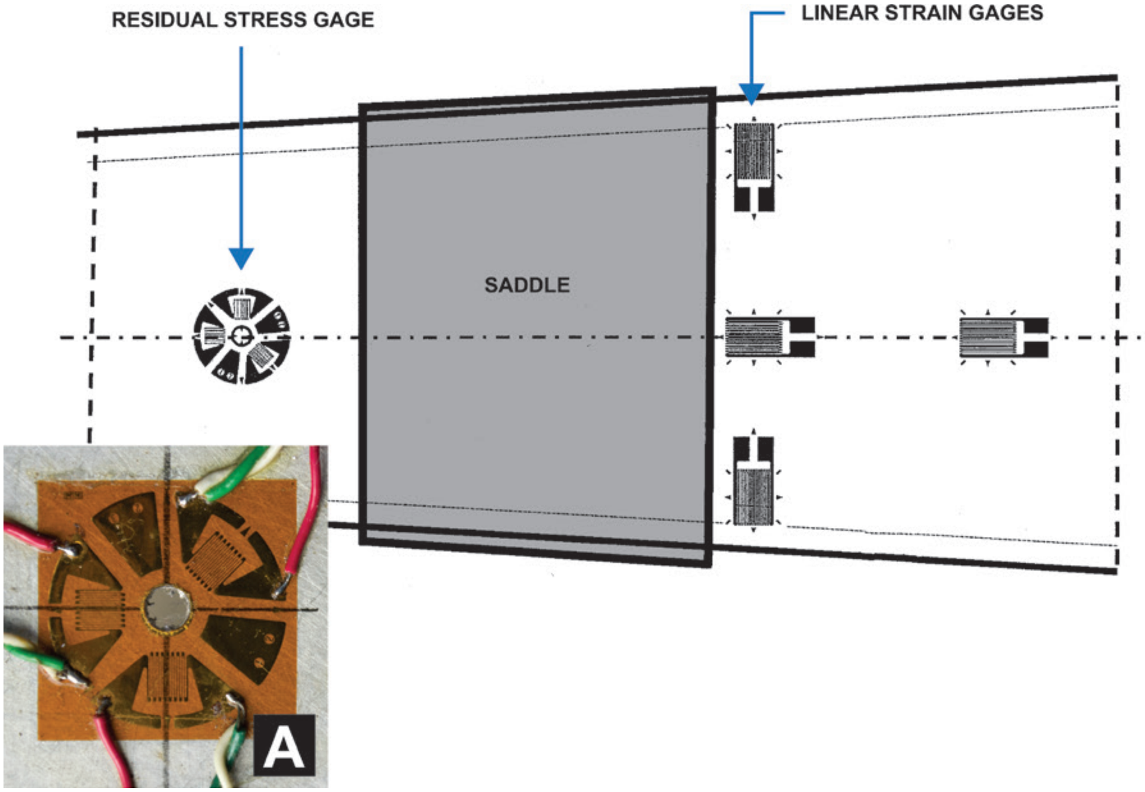

FIGURE 9. Drawing of strain gage placement on the underside of a deck beam and (A) a strain gage rosette with a hole drilled at the center. From the collections of The Henry Ford.

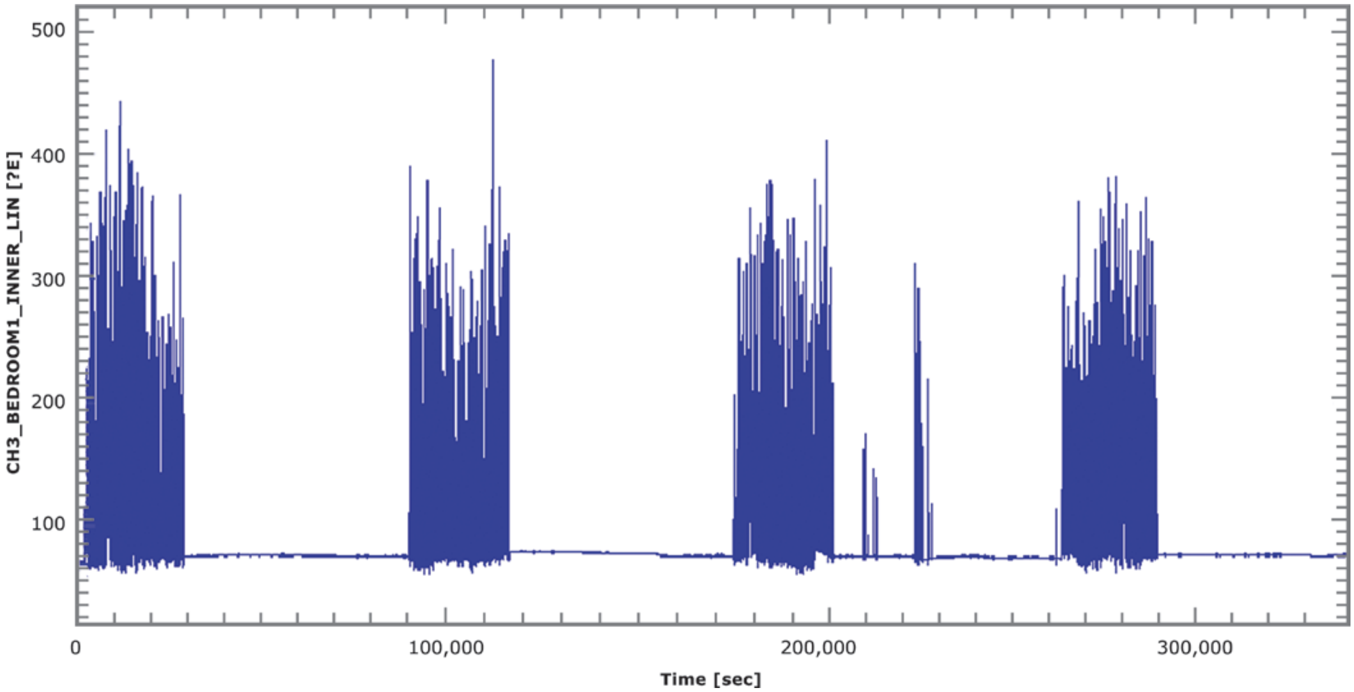

FIGURE 10. Strain measurements over a four-day period. The ordinate of the plot is the measured strain in micro-strain. From the collections of The Henry Ford.

The fatigue data are expressed as S/N curves showing the magnitude of a cyclic stress (S) plotted against the logarithmic scale of cycles to failure (N). The fatigue analysis is used to estimate the time to the initiation of future cracks and consists of the following sequential steps.

- The time history of the strain in select deck beams was measured with linear strain gages (Figure 10).
- A rainflow cycle counting analysis is conducted to establish how many times a strain cycle of a selected level occurred during the test. Rainflow counting is a method of simplifying a complex strain history into a series of strain reversals from which fatigue damage can be calculated (ASTM 2013 and US Dept. of Defense 2003).
- A proprietary Ford Motor Company fatigue life analysis program, "FLAP", the Fatigue Life Analysis Program, uses each strain reversal cycle and calculates the amount of damage done to the beam based on the material S/N curve. This is the fraction of the total maximum theoretical life of the material that the actual strain cycle range used up.
- Following Miner's Rule, the total fatigue damage is the sum of the damage increment done by each strain reversal cycle (Wood et al. 2014). Total fatigue life is the inverse of total damage (Kondo 2003).

Fatigue Analysis Conclusion

The fatigue analysis described above was conducted for all the strain data collected, and the results for each location are shown in Figure 11. The shortest time to the initiation of continued crack growth was estimated to be 144 years and located in Bedroom 1 and in the Kitchen.

CONCLUSIONS

The challenge of the Dymaxion House project was to conserve and reassemble a collection of over 3,600 parts into a structure that would be visually correct and safely support museum visitors. Treatments were determined based on the alloy, fabrication method, type of finish, installation method, deterioration mechanisms, and condition. Structural stability was paramount, but aesthetic expectations were also a high priority. The restoration protocol included re-fabrication and patching of some parts that were too badly deteriorated to repair.

Fatigue cracks occurred in the deck beams of the house because of concentrated support loads. Remedial actions were taken, and, based on measured operation strains and analyses, further crack growth is not expected for at least 144 years.

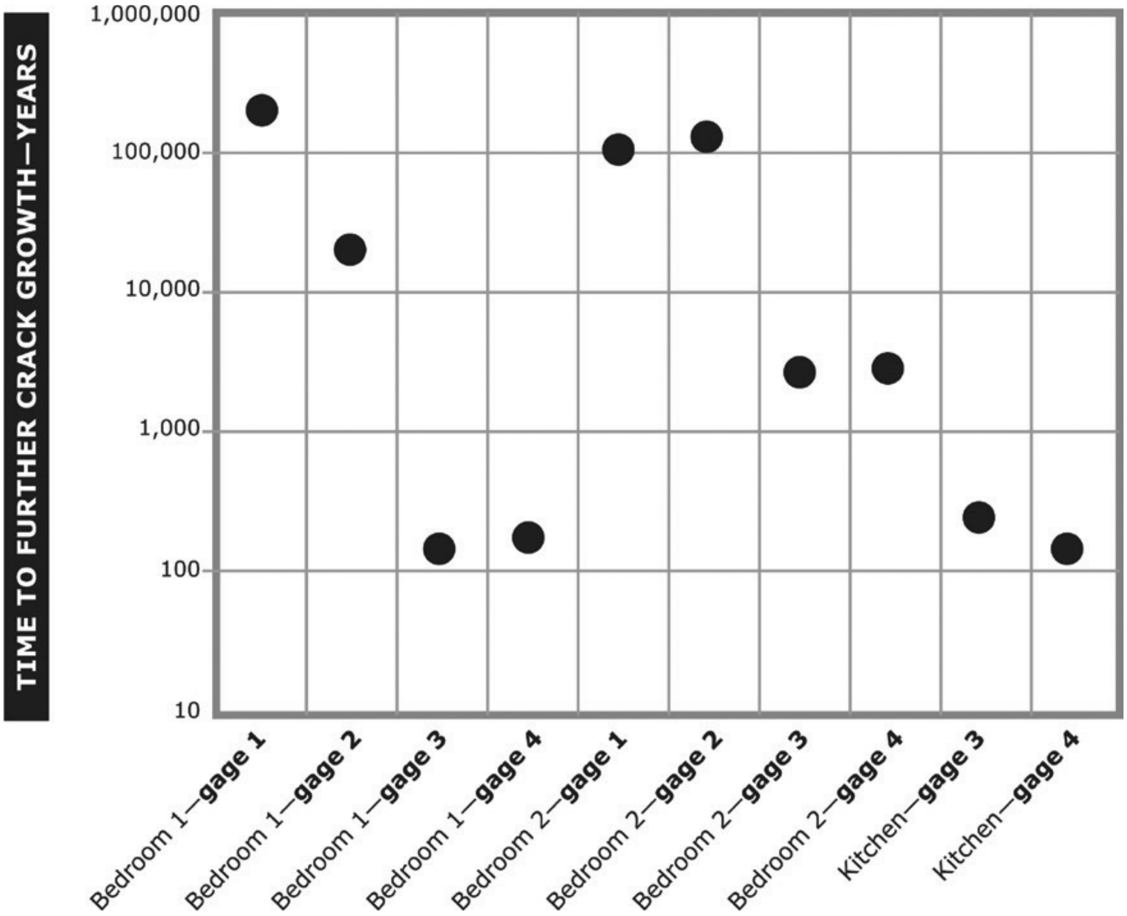

FIGURE 11. Deck beam fatigue life for each location. From the collections of The Henry Ford.

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This paper is dedicated to Richard Jeryan (1945–2015).

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Restoration of the Aluminum Night Doors and Windows at the Robert F. Kennedy Department of Justice Building in Washington, DC

Justine P. Bello, Joseph Sembrat, and Mark Rabinowitz*

ABSTRACT. The Robert F. Kennedy Department of Justice building in Washington, DC, was completed in 1935 to a design by the Philadelphia architecture firm of Zantzinger, Borie & Medary. That office collaborated closely with sculptor C. Paul Jennewein in the overall decorative scheme for the over ninety thousand square meter Art Deco office building. The building hailed a modern aesthetic with its use of aluminum in large quantities for both decorative and functional purposes. To that end, aluminum is found in a variety of forms including cast sculptures and grilles, aluminum leaf on a barrel vault, nearly 2000 window frames, and most notably, monumental decorative night doors.

Conservation Solutions, Inc. (CSI), treated five sets of night doors in 2007, and in 2014 the firm was under contract to survey and develop treatment recommendations for the restoration of the building's windows and remaining doors. This paper provides a summary of the historic research and treatment work that went into conserving the doors, which also informs recommendations for the remaining aluminum elements. It focuses on the study, testing, and treatments used to restore the doors to their original appearance, including reinstating an original paint scheme that provides improved corrosion resistance. The work balanced the preservation of the doors as decorative objects and functional elements. The challenges of navigating a complex array of logistics ranging from security concerns, complex rigging issues, and the practical issues of maintaining consistency on multiple sets of doors of large size is also discussed. A review of the doors' state seven years after treatment is provided for comparative purposes. Proposed assessment of the aluminum windows is also described, and the potential applicability of treatments used on the doors to problems on the windows is discussed.

Keywords: aluminum, Department of Justice, night doors, conservation, art deco, architecture

INTRODUCTION

The Robert F. Kennedy Department of Justice (DOJ) Building in Washington, DC, located at 950 Pennsylvania Avenue, NW, was designed by the Philadelphia architectural firm Zantzinger Borie & Medary. Construction of the building occurred between 1931 and 1935 and was carried out by the Philadelphia general construction firm George A. Fuller Company.

The seven-story Beaux Arts building has steel-frame construction, is clad in Indiana and Alabama limestone, and has a red pan-tile roof. The building contains 634,000 net square feet of office space on an 8.9-acre site. It is situated between Constitution Avenue, Pennsylvania Avenue, and 9th and 10th Streets. The site had originally been designated in the 1902 McMillan plan for municipal buildings that were never built, replacing marginal commercial enterprises relegated there on account of the area's tendency

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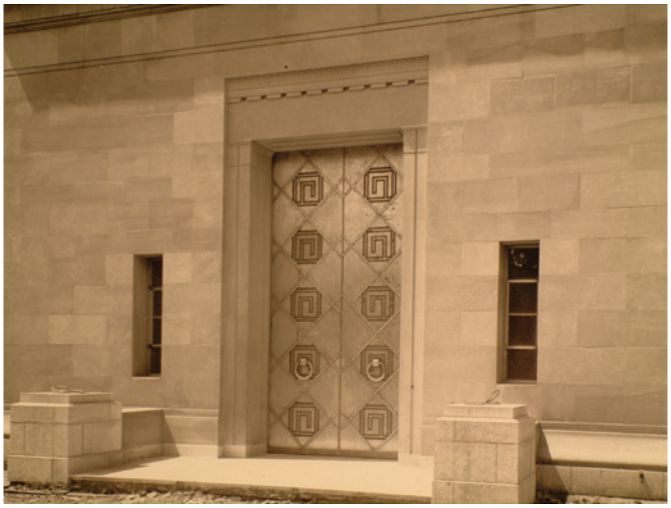

FIGURE 1. One of two sets of smaller night doors with diaper pattern on Pennsylvania Avenue around the time of the building's completion, circa 1935.

to flood. The stand-alone structure is one of a contiguous collection of nine federal buildings bounded by Pennsylvania and Constitution Avenues. Known collectively as the "Federal Triangle," these buildings were designed as an ensemble but by different architectural firms in the period from 1927 to 1938. They include the Internal Revenue Service, National Archives, Federal Trade Commission, and Department of Commerce.

Today, the building continues in its originally intended use. It initially housed the Federal Bureau of Investigation, which is under the DOJ but was moved to a separate building in 1976. The DOJ is listed on the National Register as a contributing building to the Pennsylvania Avenue Historic District. (Geier Brown Renfrow Architects, 1988: 45) (Figure 1).

THE BUILDING'S DESIGN

The DOJ is anomalous among the Federal Triangle buildings for several reasons, most of which relate to its design and elaborate interior artistic program. The building's use of aluminum in its architectural and decorative program is exceptional. The five sets of night doors, numerous interior doors, nearly 2,000 casement windows, all 10,696 light fixtures, as well as two interior sculptures in the grand hall and a fountain in the central court, were fabricated from aluminum. Other interior aluminum embellishments include grilles, railings, balustrades, and applied aluminum paint and leaf (e.g., on a barrel vault) (Figure 2).

In addition to its use of aluminum, the DOJ departs from other Federal Triangle buildings in the distinctive Art Deco style of its elaborately decorated interiors. In 1928, Milton Bermett Medary (b. 1874) was appointed architect of the building, but upon his death in 1929, his partner Clarence Clark Zantzinger (b. 1872) completely redesigned the DOJ. Their firm was not known for its work in the Art Deco style or for work on large government buildings. In fact, their practice was focused mainly on residential, ecclesiastical, and educational buildings in the Gothic Revival style.

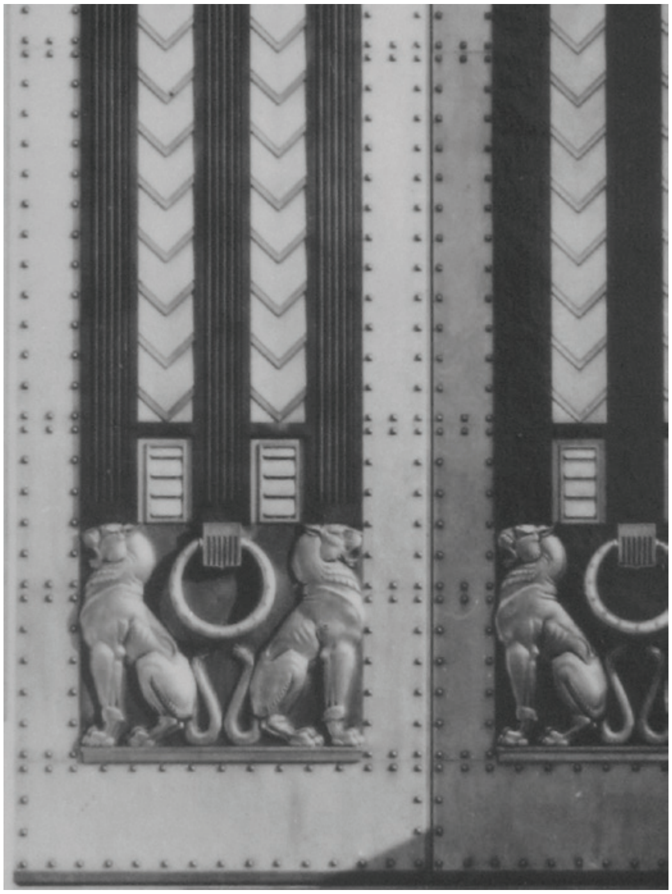

FIGURE 2. Detail of one of the larger sets of doors with heraldic lion pattern, circa 1935.

Zantzinger was aided by a large cast of artists in the creation of the elaborate interiors. John Joseph Early of Washington, DC, was responsible for the polychrome concrete mosaics; Carl Paul Jennewein designed the sculptural program; Gustav Ketterer of Philadelphia designed the interior decorative painting schemes (Geier Brown Renfrow Architects, 1988: 34–37).

None of these men had a wealth of experience with aluminum as a medium. In fact, historic records indicate that the use of aluminum for several elements was not approved until well after construction had begun. The monopoly given to the material was later attributed to Andrew W. Mellon, who as the

Secretary of the Treasury from 1921–1934 had been the driving force behind the creation of the Federal Triangle. He appointed all members of the Board of Architectural Consultants, which consisted of the architects responsible for the designs of the various buildings, and presided over their work. The following quotation from the Historic Structures Report (HSR) for the DOJ indicates one facet of the breadth of Mellon's influence on the design of the building:

> The decision to make almost exclusive use of aluminum brought considerable controversy to the Office of the Supervising Architect. Competing industries argued that the choice of aluminum stretched the project costs by $100,000 for the windows alone. The architects, however, argued persuasively for their choice, claiming that "in the long run there is a real economy to the Government in maintenance, and secondly that we greatly prefer the color of the aluminum." In a 1978 interview, Jennewein offered an unusual and unsubstantiated explanation of the choice of metal, claiming it was tied to the Secretary of the Treasury's familial ownership of the Aluminum Company of America (ALCOA): "Mellon! Mellon had the aluminum industry, and he gave the architects an order that not one bit of bronze would be used on the Department of Justice . . . Mellon gave the order . . . everything had to be aluminum." (Geier Brown Renfrow Architects, 1988:29).

ALUMINUM'S USE IN AMERICAN ARCHITECTURE

Despite its association with the white metals of the Art Deco period, aluminum had already seen a large amount of use in American buildings by the 1920s. It was famously first used architecturally to cap the Washington Monument in Washington, DC, in 1884. A method for producing aluminum in large quantities for industrial use was discovered in 1886. From this date, production and use in buildings proceeded rapidly. Some notable uses that preceded the DOJ building were in the Monadnock building in Chicago (1893), the Gothic spire of the Smithfield Street Congregational Church in Pittsburgh (1926), and the Empire State Building (1931) (Gayle and Waite, 1992).

CONSERVATION OF THE NIGHT DOORS

In 2007, CSI was awarded the contract to conserve the five sets of monumental aluminum night doors at the DOJ. The challenges of this assignment were two-fold: the implementation of the treatment itself and the logistical issues associated with the work, with the latter being perhaps the greater of the two. In the planning stages of the project, it was determined that it would not be feasible to treat the doors on site. This was confirmed during our in-situ assessment of the doors at the kick-off of the treatment phase (Figure 3). The treatment requirements were too great to effectively perform the work on site, particularly in a way that could still allow the doors to fulfill their function from a security perspective. Therefore, it was concluded that the doors should be removed to an off-site location for conservation.

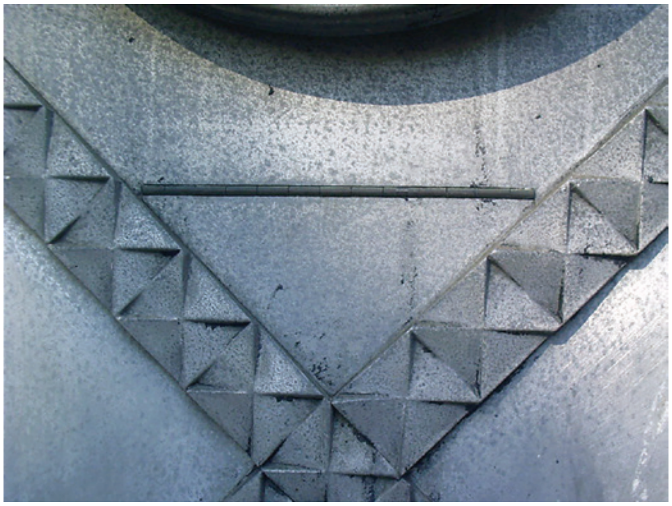

FIGURE 3. Detail of typical surface corrosion and soiling on the door surface, 2007.

Planning for the removal of the doors was complicated and challenging. The smaller two sets of doors are each 6.1 meters tall, and the three larger sets are 7.2 meters tall. The doors were expertly crafted with limited access to hinge pins and no obvious evidence of how they might have been installed originally. A transom over each entrance and a glass vestibule a few feet behind meant that the doors would have to be tilted back to clear them for removal. These factors, coupled with limited understanding of the doors' construction or knowledge of their weight, made for a great sense of uncertainty in planning a means for their removal.

Armatures inside the doors proved to be inconsistent with the archived architect's drawings (Zantzinger, Borie, and Medary, 1932) and were not fully understood by the conservation team until the doors were removed and partially disassembled. Through several careful probes, however, it became clear that an external jig could be fastened directly to the door's internal accordion-style armature through holes for fasteners, which had formed a decorative pattern on the back of the door. A complex jig was custom-fabricated that could hold the door as its hinge pins were cut and allow the ensemble to be tilted backwards enough to clear the masonry surround without hitting the glass vestibule. After the first test removal proved successful, the jig was used to remove and later reinstall all ten door leaves from the building with additional assistance from an all-terrain forklift. Once removed, the doors were shipped to an off-site facility for treatment (Figure 4).

At the facility, the back panel was fully removed from one door. Investigation revealed that the interior structure of the door was a corrugated sheet of aluminum coated with an unidentified corrosion inhibiting primer (Figure 5). Both the bent aluminum sheets and primer were found to be in stable condition, and remaining doors were treated without extensive disassembly.

FIGURE 4. The complicated removal of the Northeast set of Pennsylvania Avenue doors using a long-reach forklift and custom jig.

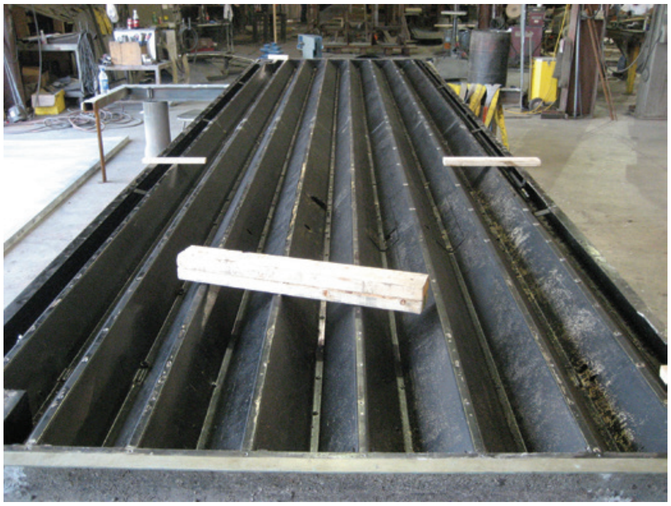

FIGURE 5. Overview of the accordion-style aluminum framework inside the door. The black coating is believed to be an original corrosion inhibitor but was not identified.

Each was determined to be structurally sound without any evidence of wracking or warping.

The accordion framework of the door is an interesting and innovative design. The original construction plans for the door show a more traditional internal armature consisting of heavy steel cross-bracing (Zantzinger, Borie, and Medary, 1932); the accordion webbing, as was actually fabricated, is a much more elegant and efficient solution. It is a lightweight alternative that naturally resists warping, wracking, and bending, much like aluminum honeycomb panels routinely used for a variety of structural purposes in the construction industry and elsewhere today. This fabrication detail, although hidden from view, is another important example of progressive use of aluminum at this site.

At the workshop, the treatment proceeded in keeping with the observations recorded during the original assessment. The budget for this project did not allow for extensive analysis of the aluminum alloy, corrosion products, or salts; however, efforts were made to characterize the materials to the greatest extent possible where needed to inform the treatment.

Anecdotal evidence suggested that the doors were fabricated from Alclad (2024-T3), an aluminum-copper-magnesium alloy introduced by Alcoa in 1931 consisting of an aluminum alloy sheet clad in pure aluminum or a different alloy to afford corrosion resistance (Alcoa Mill Products, Inc.). It generally replaced Duralumin (2017-T4) and has since been extensively used in aerospace applications. Since the date of this product's introduction coincides closely with the construction of the DOJ building, it is reasonable to believe that this new and promising alloy would have used for a major design element in the building.

One of the primary aims of the treatment was to reduce corrosion that had become pervasive across all exterior surfaces. The worst areas of corrosion, typically on the lower quarter of the door, had likely been engendered by soluble salts from sidewalk de-icing products. Prior to large-scale treatment, the efficacy of several proprietary wash solutions and water jetting techniques was tested to determine the most effective means for extracting soluble salts on the aluminum and the most desirable level of corrosion removal from the pitted surfaces. Spot tests using Hach titrator strips for chlorides on both wet door surfaces and effluent confirmed that water jetting at approximately 3000–3500 psi using heated water (82° C) was effective at reducing soluble salts to an acceptable level (below <25 ppm).

Solubility testing revealed the remnants of a failed lacquer coating on the doors, which were removed along with any other remnant paint and graffiti using a methylene chloride gel stripper (pH 10–10.5). The stripper was applied in a layer thick enough that it would not readily dry. It was allowed to dwell for at least 30 minutes and then agitated with a nylon bristle brush to break up the coating. The solubilized coating was then washed from the surface with the heated water jetting.

Then the entire exterior surface was treated with Sea-2-Sky SPC 502 Gel, a metal brightener based on phosphoric acid, which is designed to remove metal oxides along with oil residues and any weakly-adhered coating remnants; it is frequently used on aircraft components and recommended for use on a variety of metals, including iron and stainless steel. The highly acidic gel has a pH of 0.5 and works quickly in ambient temperatures between 10 and 26° C. To brighten the metal evenly, it was applied to the surface using an airless sprayer, covered with painter's plastic, allowed to dwell for 30 minutes, and flushed from the surface using the water jetting technique (Figure 6). On aluminum, the cleaner acts as a metal "brightener" by effectively removing dull, medium gray aluminum oxides and revealing a lighter and more luminous aluminum surface (Figure 7).

Finally, Cortec VpCI®-415, a cleaner/degreaser (pH 8.0–8.7), was applied in a 5% solution using a garden sprayer to help neutralize the surface and deposit additional vapor phase corrosion inhibitors (VpCI) on the metal. The degreaser was allowed to dwell for 10 minutes and again rinsed using the hot pressurized water. The pH of the effluent water was monitored with test strips to ensure that the acidic cleaner had been effectively neutralized by the alkaline degreaser.

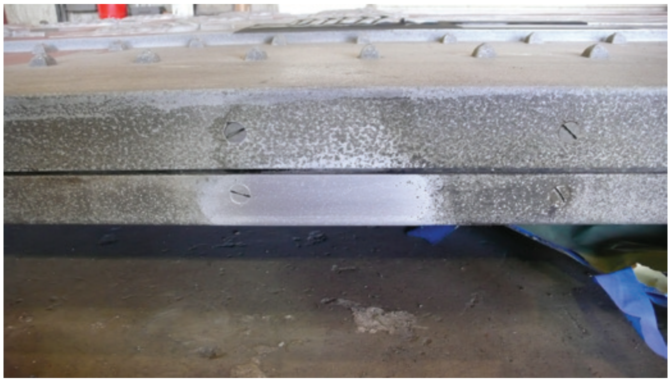

FIGURE 6. Detail cleaning test demonstrating the efficacy of the metal brightener gel, Sea-2-Sky SPC 501 gel.

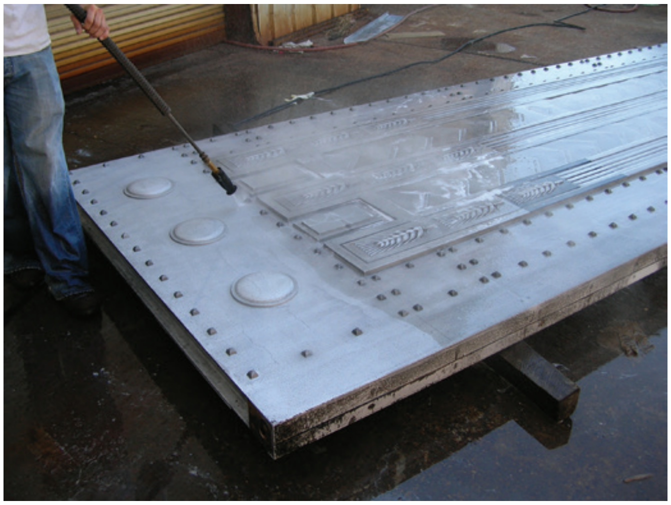

FIGURE 7. The gel cleaner is removed from the surface with heated, pressurized water.

During and after each cycle of rinsing, care was taken to prevent water from pooling on the doors, which were horizontal during treatment; after which they were dried with filtered compressed air. The result was surfaces visibly free of active, aggressive corrosion and substantially brightened, improving legibility of the sculptural elements of the doors and clarifying the artist's original intent.

The conservators were careful to avoid over-cleaning the metal. By controlling the method of application, dwell time, and premature drying of chemicals on the surface, consistent cleaning results were achieved overall. Chemical cleaning methods had been favored over mechanical methods, such as micro-abrasion, which may be more difficult to control. Using micro-abrasion, it is much easier for an operator to accidentally over-clean and more challenging to achieve the same level of cleaning overall.

Although no significant structural repairs were necessary, a variety of mechanical repairs were performed to stabilize and improve the appearance of the aluminum skin. Surfaces that had become deformed from impact were hammered to match original profiles where feasible. Most corrosion-related holes were filled with an aluminum-bulked epoxy. Dutchman repairs were fabricated and TIG welded to replace areas of severely compromised aluminum. Thick accumulations of loose corrosion found in the channels on the top and underside of the doors were first removed mechanically using a variety of hand tools and nylon abrasive pads; once the bulk corrosion had been removed, these surfaces were subjected to the same cleaning techniques as on the panels. On the front of each door, areas of severe pitting and deep scratching were buffed out using Scotch-Brite abrasive pads to produce a directional finish that matched the original. On the back, a unidirectional finish was re-created using the abrasive pads along the entire length of the door. Care was taken to maintain a consistent patina layer. Areas that were abraded from contact with stonework were lightly sanded to restore surface consistency. Sanding was kept to a minimum to avoid removing historic material.

Several kick plates were completely lost or had become so badly deteriorated that replacements were required. A sample of one of the surviving pieces was sent to an independent testing lab for alloy identification; the assay confirmed that the pieces were fabricated from nickel silver, a copper-nickel alloy that was also popular in this time period (on average, nickel silver typically contained 75% copper, 20% nickel, and 5% zinc). New plates were recreated "in-kind" to match the originals. These were attached using an industrial-strength double-sided 3-M tape, a polyester film coated with a flexible acrylic adhesive widely used in the assembly of high-performance electronics that provided adhesion and galvanic isolation between the two metals. Other repairs included rehabilitation of the hinges, drop bars, locks, and stops to restore secure operations to each of the doors.

One of the final, and most visible, aspects of the restoration was the reinstatement of a decorative paint scheme. Historic

FIGURE 8. The doors were carefully masked to facilitate painting with an airless sprayer.

photos illustrated that each of the doors had been enhanced by selectively painting some of the background, recessed areas in black while the bas-relief foreground remained bright and uncoated. This contrast between dark and light was stark and compelling in these early photographs; the client therefore requested that the paint scheme be recreated. At the same time, all parties recognized the need to provide a durable, protective clear coating on all exposed surfaces as well. It was understood that implementing the paint scheme was going to be extremely detailed, time-consuming work; for this reason, the client requested that a coating system be used that would allow the clear lacquer coating to be stripped or touched up without disturbing the black paint underneath (Figure 8).

A paint and lacquer system that met these parameters in laboratory trials was ultimately identified in collaboration with G. J. Nikolas, a coatings manufacturer, to meet the parameters specified by the client. As indicated by the Historic Structure Report and a small sample found in a crevice on one of the Pennsylvania Avenue doors, the original paint was high gloss and "rubberoid" in appearance (Geier Brown Renfrow Architects, 1988: 179). The paint identified to meet these performance and visual characteristics was a two-part catalyzed epoxy coating, GJ Nikolas 070314-C4. Testing found that the lacquer coating could be successfully removed using acetone without disrupting the paint finish underneath. To ensure compatibility, both components were ultimately sourced from this single manufacturer.

The application of both paint and clear coat was an exacting process. The doors were carefully masked with painter's tape and plastic to outline the limits of the decorative scheme. The paint was applied with an airless sprayer; small interstices were inpainted by hand with an artist's brush. The clear coating was GJ Nikolas OD Lacquer 12164 RFU, a solvent-borne, modified acrylic outdoor-grade lacquer with added corrosion inhibitors. The lacquer was applied in successive coats with an airless sprayer until the manufacturer's recommended wet and dry coating thicknesses were achieved. A matting agent was introduced to the topcoat to reduce gloss (Figure 9).

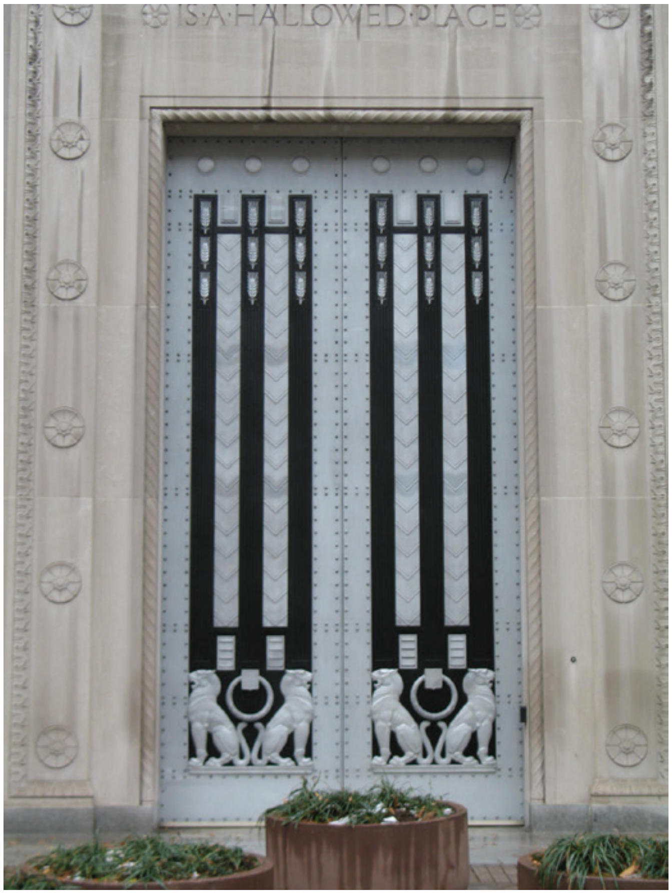

FIGURE 9. Constitution Ave doors, after treatment circa 2008.

CONDITION IN 2014

Seven years after treatment of the five sets of doors, CSI was again engaged in work on the DOJ building, this time to assess and quantify treatment for the remaining doors and approximately 2000 aluminum windows. To facilitate the characterization of the aluminum conditions of the remaining untreated doors and windows, CSI developed a schematic glossary to be used to rapidly identify those conditions requiring treatment. The intent was to define the types of conditions that will require repair in a clear, unambiguous way that could be easily understood and consistently applied by multiple surveyors. This approach was driven by a variety of factors including a tight time frame, budget, and the need to find a methodology that was manageable and reproducible for the survey of thousands of windows. The full window and door survey was expected to begin in early 2014.

The return visit provided an opportunity to review the previous treatments of the night doors. In general, all cleaned surfaces, repairs, and finishes were continuing to perform as intended. No mechanical failures of the door hardware were found, and all decorative finishes remained intact with one exception: on the set of doors that face Constitution Avenue the lacquer was flaking and showing signs of failure. The black epoxy paint remained substantially intact, and it appeared that locally removing and replacing the lacquer might be feasible without re-doing the in-painting (Figure 10).

FIGURE 10. Detail of premature coating failure, likely exacerbated by UV and salt exposure, 2014.

Two conditions may be contributing to the failure of the lacquer on the Constitution Avenue doors. This is the only entrance that faces south, which makes the doors subject to more aggressive UV exposure and thermal cycling than the other doors. As the primary visitor's entrance to the building, this entrance is the most heavily trafficked and the doors most routinely used. Furthermore, the entrance is kept open during winter months concurrent with the extensive use of sodium chloride-based de-icing salts. Sampling the doors was planned to ascertain the causes of coating failure in order to help prescribe a treatment to prevent failure from recurring on remaining windows and doors.

CONCLUSION

The conservation of the aluminum night doors at the Department of Justice was both a logistical and technical challenge that was met with a variety of creative and well-implemented solutions. It is also a project that highlights the extensive use of aluminum in Washington, DC, somewhat outside the realm of what is typically thought of as a center of progressive architecture and design in the 1930s. Evaluated seven years later, treatment of the doors is considered a success overall, with some early failures that provide opportunities for further investigation and mitigation before revised treatment recommendations are made for large-scale treatment of other aluminum elements on the building.

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Aluminum, the New Silver: Shining a Light on Gilded Age Decorative Surfaces at the Flagler Museum

Tracy L. Kamerer[1]* *and Scott W. Nolley*[2]

ABSTRACT. Henry and Mary Lily Flagler's 1902 Whitehall – a 75-room, 100,000-square-foot mansion in Palm Beach – was described as "more magnificent than any other private dwelling in the world." The Drawing Room, typical of Whitehall's sumptuous interiors, was designed in the Louis XVI style, not unlike French style salons in other period mansions. Recent testing, however, has revealed that the room is unique – the raised ornamentation on the walls, which appears to be highlighted with silver leaf, is actually aluminum leaf, and the room contains light fixtures coated with a rare aluminum amalgam.

Whitehall was built electrified, with fixtures made by Caldwell & Company of New York. There are four monumental torchieres in the corners of the Drawing Room, previously believed to be silver-plated, and past polishing campaigns attempted to brighten the darkened finish. A conservator was engaged to address accumulations of corrosion and polish residues. Initially it was thought that the degree of corrosion was the result of common silver corrosion processes, but it was instead identified as a wide range of corrosion products, largely the result of the copper alloy substrate's interaction with ammonia = based polish materials and the chlorides available in the ambient seaside environment.

It became apparent that each torchiere was surfaced with a white metal alloy that seemed oddly unaffected by on-going oxidation of the substrate metal. Micro-chemical testing and X-ray fluorescence analysis aided in identification of the metal as an unusual early twentieth century industrial alloy, a mixture of silver and aluminum applied as an amalgam. Other decorative applications of this alloy from the period have not been located.

It is obvious that this industrial alloy – like the aluminum leaf on the walls – was designed to have the appearance of silver, while remaining tarnish and corrosion free in the Florida climate. Well-intended polishing campaigns, however, had actually worsened their appearance, causing corrosion with silver polish.

Keywords: aluminum, amalgam, corrosion, white metal, Caldwell, Flagler, Gilded Age, decorative arts

INTRODUCTION

When it was completed in 1902, the *New York Herald* proclaimed that Whitehall was "more wonderful than any palace in Europe, grander and more magnificent than any other private dwelling in the world." (Anonymous, 1902:10) The 75-room, nearly 100,000-square-foot beaux-arts mansion (figure 1) was built in Palm Beach by Henry Flagler – a founding partner in Standard Oil, railroad magnate, and developer of Florida's East Coast – for his third wife, Mary Lily Kenan. Whitehall is now a National Historic Landmark and is open to the public as the Henry Morrison Flagler Museum.

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[1] Formerly of Henry Morrison Flagler Museum, Palm Beach, Florida, USA. Now at the Museum of the American Arts and Crafts Movement, St. Petersburg, Florida, USA.

[2] Formerly at the Fine Art Conservation of Virginia, Richmond, Virginia, USA. Now at the Smithsonian Institution's National Museum of American History, Washington, DC, USA.

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FIGURE 1. Whitehall, Henry and Mary Lily Flagler's 1902 mansion in Palm Beach, Florida. Copyright Flagler Museum.

Architects John Carrère and Thomas Hastings designed the neo-classical building and formal Grand Hall, and Pottier & Stymus designed and executed the remaining interiors with period rooms in styles such as Louis XIV, Louis XV, Louis XVI, Italian Renaissance, and Francis I. Henry Flagler became a major patron of both Carrère and Hastings and Pottier & Stymus, utilizing each firm on numerous projects, from his homes to hotels and churches. The New York firm of Pottier & Stymus, founded in 1859 by Auguste Pottier and William Stymus, was one of the most prominent decorating and cabinetmaking firms of its day, with clients including William Rockefeller, Leland Stanford, and President Ulysses S. Grant.

Located just off of Whitehall's Grand Hall, the sumptuous Drawing Room (figure 2) was designed by Pottier & Stymus in the Louis XVI style. While this style was utilized for French salons in other Gilded Age mansions, a closer study reveals that the room is quite unique. The Drawing Room had been painted several colors over recent decades, and until last year it was warm beige. Contemporary accounts including the 1902 *New York Herald* article, however, described the appearance of the Drawing Room differently: "It is treated in a delicate shade of gray and silver, instead of the usual white and gold. . . ." (Anonymous, 1902:10) Based on this information, the Museum commissioned cross-section paint microscopy. Analysis confirmed that the room was, indeed, originally French gray and silver, an unusual scheme for a period French-style salon. The Drawing Room's walls and matching piano were restored to their original color in the spring of 2013.

FIGURE 2. Whitehall's Louis XIV-style Drawing Room. Copyright Flagler Museum.

Testing carried out at the Smithsonian Institution's Conservation Analytical Laboratory in 1997 (Wachowiak *et al.*, 1997) determined that the leaf on the raised plaster wall ornament, which was previously thought to have been silver leaf, is actually nearly pure aluminum (figure 3). The slightly gold appearance of the leaf today is due to the original shellac coating, which is discolored but otherwise intact.

Aluminum was a fashionable yet extravagant luxury throughout most of the nineteenth century. Until late in the century its cost was high, as the metal was extracted utilizing very primitive methods. Aluminum was first produced in 1825, and for decades was more costly than gold. The metal became popular for fine jewelry, and Napoleon III owned an aluminum dining service reserved for his most important guests. In 1855, aluminum cost approximately $500 per pound. The great interest in the metal prompted rapid development in technology, however, and by 1859 aluminum was priced at $17 per pound.

In 1886 the electrolytic process was developed, drastically reducing the cost of producing aluminum, and the price fell to

FIGURE 3. Detail of the Drawing Room's overdoor plaster relief ornamentation, highlighted with aluminum leaf. Copyright Flagler Museum.

$12.00 per pound. An 1889 *New York Times* article placed the value of aluminum at $4.00 per pound, and despite the fact that it was still about four times more expensive than silver, the *Times* stated that aluminum had taken the place of silver leaf in sign painting with great success. (Anonymous, 1889:2) By 1892 it was less than a dollar per pound.

The metal was gaining popularity for industrial use, but despite the drop in prices by the end of the century, it was still an unusual material choice for decorative purposes. Some decorative applications exist dating from the 1870s to around 1910, however, and a small group of elite American homes of the period utilized aluminum in their decorative schemes instead of silver. Decorators Pottier & Stymus are known to have employed aluminum instead of silver in at least two other projects: McKim, Mead, and White's 1894 New York Metropolitan Club and the Moody Mansion in Galveston, completed in 1895.

The Louis XVI-style Drawing Room at Maymont in Richmond, Virginia, built between 1890 and 1893 by financier James Henry Dooley, incorporated both metals. The Drawing Room was originally outfitted by an unidentified company with silver-leafed wall decorations and furniture, and silver-plated light fixtures and hardware. Around 1910 to 1912, aluminum leaf was applied over the older silver leaf, probably in an attempt to add brightness to tarnished decorations. (The light gray color visible today, however, is paint applied over the aluminum during a 1970s renovation.) It is highly likely that the application of aluminum at Maymont was influenced by a visit by the Dooleys to Whitehall.

Aluminum leaf was also sometimes utilized as a stand-in for gold. At Clayton, industrialist and art collector Henry Clay Frick's home in Pittsburgh, aluminum leaf wall decorations that mimicked silver were executed by the cabinetmakers and decorators A. Kimbel & Sons of New York during an 1891–1892 renovation. But in 1903–04, a gold-toned aluminum ceiling was installed in Clayton's Parlor by New York decorators Cottier and Co. Other decorators including Louis Comfort Tiffany realized that aluminum had distinct advantages over gold – particularly that gold-toned aluminum leaf was brighter and more iridescent than real gold leaf. Tiffany utilized aluminum dyed gold in several major projects, such as the dome of the 1897 Chicago Public Library.

The use of aluminum in the decoration of Whitehall's Drawing Room – still an unusual choice in 1902 – would have been a particularly appropriate choice for several reasons. First, aluminum's rarity would certainly have served as an appealing status symbol. Second, Flagler was highly interested in technology and had mining interests, so the challenges in obtaining and processing the metal would likely have also appealed to him intellectually. But, most importantly, aluminum was a practical choice, as it was not as vulnerable to Florida's salty air as silver, and didn't tarnish. After more than a century, the leaf is still in excellent condition, except for the discolored shellac, despite the fact that Whitehall was not climate controlled until 1999.

The extensive use of aluminum in the Drawing Room is only one of the numerous modern features within the historically-veneered Whitehall, but it is not the most exciting aluminum-related discovery in the room. Whitehall was built electrified – still relatively uncommon for the time – and retains its original light fixtures made by Edward F. Caldwell & Company. Four monumental, 8½-foot tall torchieres with 13 branches are located in the corners of the room, custom manufactured to match the aluminum-leaf decorations in design and finish (figure 4).

The New York firm Edward F. Caldwell & Company was America's most prominent manufacturer and designer of custom lighting fixtures and decorative metalwork from the end of the nineteenth century until 1959, when the company closed. Edward F. Caldwell began his designing career with the help of his friend, the architect Stanford White, and in 1894 he founded Caldwell & Company with another designer and draftsman, Victor F. von Lossberg. Caldwell believed that lighting should be an artistic addition to a fine interior. The firm also embraced electricity at an early stage. Only two percent of New York City's

FIGURE 4. One of four 13-branch torchieres in the corners of the Drawing Room, made by Caldwell and Company, after treatment. Copyright Flagler Museum.

population had electricity by 1895, but those who did were a prominent and wealthy group who could afford the finest custom designs.

Caldwell & Company built a prominent clientele and created fixtures for many important buildings, such as the White House, Andrew Carnegie's New York mansion, the Waldorf-Astoria Hotel, and Saint Patrick's Cathedral. The firm was renowned for the casting and gilding of bronze and became the foundry for Tiffany & Co. Caldwell & Company worked closely with Whitehall's architects and interior decorators to create custom fixtures that harmonized with the building and its historical interiors.

Museum records indicated that the Drawing Room's torchieres were made of silver-plated bronze, but their recent conservation treatment yielded surprising information. Several past polishing campaigns had attempted to brighten the finish of the fixtures, but they still appeared darkened and corroded (figure 5).

FIGURE 5. A darkened and corroded torchiere, before treatment. Copyright Flagler Museum.

In 2011, conservator Scott Nolley was engaged by the Museum to address the unsatisfactory appearance of the fixtures.

EXAMINATION

An initial examination revealed that, rather than the dark corrosion associated with tarnishing silver, the substantial surface accumulations of corrosion products appeared as a range of granular and crystalline deposits in a variety of colors (figure 6). As a result of institutional memory and curatorial record characterizing the fixtures as silver, the presentation surfaces of the torchieres were regularly subjected to polishing – likely using proprietary, ammonia-based abrasive formulations. This assertion was supported by the significant accumulations of polish residues that were visible in the recessed details of each fixture. Viewed under magnification, beneath the significant accumulation of disfiguring corrosion products, the white metal substrate appeared lustrous and oddly unaffected.

At this point we returned to looking at the drawing room as an overall concept. The matching grand piano, for example, was manufactured by Steinway & Sons and decorated by a firm other than Pottier and Stymus. There was clearly an overall design mandate for aesthetic uniformity. Many of the design details, such as a pattern of scrollwork along the edge of the piano case, echo those found throughout the room. Similarly, the light fixtures were custom designed to correspond to the decorative motifs of the Drawing Room wall reliefs. Floral ranceau, acanthus leaf, and "lamb's tongue" patterns appear on both the fixtures and the walls, as well as repeated patterns of neo-classical urn and boss motifs that give measure to just how integrated the room's design had been.

X-ray fluorescence (XRF) analysis revealed the composition of the decorative white metal surfaces of the torchieres to be an alloy of silver, aluminum, and nickel, on a bronze substrate of copper and tin. XRF analysis also indicated that the

FIGURE 6. Before treatment, three candle cups exhibiting a range of accumulated corrosion products. Fine Art Conservation of Virginia, 2011.

Drawing Room's custom thermostats and door handles were cast in bronze and coated with this same aluminum-silver-nickel white metal alloy.

The interior surfaces of various elements of the torchieres display an interesting pattern of drip and brush marks that define the application of the white metal surface (figure 7). The characteristic pattern of drips and brush marks – plus the fact that some XRF analyses showed traces of mercury – suggests the white metal presentation surface was likely applied as an amalgam.

The relationship of mercury and aluminum in metallurgy is a notoriously aggressive one – the two elements are legendary for their structural incompatibility – but recent research into the industrial and scientific literature of the late 19th and early 20th centuries has produced several citations. Most notably, a chapter in *The Scientific American Cyclopedia of Formulas* entitled "Alloys and Amalgams" makes note of an aluminum alloy where the addition of silver serves to "harden, whiten and strengthen the metal" and "gives a metal susceptible to taking a good polish and making fine castings." (Hopkins, 1913:73)

An 1890 French language publication devoted to aluminum extolled the virtues, as well as the temperamental performance characteristics, of a similar alloy applied as an amalgam, and presenting a surface that is characterized by patterns of crystals – a phenomenon we consistently identified over the torchiere parts. (Minet, 1890:265) The composition of this alloy is consistent with the results of the XRF analysis of the torchieres' presentation surface.

Applied as an amalgam, the white metal alloy dispersed in mercury would have resulted in a surface that was somewhat matte in appearance, and examination of the various surfaces of the fixtures' components is consistent with this assertion. Areas of various components appear to have been left unpolished, while selected highlights and details of other forms were burnished to a reflective luster (figure 8). This apparently intentional use of surface luster for decorative contrast also seems to have had an effect on the varying corrosion potential of the artifact surfaces, as unburnished surfaces displayed a greater degree of corrosion than that of the more polished, lustrous surfaces of the design.

The use of the amalgam technique to deposit the white metal surface seems to have also had a significant role in the stability and corrosion resistance of the decorative surface. Typically porous, unburnished, and possessed of a characteristic texture, the white metal amalgam surface would have proved an incomplete barrier between the salt water atmosphere of South Florida and the copper alloy below. The minute voids in the aluminum-silver surface would have provided ample opportunity for the crevice corrosion that often affects textured aluminum surfaces.

This combination of conditions appears to have initiated a complex form of crevice corrosion, a prevalent corrosion cycle typical to aluminum, though in this case also involving the copper alloy below. The porosities over the amalgam surface would have been more acidic, and corrosion would have likely occurred at an increasing rate, accompanied by the continual redeposition of aluminum oxides and copper salts in a range of corrosion products over the metal surface. These appeared as irregular deposits forming a complex laminate that ranged in character from chalky green-colored deposits of copper carbonates and

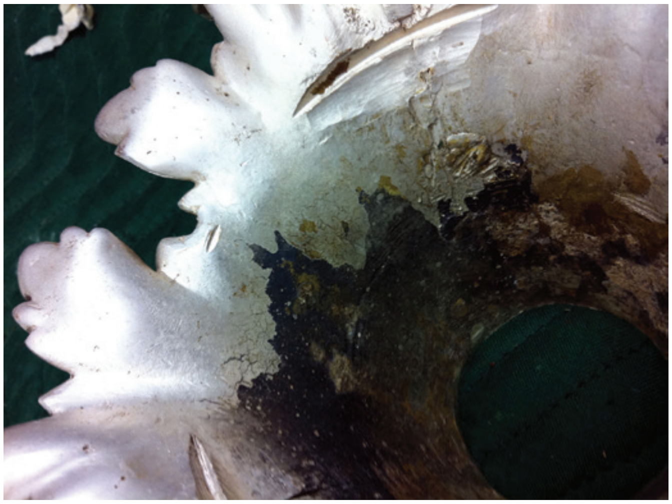

FIGURE 7. Interior surface of column "hickey" ring, showing drip and brush marks associated with the application of the white metal surface. Fine Art Conservation of Virginia, 2011.

FIGURE 8. Detail of back of lamp arm, after reduction of corrosion, showing burnished surfaces at right and unburnished surfaces at left as an intentional use of surface contrast. Fine Art Conservation of Virginia, 2011.

dark-granular accumulations of aluminum oxides, to a thick glass-like crust, trapping polish residues and, in few instances, lifting metal surfaces. Also visible were local areas of beautiful filiform corrosion that were identified not on the white metal surfaces, but rather over the exposed areas bronze alloy substrate not coated with the amalgam.

Samples of the corrosion products taken from the torchieres' surfaces were tested using micro-chemical methods and were found to test positive for a number of environmental detractors, including chloride and sulfate ions, but primarily as salts of copper, though also testing positive for aluminum.

CLEANING

As we approached and reviewed techniques for the reduction of these accumulated corrosion products, we briefly visited the idea of using an infrared laser to reclaim the decorative surfaces. Spot testing with the laser on hidden areas of the torchieres proved less than ideal, as the silver-aluminum-nickel amalgam layer was not able to withstand the mechanics of the ablation process associated with the laser. Laser testing caused intermittent delamination of the applied layer, which was likely a fragility resulting from the degree of corrosion and loss that had occurred between the bronze substrate and amalgam layer.

Cleaning tests resulted in the development of a wet-cleaning technique that proved the least invasive of any techniques considered, as crisp chasing and casting details would have succumbed to even the mildest mechanical or abrasive cleaning method. Solvent and surfactant cleaning tests led to a cleaning method that proved quite successful. By formulating a system using citrate-based chelating agents in solution and by working in the alkaline range, modifying the pH as needed, an aqueous system was designed and subsequently modified as required, to reduce soluble and insoluble salts from the artifact surfaces (figure 9). Following the aqueous phase of cleaning, each individual component was dehydrated by immersion in an acetone bath and air dried prior to reassembly.

While the successful treatment of the torchieres was both unique and challenging, what remains the subject of further continued interest is the apparently limited use of an aluminum-silver-nickel amalgam as a decorative surface. Contemporary literature that mentioned the use of such an amalgam appeared in both the United States and in Europe and extolled its beauty, but also described its temperamental working properties. It appears the amalgam's use was somewhat short lived, spanning about 30 years from the end of the 1800s into the 1920s. Other decorative applications of this white metal alloy from the period have not yet been located, however, nor have records explaining the circumstances of the creation of the torchieres or the presence of the amalgam on these decorative fixtures.

It is obvious that this unusual white metal alloy – like the aluminum leaf on the walls – was intended to have the appearance of silver while remaining tarnish- and corrosion-free in the Florida climate. But the choice of an amalgam in the application of the aluminum-silver-nickel alloy may have introduced an inherent vulnerability. The porous nature of an applied amalgam appears to have facilitated the active corrosion and, later, well-intended polishing campaigns worsened its condition and compromised the appearance of the torchieres. These unique lighting fixtures have now been returned to a matching lustre and brightness in the newly restored Drawing Room at Whitehall, coordinating beautifully with the aluminum leaf ornament, and at the same time providing an intriguing new subject for research for scholars in the fields of decorative arts, metallurgy, and conservation.

FIGURE 9. Pair of bobeche plates: before (top) and after (bottom) reduction of corrosion products. Fine Art Conservation of Virginia, 2011.

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Corrosion Prevention and Control for Aluminium Alloy Aircraft Components

Bruce R. W. Hinton

ABSTRACT. This paper provides an overview of surface treatments and coating systems used for aluminium alloy components on military aircraft. It will also discuss corrosion prevention strategies employed by aircraft maintainers, some of which may be applicable to the conservation of museum artefacts. The paper briefly summarises recent developments with innovative environmentally friendly inhibitor systems for use in corrosion prevention with aluminium alloys, in particular rare earth metal organic compounds.

Keywords: Aluminium, corrosion, prevention, inhibitors.

INTRODUCTION

The development of corrosion in aircraft structural components over their operating life is largely due to the gradual deterioration and breakdown of protective paint coatings. Unfortunately most of the high strength aluminium alloys and steels used for structural components are susceptible to corrosion. Therefore, the prevention and control of corrosion on aircraft components is a very important maintenance consideration for the operators of civilian and military aircraft and for those conserving museum aircraft.

The following paper will provide an overview of surface treatments and coating systems used for aluminium alloy components on military aircraft and discuss some of the other methods used by aircraft maintainers to prevent corrosion. A challenge facing the corrosion prevention community in general is dealing with the elimination of chromates as inhibitors in protection schemes. The paper will also summarise recent developments at both Monash and Deakin Universities, with the environmentally friendly rare earth metal compound inhibitor systems for use with aluminium alloys.

THE CORROSION PROCESS

Corrosion is an electrochemical process which develops on a metal surface as a result of local anodes and cathodes present in the microstructure of the Al alloy. Figure 1 is a simplified schematic of a localised corrosion process (e.g. pitting corrosion) on an aluminium alloy. However, the basic concept may be applied to pitting, crevice, intergranular, galvanic, filiform corrosion, or stress corrosion cracking.

Figure 1 shows the local anode and cathode separated, with aluminum going into solution at the anode as Al^{3+} ions. This anodic reaction is accompanied by a cathodic reaction e.g. reduction of oxygen, at the nearby cathode, which may be an adjacent intermetallic particle, or the mouth of a pit, crevice or crack. If oxygen is unavailable,

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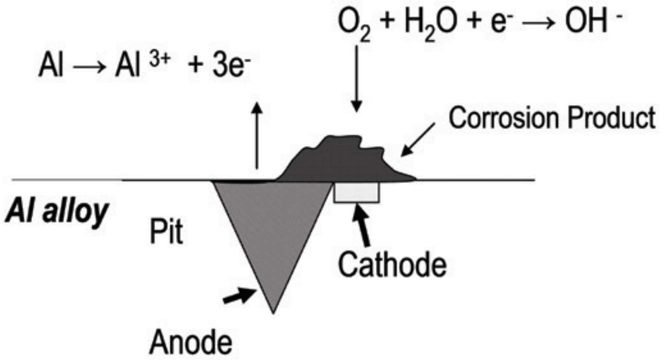


FIGURE 1. Schematic showing the mechanism of pitting on an Al alloy. The cathode is typically an intermetallic particle in the microstructure of the alloy.

hydrogen evolution is the accompanying cathodic reaction. As a result of the development of these anodic and cathodic sites, electron flow occurs in the metal and ionic transport of charge occurs in the moisture layer. Thus an electrochemical circuit is established as shown schematically in Figure 2. The rate at which an aluminum alloy corrodes is controlled by the slowest of these processes. This basic mechanism helps to understand how corrosion can be controlled or prevented and is used to explain the effectiveness of various parts of a corrosion prevention strategy for aircraft structures.

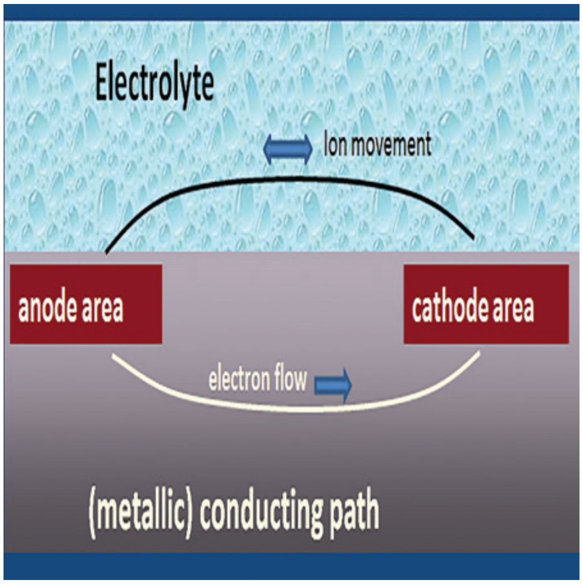


FIGURE 2. The electrochemical circuit which represents the corrosion process.

TYPES OF CORROSION

Aircraft operate in a very diverse range of environments arising from the atmosphere in which they fly and the airports from which they operate. They may be exposed to salt contamination near seacoasts, to high humidity tropical conditions and dusty dry locations. The environment inside an aircraft structure may be different to that outside, both when flying or on the ground where the aircraft is parked. In these operating environments the aircraft alloys are susceptible to corrosion. Many internal and external aircraft structural components are made from 2000, 6000 or 7000 series aluminium alloys, and because of the non-homogeneous nature of their microstructures they will always be susceptible to corrosion. The most common forms of corrosion are pitting corrosion, galvanic corrosion, intergranular corrosion, filiform corrosion and stress corrosion cracking. A comprehensive discussion on corrosion types can be found at Reference (Kaufman 2005).

CORROSION PREVENTION STRATEGIES

The durability of aluminum alloy assemblies and components in a service environment depends on many factors such as type of alloy, design and fabrication, protective coating, environmental conditions, maintenance programs and inspection requirements. With aging aircraft and museum aircraft in particular, a susceptible alloy in a structure is unlikely to be changed. In relation to design, it is important in any corrosion prevention strategy that attention is paid to any possible moisture entrapment areas and that provision for adequate drainage is considered, especially if joints, galvanic couples and stresses (stress corrosion cracking) may be present. In order to avoid corrosion, protective coatings are employed and where possible modifications made to local operating environments. These preventative measures coupled with a well-planned maintenance program and adequately trained inspection teams provide the basis for a comprehensive corrosion prevention strategy.

The nature of the environment in which an aircraft component operates can be changed to reduce its aggressiveness by removing or diluting dissolved ions such as chlorides or by the addition of inhibitors that produce protective films on the surface. Reducing the concentration of chloride ions in the environment e.g. by washing or rinsing will reduce the efficiency of ionic transport, which affects both anodic and cathodic processes (See Figure 2). Reducing moisture in an airframe using dehumidification is another form of changing the severity of the environment. These approaches will be discussed in more detail later in this paper. Modification of the environment forms a significant part of any corrosion prevention strategy.

CORROSION PROTECTION ON THE AIRCRAFT STRUCTURE

The natural passive oxide on aluminium alloy aircraft components is insufficient to protect from corrosion in service. Therefore multilayered protection schemes are used in operational environments. This section describes the various layers that make up protection schemes commonly used on Al alloy components on military aircraft.

ROLE OF PROTECTIVE SCHEMES AND CORROSION INHIBITORS

A coating not only acts as a barrier to moisture, it also provides a high resistance pathway to the movement of ions when the barrier has been permeated by water, thus restricting the flow of ions in the electrochemical circuit depicted in Figure 2. In the event that a coating is damaged or deteriorates over time and fails mechanically, moisture can penetrate to the exposed metal substrate. Inhibitor pigments contained in the pre-treatment layers of paint coatings are available to provide corrosion protection. These inhibitors can act to prevent corrosion by shutting down potential electrochemical reactions on surfaces and inside crevices, pits and cracks. Inhibitors may produce protective layers on the surface either by combination with the metal to form an oxide film for example, or by adsorption of molecules onto the surface.

Inhibitors are (i) present in conversion coatings and anodised films, (ii) incorporated into paint coatings, (iii) present in temporary corrosion protection coatings, and (iv) included in detergent washing formulations. These are chemical substances that have some solubility in water and which prevent or slow corrosion in aggressive aqueous environments. Referring again to Figure 2, the presence of an inhibitor may decrease the rate of the anodic process (anodic inhibitor), the cathodic process (cathodic inhibitor) or both processes (mixed inhibitor). Anodic inhibitors function by reacting with the aluminum to produce a thin passive film that leads to a decrease in the corrosion rate. Hexavalent chromates e.g. zinc strontium and barium chromates are extremely effective inhibitors for aluminum alloys (Frankel and McCreery 2001). Chromate does this by producing a passive corrosion resistant oxide film on the aluminum surface. This film reduces the activity of both anodic sites and cathodic sites (Frankel 2001). At the anodic sites the passive film prevents dissolution of the aluminum, and at the cathodic sites the film prevents oxygen adsorption and restricts access of electrons to oxygen for oxygen reduction to occur; thus, the electrical circuit shown in Figure 2 is broken.

Cathodic inhibitors typically affect the rate of the oxygen reduction reaction and/or the hydrogen evolution reaction. Common cathodic inhibitors for aluminum alloys are those which react with hydroxyl ions produced at cathodic sites to form an insoluble complex hydroxide layer (corrosion product) at those sites (See Figure 2). This film provides a barrier between the cathodic site and the electrolyte, which restricts access of oxygen or hydrogen ions to the site. Thus ionic flow in the electrochemical circuit is restricted and the rate of corrosion reduced. Zinc salts and the salts of the rare earth metals (Hinton, Arnott et al., 1984; Hinton 1989) may act as effective cathodic inhibitors; the latter by allowing complex rare earth metal oxides/hydroxides to precipitate at cathodic sites. More recent research showing the effectiveness of the rare earth compounds will discussed later in this paper.

Many organic compounds such as sulphonates, phosphonates, amines, quaternary ammonium salts are also inhibitors of corrosion for aluminum alloys (Hinton, Trathen et al. 1982; Hinton, Ryan et al. 1984). They function by chemisorbing onto the metal surface either at anodic, cathodic sites or both. The adsorbed layer effectively acts as a barrier to the environment by preventing access of water, chloride ions and oxygen. While many compounds are known to be effective inhibitors of aluminum alloys, they are not as effective as chromates.

PAINT COATING SYSTEMS

PRE-TREATMENTS

The corrosion protection systems used on aircraft generally consist of an anodized or chromate conversion coating pretreatment, a primer and a finishing top coat. In some areas of internal structure a primer only is applied, but in areas where moisture and aggressive contaminants collect such as under floors, around toilets and galleys several layers of top coat may be applied. The main purpose of the pre-treatment process is to provide a coating with some level of corrosion protection capability, and improved adhesion for the following paint coating. The pre-treatment process is most important because it removes contaminants, which may affect the adhesion of the paint coatings. The two pre-treatment processes used in the aircraft industry are conversion coatings and anodising. References (Biestek and Weber 1976; Wernick, Pinner et al. 2007.) provide detailed descriptions of the characteristics of these coatings and how they are produced.

CHROMATE CONVERSION COATINGS (CCCS)

Chromate conversion coatings have been widely used in the aircraft industry for over 80 years. They are produced by immersion, spraying or swabbing with an acid solution containing the salts of hexavalent chromium ions (chromates). The process produces a film consisting largely of hydrated chromium oxide (Hughes, Taylor et al. 1997). The film also retains some soluble hexavalent chromate ions. Common trade names for the CCC process are Alodine™ and Iridite™.

Non-Chromate Conversion Coatings

Due to environmental, health and safety concerns (Costa 1997) there is increasing legislative pressure in various parts of the world to limit and prevent the use of chromates. Many alternatives to CCCs for use on aluminum alloys have been discussed over recent years (Hinton 1991; Hinton 1991; Hughes, Hardin et al. 2003; R.G.Buchheit and A.E.Hughes 2003), however as yet most of these do not match the corrosion protection performance of CCCs, especially on corrosion prone alloys such as the 2XXX and the 7XXX series alloys.

Anodised Coatings

These are produced by electrochemical polarisation in an electrolyte containing chromic acid, phosphoric acid or sulphuric acid. Anodising produces a thick oxide film up to 10µm thick depending on the acid anodising bath (Biestek and Weber 1976). These films provide better corrosion protection than chromate conversion coatings; however they can be more brittle. Because of this, conversion coatings or anodised coatings may be used on different parts of an aircraft structure depending on structural and loading considerations.

Primers

The primer is the primary source of protection in the paint coating system and provides improved adhesion of subsequent top coats. The one most commonly used in aircraft structure is based on a two-part epoxy polyamide polymer. It consists of an epoxy resin binder and a polyamide resin hardener. For many years, the most common corrosion inhibition pigment used in this primer was strontium chromate. This pigment provides a source of the powerful hexavalent chromate inhibitor ions. These ions may leach from the coating particularly at points where the coating is damaged or cracking occurs and thereby provide protection. Unfortunately, the chromate ion is now known to be toxic and carcinogenic. The primer coating is typically 15 to 25 µm for a single dry coat.

Many non-toxic alternatives to chromates as pigments in paints have been investigated, such as zinc phosphate, borates, molybdates and silicates (Twite and Bierwagen 1998). Although these pigments have been shown to provide some level of inhibition, none has been shown to be as effective as chromates (Twite and Bierwagen 1998). However, some combinations of inhibitors have provided levels of inhibition similar to that provided by chromates when included in coatings (Spadafora 1997).

The salts of the rare earth metals such as cerium and lanthanum are known to be very effective inhibitors of corrosion of aluminum (Hinton 1989; Forsyth, Markley et al. 2008). Over recent years considerable research has been conducted on the protective performance of coatings, such as epoxy polyamides containing rare earth metal salts, e.g., cerium sulphate and formate (Smith, Baldwin et al. 1993); cerium nitrate (Morris, Stoffer et al. 1999); cerium diphenyl phosphate (Hughes, Mol et al. 2005; Markley 2008); and other compounds, e.g., Hydrotalcites to which REM salts have been attached (Williams and McMurray, 2003). While all of these formulations showed significant levels of protection none was found to be as effective as chromate pigments coatings.

Top Coats

For external aerodynamic surfaces on aircraft such as in landing wheel bays and on fuselages, tails and wings, a polyurethane top coat is applied over the primer. This top coat is a two-part system consisting of an isocyanate resin and a hydrolated polyester hardener. The function of the top coat is to protect the primer against ultra violet radiation, to provide general chemical resistance, and to be durable and flexible. Polyurethane top coats are generally applied to a dry film thickness of around 50µm. Over time, top coats may degrade due to weather exposure, temperature excursions from high altitude flight, soil accumulation and stressing. This degradation leads to discoloration, chalking and cracking; the latter particularly in areas of structure where flexing can occur.

Sealants

Another important part of the aircraft component protective scheme is the use of sealants. As mentioned above, all paint coatings harden and crack eventually. The cracks allow moisture to penetrate through to the alloy substrate. As an added layer of protection, sealants are used particularly in highly stressed regions such as joints and fastener holes. They are based on organic compounds such as polysulphides and polythioesters, with properties such as excellent adhesion and high elasticity at low temperatures. All internal and external locations on an aircraft structure which could collect moisture are typically protected using flexible sealants in addition to paint coatings.

PROTECTIVE SCHEME FAILURE

Corrosion will not occur until the protective coating system fails. All paints on aircraft structures will admit moisture over time, as they degrade due to weather exposure, UV, temperature excursions from high altitude flight, soil accumulation and stressing. Evidence of degradation is discoloration, chalking and cracking. As they age and degrade they harden, and cracking develops particularly in areas of structure where flexing can occur e.g. within the joints, inside fastener holes and on mating surfaces. The network of cracks formed will allow all constituents of the atmospheric environment to penetrate through to the substrate metal. Chromate ions leached from the primer and conversion coating at the point of cracking will eventually be exhausted and corrosion will occur.

CORROSION PREVENTION AND CONTROL WITH CORROSION INHIBITING COMPOUNDS

Even with a comprehensive protective scheme in place, coatings will eventually fail given time. It is now common to apply an additional layer of protection using corrosion inhibiting compounds (CICs) in some parts of aircraft structures which are prone to corrosion. These are organic formulations consisting of a low surface tension carrier solvent containing a dissolved film former such as oil, wax or resin, and some organic-based corrosion inhibitors such as phosphonates and sulphonates. CICs are typically sprayed onto the structure after the full protective system is in place. When the solvent evaporates, a film of oil, wax or resin is left together with the inhibitors. They therefore provide an additional barrier layer for protection and a source of corrosion inhibitors when moisture is present. Some CICs also have water displacing and repellant properties, which enable them to be used to prevent moisture accessing exposed metal at cracks in paint coatings and sealants within joints and holes, or to remove moisture. Many CICs remain mobile on the surface for some time and can provide protection when cracks form in the underlying paint coating.

These products do have excellent corrosion prevention properties and they are able to arrest the growth of existing corrosion process including stress corrosion cracking (Hinton, Trathen et al. 1996; Hinton, Trathen et al. 2000). Examples of their corrosion protection performance are shown in Figure 3. These results are from specimens of AA2024-T3 plate coated with CICs and exposed on a flight deck of a Royal Australian Navy frigate for 10 months (Hinton, Trathen et al. 2000).

These data show how effective CICs can be in a very corrosive environment in the absence of any other coating. An important property of CICs identified by Defence Science and Technology Organization, Australian Department of Defence (DSTO) was their ability to slow the growth of corrosion processes (Salagaras, Hinton et al. 2001). One of the most common forms of corrosion on military aircraft operating in humid, salt laden environments is filiform corrosion. Figure 4 shows how the application of CIC to growing filiform corrosion can reduce the propagation rate.

This result also indicates how effective CICs can be as a means of temporarily reducing or retarding a corrosion process. This has important implications for saving maintenance time. Over the past 20 years some twenty cases of existing corrosion in many different Australian Defence Force (AFO) aircraft have been treated with CICs. It should be noted that while effective in arresting or retarding growth, the CICs did not stop the corrosion process completely. Therefore CICs should only be regarded as a temporary form of corrosion protection and a treatment for slowing the growth of corrosion.

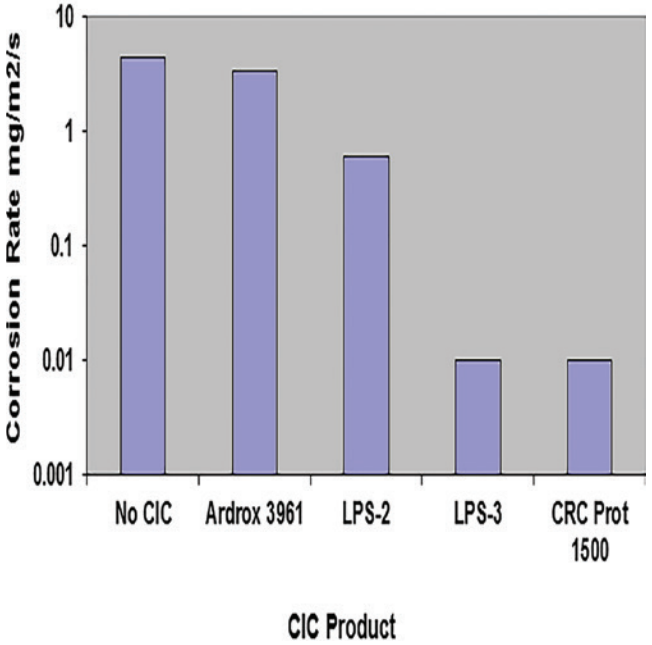


FIGURE 3. The effects of various coatings of CIC on the corrosion rate of Al alloy AA2024 specimens which had been exposed on a navy ship for 10 months. (NB Corrosion Rate is a log scale).

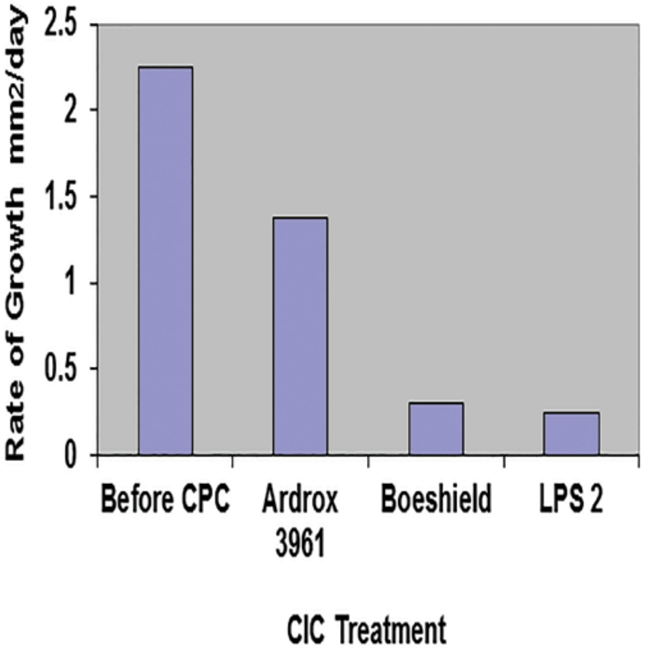


FIGURE 4. The effects of various CICs in reducing the rate of filiform corrosion on Al alloy 7075.

CORROSION PREVENTION AND CONTROL BY AIRCRAFT WASHING

Another corrosion prevention and control strategy for temporary corrosion protection and arrest is the use of the common maintenance action of periodic aircraft washing. Detergent washing formulations contain surfactants some of which are very surface active and penetrating, and have corrosion inhibiting properties (Hinton, Rohan et al. 1995). Figure 5 shows constant immersion corrosion rate data obtained for AA7075-T651 in NaCl solution, and the effects of various concentrations of commercially available detergents when added to the test solution. The detergent ZI400™ reduced the corrosion rate to almost zero at a concentration of 15%. Figure 6 shows data obtained from a galvanic corrosion test with a copper electrode and an electrode of AA7075-T651 (equal areas) in 0.1M NaCl solution. The current flowing in the cell is related to the corrosion rate of the aluminum alloy. It can be seen that the addition of a detergent to the solution (at a 10% concentration) in which galvanic corrosion was occurring, reduced the current in one case by almost an order of magnitude. The spike in the data was due to a perturbation of the system following the addition of the detergent. These data not only demonstrate the corrosion inhibiting ability of detergents, but also their ability to retard or slow the rate of an existing corrosion process.

Washing not only washes away salt contaminants and dirt, but also applies a corrosion inhibitor to the outside of the aircraft. An inhibitor in a detergent formulation would find its way into cracks in coatings along seams and around fastener heads, and counteract the deleterious effect of any chloride ions.

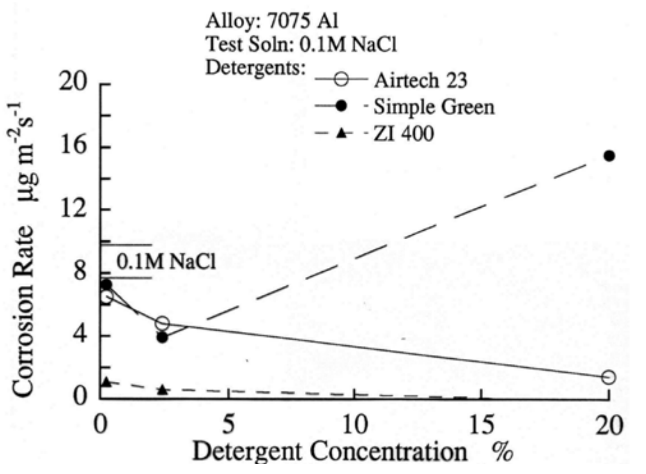


FIGURE 5. The effects of an addition of aircraft washing detergent on the corrosion rate of AA 7075 in a NaCl solution.

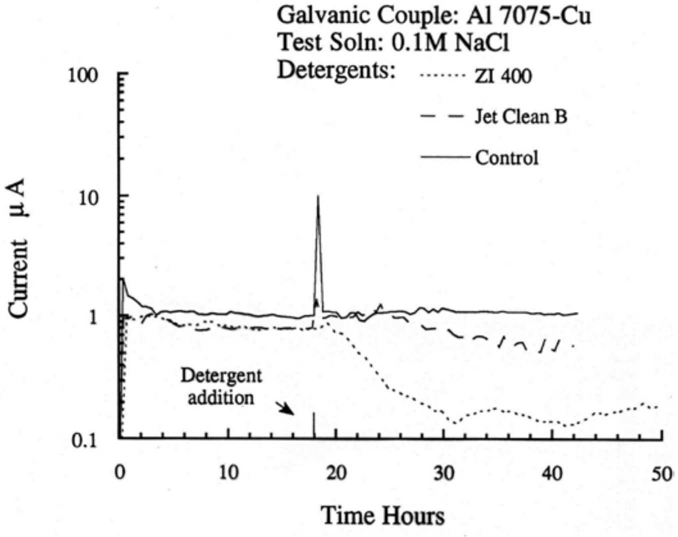


FIGURE 6. The effects of detergent additions to a corrosive on reducing the rate of corrosion of galvanic corrosion on AA7075 in a NaCl solution.

PREVENTION AND CONTROL BY DEHUMIDIFICATION

The presence of moisture is essential for corrosion to progress (see Figure 2 As Figure 7 shows, more corrosion occurs at higher humidity if salt contaminants exist on a metal surface. If the relative humidity is reduced to below around 35 % most corrosion can be prevented. Many studies from around the world with military equipment have shown that a significant reduction in failure rates were possible by dehumidifying the air within avionics system, and a reduction in maintenance times by the storage of army vehicles in dehumidified garages. The data in Figure 8 shows how an existing corrosion process as measured by corrosion current (corrosion rate) in an electrochemical test can be arrested by reducing the relative humidity. DSTO studies have shown that by blowing dry air through aircraft structures the relative humidity even in the remote parts of the aircraft can be reduced to below 35%. As a result of the various DSTO studies and overseas military experience, the ADF now routinely pass dehumidified air through aircraft structure while in maintenance or store aircraft in dehumidified hangers. Dehumidification units of various capacities are commercially available. Dehumidifiers and temporary shelters are now commonly used also for storage of military equipment and spare parts such as aircraft engines to prevent the onset of corrosion, or to stop or slow down the propagation of existing corrosion.

FIGURE 7. The effects of relative humidity (RH) level in an air environment on the corrosion of mild steel doped with NaCl solution which was allowed to dry before exposure in the air environment. (a) 40% RHG, (b) 60% RH and (c) 80% RH.

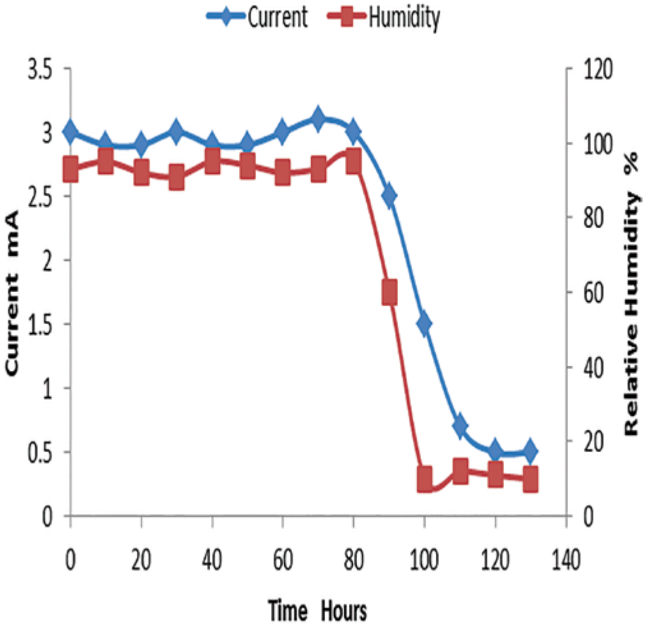


FIGURE 8. The effect of reducing the relative humidity on the current flowing between a galvanic couple of copper and tin when exposed in an air environment. The couple had been doped with NaCl. Current is a measure of corrosion rate.

MAINTENANCE AND TRAINING

Maintenance personnel are trained to look for the "failed state," which is corrosion damage. Unfortunately finding the "failed state" is too late, because expensive repairs and component replacement is required at that point. Training should involve instruction in identifying (i) the precursors of corrosion, (ii) indicators of a deleterious environmental presence, (iii) the signs of potential coating degradation and failure, and (iv) the action to be taken to prevent corrosion before the next inspection period (S. Miah and B.R.W. Hinton 2007). Precursors are chipped, cracked and degraded paint coatings, water stains, pooled water and surface contaminants. This proactive approach to corrosion prevention maintenance may mean in the short term extra maintenance hours, because the existing culture does not include looking for precursors to corrosion. However, in the long term less time would be spent repairing corrosion damage and repainting.

NEW DEVELOPMENTS IN CORROSION INHIBITION FOR AL ALLOYS

For almost 30 years, research has focused on finding a single environmentally acceptable replacement for chromates in each of these metal finishing applications. Considerable progress has been made (Twite and Bierwagen 1998; Sinko 2001), and the salts of the rare earth metals offer possible alternatives for many of these applications (Forsyth, Markley et al. 2008).

Forsyth et al (Forsyth, Wilson et al. 2002) hypothesised that the combination of the rare earth metal ions with an effective organic inhibitor could provide new compounds that suppress both anodic and cathodic reactions (i.e. a mixed inhibitor), with a degree of synergy that would lead to vastly improved corrosion protection. For aluminium alloys, Ho *et al.* (Ho, Brack et al. 2006) and Markley *et al.* (Markley, Hughes et al. 2007; Markley 2008) demonstrated that cerium diphenyl phosphate ($Ce(dpp)_3$) and cerium dibutyl phosphate ($Ce(dbp)_3$) were very good inhibitors of corrosion of aluminium alloys.

This section of the paper will provide a brief review the work undertaken with these new inhibitors, indicating their effectiveness in reducing corrosion on aluminium alloys, and outline our understanding of the inhibition mechanism.

CORROSION UNDER CONSTANT IMMERSION CONDITIONS

High strength aluminium alloys such as AA2024-T3 and AA7075-T651 are known to be very susceptible to corrosion. Optical profilometry data for AA7075 (Figure 9) (Varela et al., 2009) clearly demonstrate how effective an inhibitor $Ce(dpp)_3$ is, particularly of pitting corrosion when present in a 0.1M NaCl solution during 30 days of immersion.

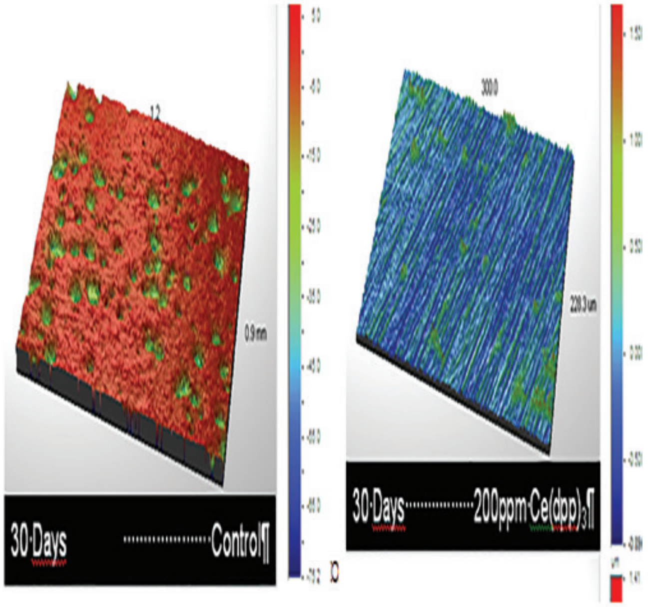
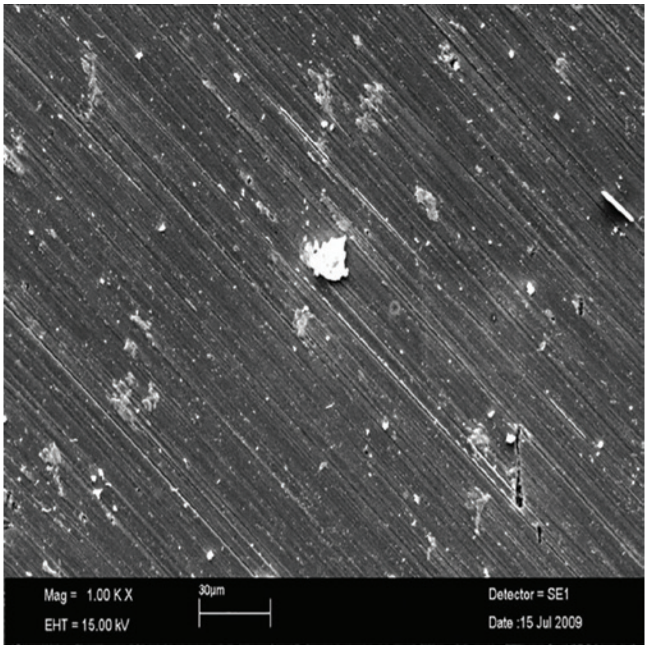


FIGURE 9. Images produced by optical profilometry of a Al alloy specimen exposed for 30 days in the control solution of NaCl and in a solution of NaCl containing the Ce inhibitor Ce(dpp)$_3$. The color scale shows the depth of the corrosion pitting. (Varela et al 2009). Reproduced by permission of the Australasian Corrosion Association.

The inhibition is the result of the formation on the surface of a complex film (See Figure 10) consisting Ce-O, O-P-O groupings in this complex film (Markley, Forsyth et al. 2007), thus proving that both the *REM* and the organophosphate units had deposited on the alloy surface.



POTENTIODYNAMIC POLARISATION BEHAVIOUR

Electrochemical tests were carried out to determine the mechanism by which these inhibitors protect aluminum alloys. Data for AA7075-T651 in constantly aerated 0.1M NaCl solution with various concentrations of Ce(dpp)$_3$ show that Ce(dpp)$_3$ is predominately a cathodic inhibitor (Figure 11) (Varela, Hill et al. 2009).

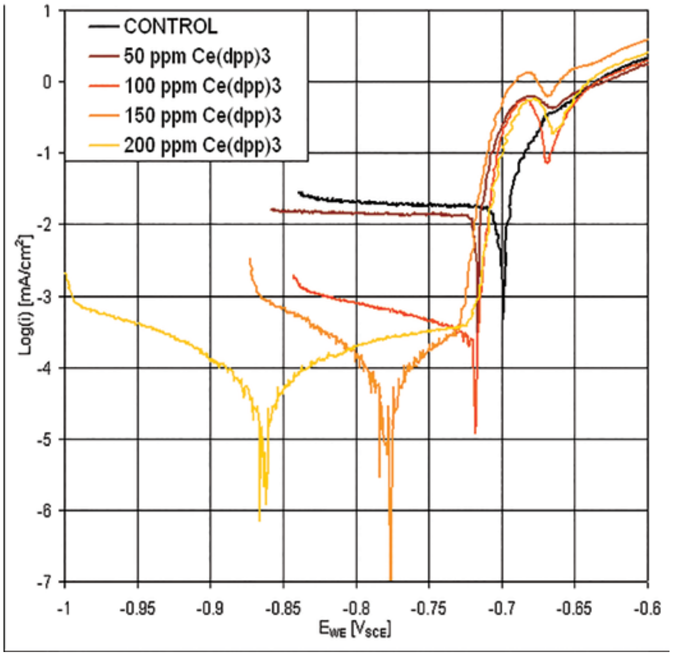


FIGURE 11. Polarisation curves for AA7075-T651 tested in continuously aerated 0.1M NaCl solution (Control) and in 0.1M NaCl with various Ce(dpp)$_3$ concentrations. (Varela et al 2009). Reproduced by permission of the Australasian Corrosion Association.

FIGURE 10. A scanning electron micrograph of the surface of a specimen after exposure to a NaCl solution containing Ce (dpp)$_3$. The large white particle and the smaller white particles contain Ce. The grey particles are intermetallic particles, which form part of the alloy microstructure. NB. the polishing marks from specimen preparation indicate the near absence of corrosion (Varela et al 2009). Reproduced by permission of the Australasian Corrosion Association.

INHIBITION OF STRESS CORROSION CRACKING

Stress corrosion cracking (SCC) is typically associated with corrosion processes in either the initiation or propagation stages. The slow strain rate test is a very effective tool for quantifying the effects of inhibitors on SCC. In Figure 12, fracture stress values are shown for AA7075-T651 specimens tested in air, NaCl solution and in NaCl with $Ce(dpp)_3$ (Varela, Hill et al. 2009).

FILIFORM CORROSION INHIBITION

Corrosion inhibitors may be added as pigments to paints in order to leach out and prevent corrosion at defects within the coating. Filiform corrosion is often observed at such defects. In work by Ho et al (Ho, Brack et al. 2006) and Forsyth et al. (Forsyth, Markley et al. 2008), it was shown that the $Ce(dbp)_3$ and $Ce(dpp)_3$ were able to suppress filiform corrosion growth from a scribe in an epoxy coating on AA2024.

MECHANISMS OF FORMATION OF INHIBITING FILM

The electrochemical and surface characterization evidence shows that inhibition by REM organic compounds results from the formation of a protective surface film. This film has a complex structure that depends on the chemistry of the inhibitor and the underlying alloy microstructure and consists of a mixture of rare earth oxide/hydroxide and adsorbed Al-REM bimetallic complexes. Our current understanding of the mechanism by which this film forms is provided by Forsyth, Seter et al. (2011).

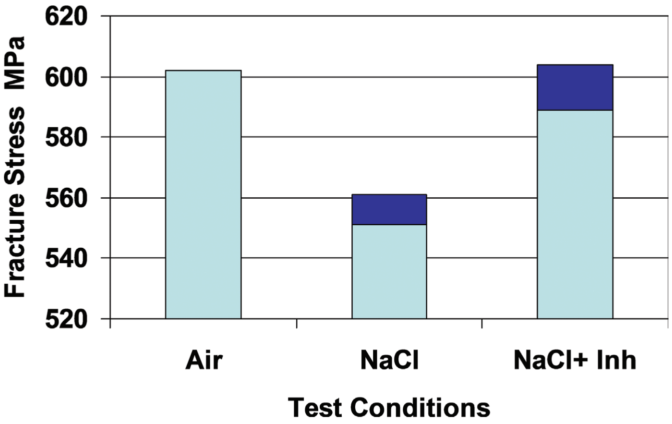


FIGURE 12. Fracture stress results for AA7075-T651 after testing in Air, in 0.1M NaCl with or without $Ce(dpp)_3$ inhibitor (Varela et al 2009). Reproduced by permission of the Australasian Corrosion Association.

CONCLUSION

The protective coating systems used on military aircraft consist of several layers: conversion coatings, primers, top coats and sealants. They all have a role in preventing corrosion from developing. However, these coating systems do break down with age and exposure to operating environments, and corrosion will eventually develop. The major ingredient in these coatings is the chromate ion, and research has been in progress for many years to find replacements because the chromate ion is toxic and carcinogenic. Inhibitors based on rare earth metal compound chemistry have been found to be most promising as replacements. To cope with the inevitable protective coating breakdown, other strategies have been employed, including the use of CICs, aircraft washing and dehumidification. These approaches coupled with better corrosion inspection techniques help aircraft operators extend the life of aging aircraft beyond the original design life. All of these methods of dealing with corrosion and preventing it from occurring would be applicable to those who role it is to conserve museum aircraft.

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In-Situ Micro-Abrasion Cleaning of a 1932 Cast Aluminum Porte Cochere

Mary Oehrlein, FAIA

ABSTRACT. The beautifully detailed and fabricated 1932 cast aluminum porte-cochere at the west elevation of the Longworth House Office Building in Washington, D.C. suffered from 80 years without maintenance. The metal was so heavily soiled and corroded that it was initially mistaken for bronze. Working with limited funding and an even more limited time frame for completing the cleaning, testing was performed using a variety of chemicals and mechanical methods to determine how best to accomplish the cleaning without damage to the metal. In addition to money and time constraints, the entrance needed to remain open to pedestrian traffic on a 24/7 basis. Cleaning with sodium bicarbonate micro-abrasion proved to be the safest, fastest means of restoring the original aluminum finish, but it was not without problems. This paper details both the successes and failures of the micro-abrasion cleaning that was undertaken.

Keywords: Architectural conservation, 1932 cast aluminum, micro-abrasion cleaning

INTRODUCTION

The ornate, cast aluminum porte-cochere is original to the 1932 construction of the Longworth House of Representative Office Building in Washington, DC. The original construction specifications for the aluminum required an alloy consisting of a minimum 96.5% aluminum, 0.45–0.8% magnesium and 1.2–1.6% silicon with minimum tensile strength of 45,000psi, minimum yield strength of 30,000psi and elongation of 10% in 2"(Figure 1). The aluminum specifications also stated that the aluminum "shall have no finish other than that involved in the process of fabrication, except as noted on the drawings or as specified herein" and further, "all exposed metalwork of the porte-cochere shall be of sandblasted aluminum."[1]

There are no records of treatment of the aluminum since the 1932 installation. Prior to cleaning, the metal was heavily soiled and disfigured by significant pitting and other forms of corrosion at surfaces not regularly washed by rain and on interior areas subject to condensation.

The porte-cochere covers an active entrance and point of egress for the Longworth House Office Building that is occupied 24 hours a day, year round. As such, the entrance could not easily be closed for more than a few hours. From a conservation point of view, the cleaning materials and methods needed to adequately clean the aluminum without adverse effects (Figures 2 and 3). From a facilities point of view, the cleaning needed to generate minimal noise and odors, could not use volatile chemicals or other materials prohibited by the Architect of the Capitol Safety and Environmental Office, could not adversely affect the historic magnolia trees immediately adjacent, needed to be accomplished during the summer congressional recess period, and needed to be accomplished at a reasonable cost. Bottom line: get it clean, but do it safe, fast and at minimum cost.

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FIGURE 1. View of the 1932 cast aluminum porte-cochere on the Longworth Office Building prior to cleaning. It protects an active pedestrian entrance/egress for an occupied building that could not be closed. The health of magnolia trees at the left was a consideration in the selection of the cleaning method (Architect of the Capitol).

FIGURE 3. Detail of the cast aluminum prior to cleaning. Soffits and interior surfaces not subject to regular washing by rain water and surfaces on which condensation forms exhibited heavier soiling and corrosion (Architect of the Capitol).

MATERIALS AND METHODS

Testing was conducted at several areas using a variety of materials and methods, including medium pressure water, detergent applied with fiber brushes, oxalic acid combined with pumice applied with abrasive scrubbing pads, Ethylene-diamine-tetraacedic acid (EDTA) with scrubbing pads, low pressure plastic bead micro-abrasion, and low pressure sodium bicarbonate micro-abrasion.

FIGURE 2. Detail of the cast aluminum prior to cleaning (Architect of the Capitol).

Materials and methods other than micro-abrasion were ineffective in removing the soiling and corrosion. Hand cleaning using the abrasive pads with enough pressure and duration to remove the soiling altered the original sandblasted surface texture of the aluminum and was impractical for removal of the soiling in the recesses of the ornamental castings. The plastic bead micro-abrasion was effective and resulted in no alteration of the aluminum surface, but cleaning was slow and the bead material is costly relative to sodium bicarbonate, particularly in an exterior environment where the beads could not be easily and cleanly captured and recycled. The decision was made to proceed with micro-abrasion cleaning using sodium bicarbonate as it proved to be the most effective cleaning technique, it was relatively fast, it was cost effective, and it presented limited environmental concerns. Because it is readily soluble in water, residual particulate matter was mitigated by thorough rinsing, thereby reducing the possibility of corrosion and potential coating failure associated with sodium bicarbonate residue (Figure 4).

Cleaning was conducted over a four week period using IBIX Helix 9 and 25 air-media blasting delivery systems with water (www.ibixusa.com). Water was used to reduce drift of the blasting media beyond the immediate work area. Dust, overspray, and bounce back were limited to 18–24" beyond the delivery nozzle. Landscaping adjacent to the porte-cochere was covered with plastic sheeting to prevent alteration of the soil pH levels. The health of two large magnolia trees, which are acid loving vegetation with shallow root systems, was of particular concern.

FIGURE 4. Test area at the center using sodium bicarbonate abrasive medium with the Ibix (Architect of the Capitol).

The air compressor used was IBIX model 200 which is very quiet compared to standard gas powered air compressors. Noise level at the interior of the nearest offices was minimal and was tolerated by the occupants without complaints. Abrasive materials used were Armex Maintenance Formula and Maintenance Formula XL. The Maintenance Formula particle size distribution is: 8% max retained on 60 mesh sieve (250 microns), 55% minimum retained on 100 mesh sieve (150 microns) and 93% minimum retained on 170 mesh sieve (90 microns). The XL Formula particle size is coarser: 8% max on 40 mesh (425 microns), 60% minimum on 60 mesh (250 microns), 70% minimum on 100 mesh (150 microns), 80% minimum on 200 mesh (75 microns) and 90% minimum on 325 mesh (45 microns).

Cleaning at the areas with less corrosion was done with IBIX 9 and the Maintenance Formula using a 4 mm diameter nozzle at approximately 60 psi. The mix of air and media was approximately 23 cfm at a rate of 1 pound per square foot. The IBIX equipment allows adjustment of both air flow and media flow. The standard Maintenance Formula and the flow rate of the IBIX 9 proved ineffective at removing heavier soiling and corrosion at the cornice soffits and other surfaces not regularly rinsed by rain. Those areas were cleaned with IBIX 25 equipment, a 7 mm nozzle and the courser XL Formula soda at 80–90 psi. Air and media flow was approximately 80 cfm at a rate 1–1.5 pounds per square foot (Figures 5 and 6).

General, overall cleaning of the aluminum was done first, during which the surfaces were washed down regularly with water using typical garden hose pressure so that the level of cleaning could be continually assessed. The entire work area was washed down at the end of each work day with copious amounts of water to remove the blasting residue from the aluminum. The ground area was swept, debris shoveled up and removed from the site. After general cleaning, remaining soiling, corrosion and shadowing was selectively targeted to prevent over cleaning or alteration of the original sand blasted aluminum surface texture (Figures 7, 8, 9 and 10).

FIGURE 5. Lightly soiled/corroded areas were cleaned using the IBIX Helix blasting system with water using a 4 mm nozzle at approximately 60 psi. Blasting media was Armex Maintenance Formula which has a Mohs hardness of 2.5 (Architect of the Capitol).

FIGURE 6. Heavily soiled/corroded areas were cleaned using IBIX Helix, an air-media blasting delivery system with water using a 7 mm nozzle at 80–90 psi. Blasting media was Armex Maintenance Formula XL (Architect of the Capitol).

FIGURE 7. Aluminum after the initial overall cleaning and rinsing. Remaining soiling was removed with targeted cleaning (Architect of the Capitol).

FIGURE 8. Aluminum after general cleaning. Dark streaking at cornice entablature resulted from leaking of the roof gutter and the vertical drain located in the corner column. Dust and overspray were very minimal due to the use of water in combination with the sodium bicarbonate, therefore protection was minimal. Although the Armex blasting media has a pH of 8.2, the soil at the trees was covered to avoid raising the pH of the soil and potentially impacting the health of the magnolia trees. Blasting media was swept and shoveled up at the end of each work shift and removed from the site. Remaining residue was washed away using power washers (Architect of the Capitol).

FIGURE 9. The aluminum porte-cochere enclosure after initial cleaning and rinsing. Remaining soiling and shadowing was removed by targeted cleaning after the general cleaning (Architect of the Capitol).

FIGURE 10. Side by side detail of the cleaned and un-cleaned aluminum. The sodium bicarbonate micro-abrasion effectively removed the soiling and light corrosion without removal of the aluminum or alteration of the original mold and sandblasted finish (Architect of the Capitol).

The combination of media, nozzles, delivery pressures, and media flow rates proved successful in removing the heavy soiling and corrosion at the exterior surfaces of the porte-cochere, but did not remove the much heavier corrosion at the interior of the structure. If there had been more time available to complete work, the contract could have been modified to test other media and to adjust the cleaning materials and methods to remove the corrosion from the interior aluminum. Further testing and cleaning will be done in future years.

LESSONS LEARNED

Although the cleaning was deemed successful, there were missteps and opportunities for improvement. During testing, the glass in the porte-cochere was blasted to assess what damage would occur and to determine if the glass should be removed for cleaning. The glass stops, like the decorative grills are installed with aluminum screws that are easily removed. During testing, there was no damage to the glass. It was not known, however, that the interior face of the glass had been treated with a shatter resistant security film. The micro-abrasion damaged the film, which could not be removed from the glass, requiring that all of the glass be replaced. When the glass was replaced, the staff did not allow sufficient space between the glass and the aluminum frame for expansion and contraction of the aluminum; multiple panes of glass have subsequently cracked as a result. The porte-cochere is made up of multiple cast aluminum parts assembled around a steel frame. While the joints appeared to be tight and are indeed generally watertight, there is enough gap that the fine particles of the sodium bicarbonate media were able to penetrate to the interior of the assembly. A year later, the soda continues to filter out of the joints in the aluminum. For future cleaning, disassembly of portions of the aluminum will be done, particularly at the sash muntins and glass stops. Additional dry brush cleaning and water washing has also be done in the months following the cleaning to more thoroughly rid the structure of the blasting media.

CONCLUSION

The 1932 cast aluminum porte-cochere was cleaned using low pressure sodium bicarbonate micro-abrasion with good overall success. The materials and methods accomplished the cleaning with minimal impact on the building operations and occupants, within the time allotted, at a reasonable cost, and without alteration of the original sandblasted aluminum texture and finish or any apparent long term damage to the aluminum. Areas of heavy corrosion at the interior surfaces were not fully cleaned using the media and pressures specified for the contract work, but further testing and cleaning can be undertaken in the future.

NOTE

1. Historical Records of the Architect of the Capitol, "Longworth House Office Building HL-1", David Lynn (Architect of the Capitol) and The Allied Architects of Washington DC, *Specifications for a New Office Building, House of Representatives*, 1929, Architect of the Capitol, Washington, DC.

REFERENCE

Lynn, D., and Allied Architects of Washington DC. 1929. "Historical Records of the Architect of the Capitol, Record Group 40, Art and Reference, Series 40.3: Longworth House Office Building HL-1, Construction Records 1929–1932." In *Specifications for a New Office Building, House of Representatives*. Washington, DC: Architect of the Capitol.

Redesign: A Recipe for Results: 1930s Architectural Aluminum Finishes, Restoration and Conservation

Xsusha Carlyann Flandro

ABSTRACT. This paper illustrates the challenges of architectural aluminum conservation through three case studies of three structures in New York City: a spandrel arch at an elevated subway station in Brooklyn, decorative panels on a bell tower at the Church of the Most Precious Blood in Queens, and art deco light fixtures and clocks on a public bathhouse at Orchard Beach in the Bronx. Condition issues, past interventions, and the goals of conservation and restoration are detailed for each case study. Original finishes, paint removal, aluminum alloy treatments, and reinstatement of finishes are described. The conservation and restoration of one structure in-situ presented difficulties because of the need to maintain public access, which prevented abrasive blasting to replicate an original method of finishing. A survey of typical 1930s architectural aluminum finishes used in the United States by the Aluminum Company of America is included.

Keywords: aluminum finishes, architecture, 1930, conservation, corrosion

INTRODUCTION

In the 1930s aluminum was hailed as the new wonder material capable of withstanding weathering and structural stresses. Advertisements of the Aluminum Company of America (ALCOA) claimed that “rain, hail and snow fight ALCOA aluminum and lose” (ALCOA Advertisement, 1932). As a result, aluminum was used for a wide variety of architectural features including windows, doors, spandrel panels and decorative elements.

Key to approaching the conservation of architectural aluminum is the understanding of early architectural aluminum finishes, what they were and how they were applied. Typical mechanisms of aluminum corrosion must also be recognized and understood to slow deterioration. In an effort to help conservators with these two issues, architectural aluminum finishes used by ALCOA during the 1930s are presented, and three types of corrosion found on coastal aluminum are briefly described.

To illustrate the many challenges of architectural aluminum conservation and restoration, three architectural aluminum projects in New York City and their restoration goals are described: an aluminum archway at an elevated subway station (1932) of the New York City Transit System in Brooklyn (Figures 1, 2),[1] decorative bell tower screens at the Most Precious Blood Roman Catholic Church (1932) in Queens (Figure 3), and Art Deco light fixtures and slim-line clocks at the Orchard Beach Bathhouse (1938) in the Bronx (Figure 4). While the three projects are different in size and scope, all three structures are located in marine environments (the farthest site is less than five miles from the ocean). Corrosion, cracks, and losses on their aluminum provide evidence that the metal is not as weather-resistant as ALCOA advertised.

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FIGURE 1. Elevated subway station arch (1932), Brooklyn, NY, prior to restoration, ca. 2008.

FIGURE 2. Elevated subway station arch, nearing complete restoration, ca. 2015.

FIGURE 3. Detail of cast panels on the bell tower, Most Precious Blood Roman Catholic Church (1932), Queens, NY, ca. 2013 after conservation.

FIGURE 4. Detail of a clock, Orchard Beach Bathhouse (1938), Bronx, NY, during examination, ca. 2013.

CORROSION ON COASTAL ARCHITECTURAL ALUMINUM IN NEW YORK CITY

Surface Corrosion

The most common surface corrosion noted on the three structures was a passivating layer of aluminum oxide, which forms immediately when unprotected aluminum is exposed to the Although aluminum oxides are white, at the three sites in New York City they generally appeared rough, absorbent and dark gray from incorporation of atmospheric soiling (Figure 5). Surface corrosion seemed more severe on architectural elements that were cast or sandblasted, apparently because of water-retaining texture and greater surface areas.

Pitting Corrosion

Pitting corrosion occurs in localized areas where chloride ions are present; on architecture it is frequently identified where aluminum is in direct contact with wet masonry. Masonry often

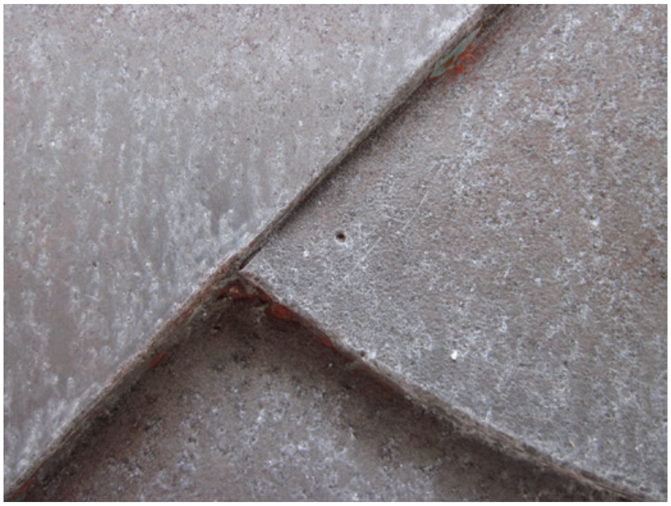

FIGURE 5. Detail of general surface corrosion with some pitting, elevated subway station archway before treatment.

FIGURE 6. Detail of severe corrosion where sheet aluminum was in contact with wet backup masonry, the elevated subway station archway before corrosion removal treatment.

contains chlorides either absorbed from the atmosphere and ground water or present at the time of construction, e.g., in concrete. Crevice corrosion is a severe form of pitting corrosion that occurs where oxygen is restricted, as in crevices. It is depicted in Figure 6 where aluminum sheet metal was in contact with wet backup masonry on the subway station arch. If alloy constituents are attacked by a corrosive medium (e.g., saline water), the corrosion velocity will be most rapid where the distribution of the medium is non-uniform, such as at an isolated area of contact with wet masonry. Any conducting impurity may increase the velocity of the corrosive attack. In the case of the subway station, crevice corrosion was observed to spread quickly, expanding in one area from 0.5 cm in diameter to 1.5 cm in less than four weeks once paint was removed.

Exfoliation Corrosion

Exfoliation corrosion (also referred to as layer or lamellar corrosion) was noted only on architectural elements next to wet masonry made from Duraluminum, an aluminum alloy containing between 3.5 and 5.5% Cu (Stratton, 1919: 80). On the Orchard Beach Bathhouse, Duraluminum components exhibited severe delamination, to the point that the metal had almost a hair-like surface texture with only fibers of metal still attached to each other (Figure 7). Exfoliation corrosion typically occurs on copper-containing wrought aluminum alloys with highly cold-worked elongated grain structures, such as extruded and rolled pieces.

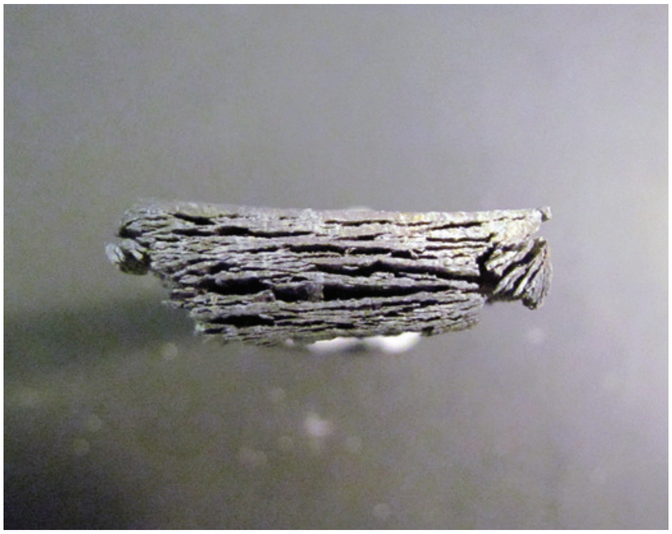

FIGURE 7. Cross section of exfoliation corrosion from the Orchard Beach Bathhouse clock hand exhibiting foliation corrosion.

1930S ARCHITECTURAL ALUMINUM FINISHES

During the 1930s finishes for aluminum were more limited than they are today and not overly complex. ALCOA held a monopoly over aluminum production in the United States and in 1932 published a promotional booklet titled *Aluminum in Architecture* for architects, manufacturers and designers; it details different uses and types of finishes available for the company's aluminum. As information in the booklet is invaluable and there are few remaining copies, excerpts from pages 117–129 are reproduced here with this paper author's notes in brackets [ ]:

> As-Cast: An as-cast finish is the natural finish created by the casting process in the foundry. This finish was not typically used as a final architectural finish but is found on architectural elements such as benches. "As-castings" always show some varying discolorations on the surface after they are removed from the sand.
>
> Sandblasted: A sand-blasted finish is achieved by bombarding the aluminum surface with an abrasive medium under pressure to create a matte, even, rough, pocked surface. [All trade documents during the period refer to this finish as "sand-blasted," but the term may be a bit of a misnomer as media other than sand can be used to abrade aluminum.] A sand-blasted finish is divided into three grades; coarse, medium and fine, the choice of grade is dependent upon the aggregate makeup and size and the air pressure used. [Historically for coarse and medium finishes, crushed silica (6–20 sieves) was utilized at 60–90 psi; for finer finishes, 100–200 sieves at 60–75 psi.]
>
> Deplated Finish: A deplated finish is a dark gray, electrolytically-formed oxide coating on sandblasted pieces. After sandblasting, the surface of the aluminum is anodically oxidized by electrolytic treatment in a sulfuric acid bath of low concentration, after which the piece is coated with a clear lacquer. [The term "deplated" disappears from use by the 1940s, likely because the process fell under anodizing.]
>
> Highlighted Finish: Highlighting is a satin, or polished mechanical finish applied only to raise sections of the aluminum design subsequent to the application of a base finish such as sand blasting or deplating [see Figure 8]. Two general methods used for highlighting are abrasive rotary wheels and belt sanders. The abrasive rotary wheels used for highlighting are sized between 6-inches to 12-inches, and are composed of sewn muslin buffs or other materials. Various grades (also called grits) of emery are used with these wheels, and are graded coarse to fine. ["Emery" refers to papers or cloth impregnated with corundum and magnetite or aluminum oxide. Cloths are graded by grit level and generically referred to in categories of fine, medium and course. Common grits range between 80 (coarse) and 12,000 (very fine).] The higher the number of grade used the finer the grit is. Coarser wheels use no.60 to no.120 emery, while the finer wheels use between no. 140 to no. 180 emery. The wheels are operated at speeds between 3400 to 4000 R.P.M.
>
> A belt sander, a machine or handheld device that uses strips of moving abrasives, is used where plain flat surfaces must be highlighted absolutely smooth and free from ripples. Emery belts of no. 80, 120, 140 and 180 emery are used in increasing order, depending on the desired finish. Number 0 buffing tallow (animal fat) mixed with a small amount of machine oil, or a thin paste of paraffin and turpentine are common cutting lubricants.
>
> Wire Brush: The wire brush finish is generally applied after a fine or medium sand blast. Wire brushes are composed of nickel, stainless steel, or German silver wires on a rotary wheel. Wire wheels typically measure between.006 inches to .014 inches in diameter. The speed of the wheel is important with best results being obtained between 450 and 600 R.P.M. [ALCOA recommended that large flat surfaces of aluminum be finely sandblasted before wire brushing to obtain a more uniform appearance.]

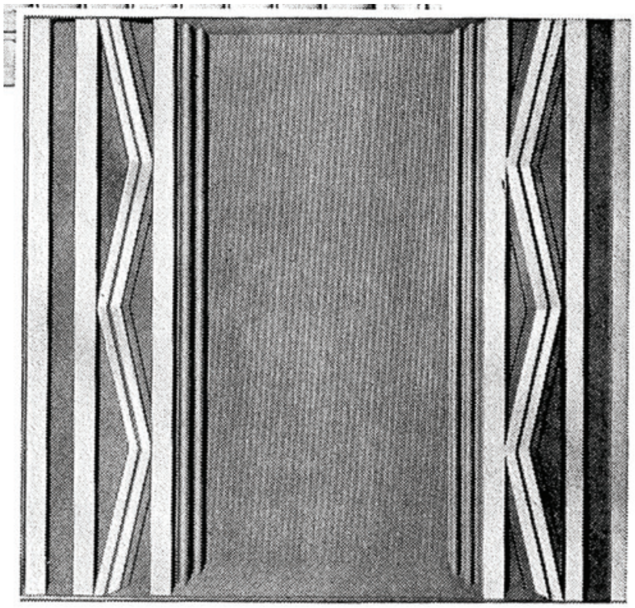

FIGURE 8. A 110-pound spandrel 4'8" × 4'4" that was deplated and highlighted. Unidentified location. From Aluminum Company of America, 1932.

Satin Finish: A satin finish gives a texture and luster with less reflectivity than a highly polished surface. The finish is created by imparting unidirectional scratched lines using various grades of abrasives or by means of a wire wheel. The surface is first finished using the Highlighting techniques, subsequently the aluminum is rubbed with emery clothes (various grades), or hand polished with a polishing paste of pumice and oil.

Hand-hammering: Also referred to as a "forged" finish, hand-hammering of aluminum is the processes by which the aluminum is repeatedly struck with a round metal hammer, creating small alternating convex and concave areas on the surface.

Oxidized Highlighted Finish: This is a multiprocess finish. The piece is first sand-blasted and the raised areas are highlighted. An electrolytic oxide coating is then applied to the piece. The sandblasted background develops a slate gray color similar to a deplated finish. The highlighted areas develop a satin gray color similar to a pewter finish. The shade of gray produced on the highlighted areas depends on the grade of abrasive used.

Painting and Lacquering: Applied paint or lacquer are used for both decorative and protective purposes. Transparent varnishes or lacquers are used to preserve aluminum finishes (As-cast, sandblasted, satin, highlighted, wire-brushed, hand-hammered, deplated) by keeping the surface from corroding. These materials are applied using the same techniques as on other coating materials. The surfaces are first cleaned off of all debris, oil and contaminants before coating applications. [ALCOA recommended the use of chemical cleansing agent such as Oakite Aviation Cleaner or Deoxidine.]

Dyeing: The electrolytic process of oxidation finds many applications. The film is remarkably hard and resistant to abrasion and is absorbent, which allows it to be colored by dyes and pigments. Dyeing is performed by pre-treating the aluminum with an acid solution with an electrical current and then dipping the aluminum in an organic or inorganic dye. [The company notes that there is insufficient experience to determine if dyed oxidation layers are suitable for outdoor application and that details of their process are proprietary. By the early 1940s the process was referred to as anodizing.]

Frosted Finish: A frosted finish to aluminum is achieved by etching the aluminum in a hot solution (120°F) of sodium hydroxide (caustic soda) followed by dipping treatment in a strong nitric acid bath.

Etching Designs on Aluminum: Hydrochloric acid is a rapid solvent for aluminum and can be decoratively used in special cases. The aluminum is first uniformly cleaned. Areas not to be etched are coated with a "resist" (any material not affected by the acid). The piece is then dipped in the acid bath. The resist is removed, the unetched areas which were protected by the resist, now form the desired pattern.

Electroplating: Electroplating aluminum coats the base aluminum with another metal. When electroplating aluminum, an initial deposit of nickel is recommended (to prevent galvanic actions) then the desired plating metal can be applied over the nickel. Electroplating is generally recommended for indoor use, as small pores can open up and in an outdoor setting, it would allow moisture to penetrate down to the base metal causing it to corrode, resulting in the peeling of the plating layer.

CHALLENGES OF CONSERVING AND RESTORING ALUMINUM: THREE CASE STUDIES

Conserving and restoring architectural aluminum and its finishes present numerous challenges, some of which are illustrated using the following three case studies. The first challenge of all architectural conservation projects is access for a condition assessment of the materials. For the subway station this required stripping away over 30 layers of paint to determine the state of the aluminum substrate. For the bell tower an elaborate scaffold had to be constructed to gain access to the screens. And because beachgoers are present during other seasons, the beachfront bathhouse could only be inspected in winter, with snow plowed up against the base of building elements.

Elevated Brooklyn Subway Station Archway

At the Brooklyn subway station (1932), a 30-foot-wide aluminum archway had been created to span a four-lane street. Review of historic construction specifications and drawings indicated that a deplated finish had been applied to stamped and cast aluminum surfaces after sand blasting, while extruded aluminum elements received a satin finish. Paint removal confirmed that these finishes had indeed been applied. The goal of the project was to match the arch's original appearance, while retaining as much historic aluminum as possible.

Smart Strip Pro (manufactured by Dumond Chemicals), plastic spatulas and pressure washers were used to remove the majority of the paint from the aluminum. A dry ice blast was used to remove any remaining paint in areas difficult to strip, such as small crevices. As the majority of the paint layers contained lead, containment of the effluent was crucial for hazardous waste disposal and personnel protection.

After paint removal, a tenacious, thick and absorbent gray corrosion layer was observed on the aluminum overall (Figure 5); original finishes remained intact only in areas protected by additions to the structure, such as behind telephones and signage. Lost elements and areas of severe aluminum corrosion were also noted in some locations (Figure 6). Holes, some of them as large as 15 cm by 15 cm, were present where the aluminum had been severely corroded in contact with repeatedly wetted masonry.

Large areas of severe corrosion were repaired by cutting them out using a Dremel rotary saw, and new aluminum sheets were welded in the voids by a certified welder with vast experience working in aluminum. Welding aluminum is difficult because of its low melting point: it is easy to blow holes in the metal, and warping and bowing of flat pieces is unavoidable. After welding flat areas, the aluminum had to be flattened either in a shop (for smaller elements) or on site. The new aluminum alloy was not an exact match to the original aluminum, but the difference in color was considered negligible. Where backup masonry touched the aluminum and had caused severe corrosion, the masonry was cut back to create a void between it and new aluminum to prevent contact corrosion in future. The aluminum was made as watertight as possible adjacent to the masonry.

Since most original finishes had been obliterated by corrosion, complete recreation was required, and the goal of the project was revised accordingly. Using period trade manuals and the original specifications and drawings for the project, methodologies for recreating the original finishes were determined and outlined for use in situ by the contractor. Deinstallation of the aluminum for shop refinishing was not an option, which precluded a true "deplated" finish on stamped and cast aluminum surfaces, because deplating requires an electrolytic bath.

Recreating the deplated finish required the most creativity. First, corrosion was removed. In a few places the blasting medium could be effectively contained, as required by the owner, and the original sandblasted surfaces were simulated by blasting with a fine aluminum oxide powder at low pressure (Figure 9). Most areas could not be closed to the public, however, and a hand-held wire-wheel rotary brush less successfully simulated the original surfaces. A belt sander was also tested, but it warped the metal and only affected raised surfaces.

"Aluma Black," a cold patina formulation manufactured by Birchwood Casey (pH < 1.0), was used to simulate the dark gray "deplated" finish. Working in small areas, the patination chemical was applied with a sponge cut to the width of the element being treated and allowed to dwell on the surface for one minute before rinsing to neutralize the surface. As the Aluma Black patina results in a deep black color rather than the gray of a deplated finish, the patinated areas were lightly hand buffed using 3M "fine" pads to lighten the coloration. After wiping the area with acetone, three coats of a VOC-compliant lacquer (Permalac-EF, manufactured by Peacock Laboratories) were immediately spray applied (Figure 10).

For cleaning extruded areas that originally had satin finishes (Figure 11), unidirectional sanding was done using 80, 100, and 120 aluminum oxide papers on hand blocks. Immediately after resurfacing, the metal was wiped clean of all oil and sanding grime using acetone on a lint-free rag, and three coats of the lacquer were spray applied.

FIGURE 9. Example of a medium sandblasted surface, elevated subway station.

FIGURE 10. Detail of the elevated subway arch after completion of the faux deplated finish using a cold patina.

FIGURE 11. Original satin finish on the elevated subway arch.

Most Precious Blood Church Bell Tower Panels

Six bell tower screens on the Most Precious Blood Church (1932) are curved, perforated cast-aluminum panels [approximately 6' × 8' (1.8 m × 2.4 m)] to which cast decorative features are attached (Figure 3). Visual assessment indicated that the screens were anchored to and pressed against a masonry substructure and that they had a sandblasted finish. Damage to the aluminum consisted of general surface corrosion that appeared absorbent, a few small stress cracks, and two loose pieces of ornamentation. Of most concern were severely corroded ferrous anchors used to attach the screens to the masonry. The structural engineer for the project recommended that the panels be removed and reset using a different anchoring system.

A more conservative conservation approach was taken for the bell tower screens than on the much larger archway, and the goal for the aluminum was conservation rather than full restoration. The panels were stabilized where needed by a few welded crack repairs, and loose elements were secured mechanically with aluminum fasteners.

The panels were cleaned with a 2% solution of Orvus WA Paste (manufactured by Proctor and Gamble) and warm water. The general corrosion layer was a concern as its absorbent surface was found to retain moisture, and a lacquer coating was recommended to inhibit further corrosion. However, the owners were hesitant about maintaining a coating on the 90-foot-high structure. The resulting decision was to wax the panels instead, providing temporary (1–2 years) moisture deflection, while meeting the requirements for maintainability by the owner. The panels were waxed using three coats of a heated clear paste wax, and no visual surface change was noted. All elements were reinstalled after the masonry substructure was properly waterproofed, thereby eliminating direct masonry and aluminum contact.

All different metals and materials were separated with either bituminous paint or neoprene gaskets to reduce the risk of future galvanic corrosion. New anchors were "wet-set" in the aluminum screens by coating them with silicone immediately prior to insertion.

Orchard Beach Bathhouse

Constructed through the Works Progress Administration, the Orchard Beach Bathhouse (1938) served as a large public facility for beachgoers. Wrought rolled sheet and extruded aluminum were used to create satin finished Art-Deco light fixtures and slim-line clocks at the Bathhouse. In 2013 the New York City Parks Department instigated extensive investigations into re-opening and re-utilizing the site through a Master Planning Study; at the time of this paper, however, restoration of the site had not yet begun.

At the outset, the goal was to determine if the aluminum elements could be salvaged and if so, how. A review of the original specifications revealed that metal features on the two clocks were constructed of "Duraluminum," a trade name for aluminum alloyed with approximately 4% copper (Sperry, 1911:437). The light fixtures were constructed of sheet and wrought aluminum.

The light fixtures had general surface corrosion with only small areas of pitting, measuring less than 2 mm square. Approximately 85% of the original satin finishes appeared stable and unaltered. Conservation recommendations for these elements included spot removal of the corrosion using unidirectional hand sanding with emery pads of decreasing coarseness until adjacent original satin finishes would be matched. This process is typical for restoring satin finishes on architectural metals but must be done carefully by a qualified technician or conservator to avoid marring of adjacent surfaces. All fixtures would then be cleaned using acetone and given three spray applied coats of the Permalac EF lacquer.

Unfortunately, the Duraluminum clocks were found to be unsalvageable. Exfoliation produced by intergranular corrosion of the wrought sheet hands and numbers had occurred to the point that they could be pulled off the structure with little effort (see Figure 7). While Duraluminum's copper content imparts structural strength, the alloy is not considered suitable for marine environments, where high moisture and chloride salts accelerate intergranular corrosion. A more suitable "nautical" aluminum alloy with a satin finish was recommended for replacement clocks.

CONCLUSIONS

These three projects, with aluminum elements ranging from large to small, illustrate different conservation approaches that can be taken when restoring architectural aluminum. These approaches were influenced by both an understanding of the original intent of the structures through historic documentation and the actual physical conditions of the aluminum. The goal for the archway was complete recreation of finishes while saving as much historic aluminum as possible and simultaneously making the structure watertight. In contrast, the conservation goal for the bell tower decoration was to preserve and stabilize the aluminum "as is." For the Bathhouse, the goal was to determine if elements were salvageable and how best they could be repaired or replaced.

As is often the case, compromises had to be made on all three projects. In-situ rather than workshop treatment of the arch proved challenging, in so far as it affected the method used for removing corrosion and resulted in application of a cold-applied conversion coating rather than replication of the original "deplated" finish. At the bell tower, the screens were structurally stabilized by making improvements to the support system, although questions were raised as to how best to slow deterioration of the surfaces while keeping within the owners maintenance requests. At the Bathhouse, it was found that while the light fixtures could be easily restored, the clocks would require complete replacement using a different alloy.

There are many options for the conservation of architectural aluminum ranging from total recreation to general maintenance, and it is often difficult to know how far to go. Too little intervention, and there is the risk of further material loss. Too much intervention, and irreplaceable surface finishes could be lost. Without research into historic documentation and knowledge of period specific aluminum finishes and corrosion mechanisms, conservation of these sites could not have proceeded appropriately. The main achievement of these three projects may not have been the end product, but the knowledge gained through research, discussions with the project teams and owners about what the goals for historic aluminum should be and how best to achieve them. By clearly defining a goal for each project, conservation and restoration treatments were directed fittingly.

NOTE

1. The New York City Transit Authority requested that the exact location of the station not be included in this publication.

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Preventive Conservation and Maintenance of Aluminium Artefacts and Collections

David Hallam

ABSTRACT. Aluminium alloys have vastly different metallographic structures and material properties depending on composition and heat treatment regimens; therefore, one preventive conservation approach will not cover all alloys. Current museum approaches to preventive conservation of aluminium alloys (both published and unpublished) are reviewed along with industrial and military practices. Methods considered include desert storage, dehumidification, the use of Volatile Corrosion Inhibitors (VCI) and Water Displacing Corrosion Preventatives (WDCPs). Best practices for storage and display, including environmental standards, are illustrated with both highly successful and catastrophic examples. Occupational health and safety hazards in relation to aluminium are addressed.

Keywords: aluminium, preventive conservation, corrosion, surface finishes, significance, hazardous materials

INTRODUCTION

In terms of volume of production, aluminium is the world's leading nonferrous metal. Because of its lightness and unique physical and chemical properties, its suitability for the construction of aircraft was recognised early last century. As a construction material it was essential to have stable and resistant surface finishes. Surface finishing techniques developed rapidly in both Europe and the U.S., so much so that it is now thought of as an extremely stable material. However, the passivating oxide film on aluminium can break down in a wide variety of circumstances that lead to rapid deterioration.

The physical, chemical, electrochemical and mechanical properties of aluminium and its alloys all vary in accordance with composition, heat treatments and environmental exposure factors. With more than 100 variations in the composition and heat treatments, a large number of preventive conservation options needs to be exercised accordingly.

In a museum context, literature on the preventive conservation of aluminium is scant and covers mainly sculpture, building heritage and large technological objects (LTOs). An electronic search showed that it is dominated by the creation of structural conservation supports for historic objects (Mazzolani, 2009). Discussion of aircraft is rare.

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BACKGROUND

It is only through an understanding of the construction of an object, its significance and its deterioration, that appropriate preventive treatments can be developed. Aircraft are usually made up of a body that is predominately one form of aluminium alloy, and paints and primers will cover aluminium surfaces on aircraft in all cases. For most WW2 aircraft in the U.S., for example, the main aluminium alloy would be 2024 T3 for the skin and 7075 alloy parts; both covered with a thin laminate of pure aluminium called Alclad. A Japanese WW2 binocular will be made from aluminium cast alloy that is copper plated, to which a "crinkle coat" of nitrocellulose black paint would be applied. On a British seaplane, the surface would be a synthetically grown aluminium oxide (anodized in chromic acid) to which a good dose of zinc chromate paint was added. A German aeroplane of the same period would have clad sheeting, chromic acid anodized aluminium, and an alkaline chromate conversion coating called a Modified Bayer Vogel (MBV) coating. On a late war German aircraft, zinc chromate paint will also be present in a nitrocellulose or acrylic base. Modern examples of the importance of surfaces on aluminium are the MacBook computer surface made by chemical etching and abrasive blasting to give a mat finish, then bright anodizing - a technique it shares with the brightwork on a 1970 Volvo wagon (Figure 1).

Today these historical finishes can offer important historical clues and technical information. They are complex and what make an object special. They are the interface to your senses. They need to be understood before any preventive treatments are even considered. As intrinsic parts of an object, every effort should be made to devise conservation strategies to retain them and other evidence.

Aluminium was used for the dome at the San Gioacchino Church in Rome in 1897. The alloy (98.3% Al with Fe and Si) has proved reliable with minimal corrosion over the last 100 years and was the parent of the 1000 series alloys, which contains 99.5% pure aluminium (Vargel, 2004:277). But when aluminium fails, it can be quite spectacular (Figures 2 and 3). I remember showing a visitor a Zero aircraft with Extra Special Duralumin (ESD) spar caps. The visitor commented that it was amazing that they were still using wood in the structure, having totally mistaken the corroded metal for an organic material. The ESD had severe intergranular corrosion and looked just like bleached degraded wood. United States and German WW2 aircraft deteriorate in the same way, as Figures 2 and 3 illustrate.

Aluminium alloys have failure mechanisms that include pitting, galvanic, and filiform corrosion; in the 2000–7000 series of age-hardened alloys, major factors are exfoliation and stress corrosion (Vargel, 2004). Corrosion rates are minimal till the RH exceeds 60% (Dean and Rhea, 1982). Pollutants such as SO_2, NH_3, and Cl increase the corrosion rate and promote pitting and crevice corrosion while reducing the threshold at which corrosion rates start to increase. When exposed to very high SO_2 concentrations and relative humidity above 50%, most aluminium alloys will corrode rapidly, forming a hydrated aluminium sulphate. Dust deposits attract moisture and pollutants resulting in increased corrosion rates. In some cases this may lead to pitting of upper surfaces of objects in unprotected storage.

Water staining of aluminium is possible due to its thermal conductivity, which promotes condensation on objects; when condensation occurs in void spaces, high corrosion rates result. In aqueous solutions the stability domain of the oxide coatings that passivate aluminium surfaces is in the region 8.4<pH>4 (Pourbaix, 1966) (Deltombe and Pourbaix, 1958).

FIGURE 1. Bright anodized aluminium a 1970 Volvo Wagon.

FIGURE 2. P-38 Lightning main spar showing spar cap delamination where it was immersed in a swamp.

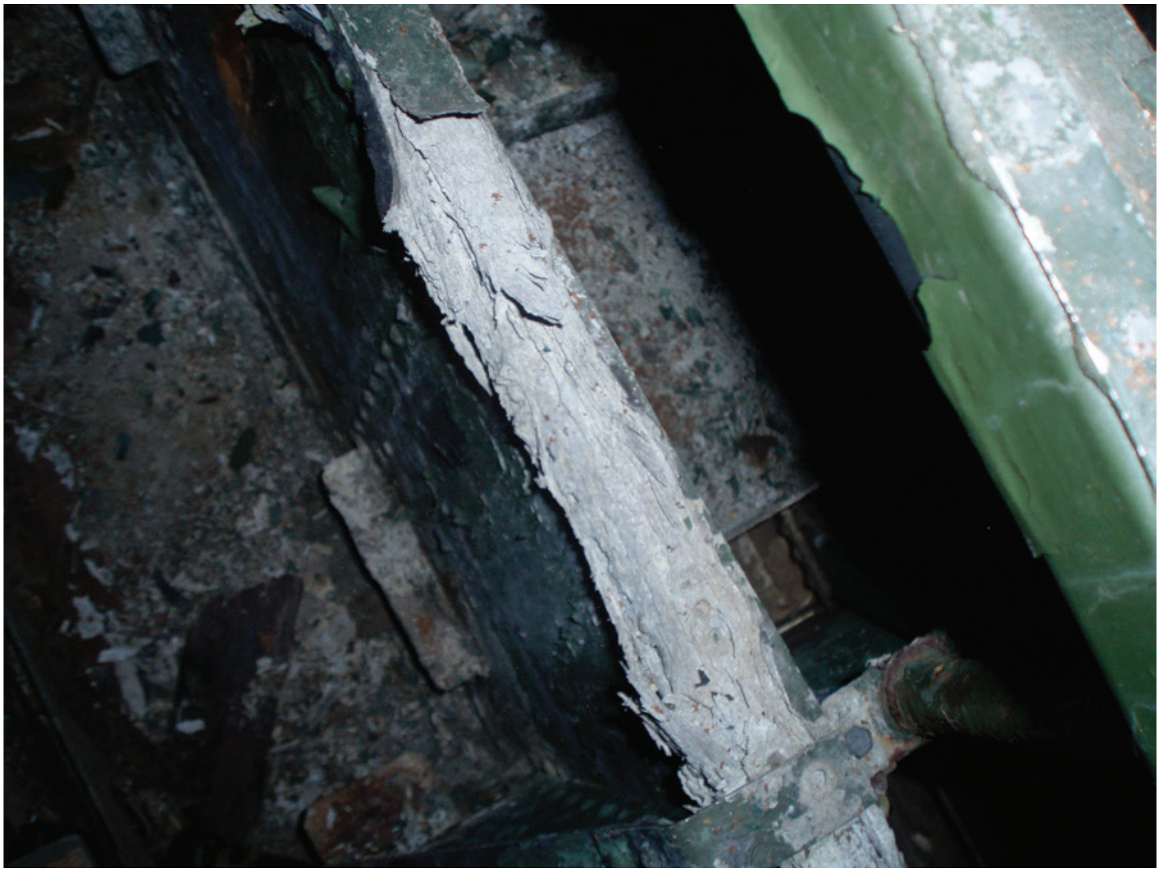

FIGURE 3. Inter-granular corrosion caused by chloride, high RH and the alloys type and heat treatment.

PRESERVATION APPROACHES

Technology preservation has always followed engineering and technical practice. It is only really recently, in the last two to three decades, that conservation practice has made a dent in the treatments and approaches of technological object conservation. As early as the 1970s, the preservation of aircraft stored out-of-doors was a concern of the Smithsonian's National Aeronautical and Space Museum (NASM) and curator Bob Mikesh (1971, 1989, and 1997). By the mid-1980s, the conservation of technology was well established as a growing theme in materials conservation. MacLeod (1983), Degrigny (1993), and Degrigny and Bailey (2004) wrote about the problems of aircraft recovered from the sea. Adams and Hallam (1993) and Ashton and Hallam (1990) looked at original surfaces and approaches to technological conservation. Preventive approaches for aircraft continues today with the work of Schwarz and Fix (2011) and Macleod (2006). Brunott et al. (2011) worked on conservation maintenance programs for functional objects and Hedditch et al. (2011) on the problems of corrosion in braking system. Otieno-Alego et al. (1998) did a lot of work on demonstrating how waxy and commercial coatings were useful for conservation treatments in museums.

Mechanics and engineers, architects and artists, corrosion scientists and craftspeople all use aluminium and will approach it's preservation from perspectives differing from conservators. Having seen some of the failures in industry, they tend to take a non-preventive approach. Their "corrosion is cancer" or the pragmatic "just blast clean it" approach will not win unified support from conservators. Neither will the "cotton bud" approach of conservators in turn win them over with its effectiveness. A logical decision making approach is needed to address the real needs of an object's preservation.

DECISION MAKING

Decisions about treating museum objects should not be based purely on their physical state or the science of preservation. Many other factors come into play in the decision making process (Figure 4).

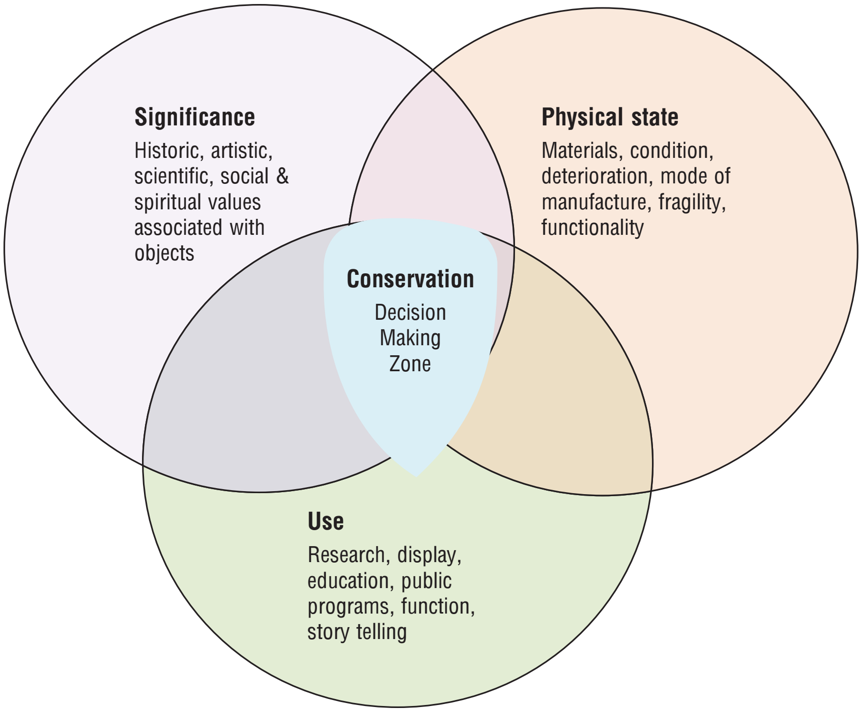

FIGURE 4. Schematic representation of the conservation decision-making zone (after Humphrey, 2012).

A significance assessment in accordance with the methodology outlined in *Significance 2.0* (Russell and Winkworth, 2010) is recommended as a key element in planning a preservation strategy. It provides a rational basis for retention of objects in a collection kept in a vast array of conditions by determining what is significant about an object and what needs to be preserved. It is a mechanism for reconciliation of material needs and preservation approaches.

For assessment, conservation treatment decisions should be made at the intersection of the following areas:

- Significance – scientific, artistic, historic, functional, spiritual, community
- Use – research, display, education, function, type example
- Physical state – material, condition, deterioration, functionality, integrity.

Each object has a life, and things that have happened to it over that life can be read from the object. Conservation treatments have to be carefully crafted so that the evidence of the object's "life" is not damaged. There may be connections or evidence of important historic events, cultural or religious practices, and ownership or use by an important national figure.

This requires an understanding of the values that make the object significant and a decision about what stage in the object's life will be represented after work is complete. Significance and value should be the primary determinates of the treatment approaches to be taken with an object or collection of objects. We need to ensure that the risk of damage to significance is minimised by our treatment approaches. Hence we need a collaborative workspace as shown in Figure 10.

A Wankel engine generator held by the National Museum of Australia, for example, tells the story of its use in the red sands of the Australian outback, not the technological mastery of the Wankel engine. Hence, the preservation of the red sand on the surface of the engine is important (Figures 5 and 6). With some community held objects, a pure conservation approach may be

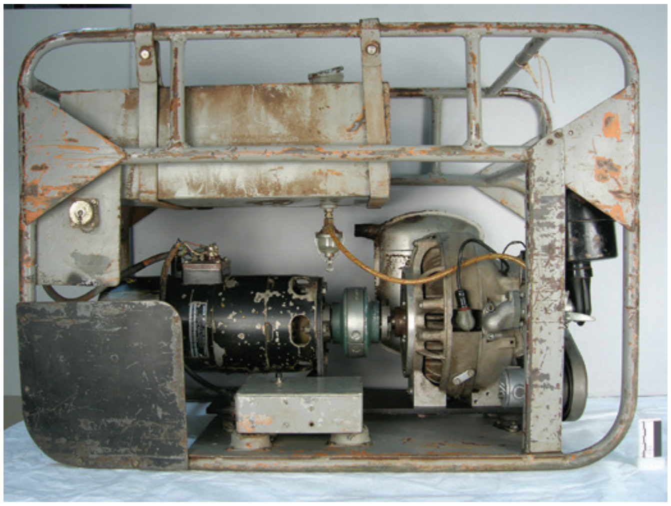

FIGURE 5. A Wankel engine generator after conservation treatment and inhibition tells the story of its use in the red sands of the Australian outback rather than the technological mastery of the Wankel engine.

meaningless if minimal gain in stability and preservation of original materials is at the expense of the object's significance as a focal point of a community and its continuing cultural tradition of interaction and restoration (Wain, 2012). Aluminium objects are no different: significance assessment is an important part of the preservation process.

FIGURE 6. Close-up of the adhered red dirt on the fuel tank paint of the Wankel engine. The weld in the tank adds to the surface information.

RISK ASSESSMENT

Risk assessment in industry is a well-managed process (Fujiyama et al., 2004). Getting conservators to place formal risk assessment into a practical framework is challenging. An attempt at visualising risk assessment shown in Figure 7 needs to be developed as a standard methodology (Brunott et al., 2010).

Having effective methods for assessing the environment of storage and display areas would mean that resulting data could be used to predict the maintenance requirements of the objects, rates of decay, and lifetimes in a meaningful way (Ryhl-Svendsen, 2008). This kind of approach has been used in the Australian Defence forces to predict maintenance requirements of the fleet and plan budgets. Museums can do the same.

Looking at the objects and their preservation environments is the best method of accessing the risks of deterioration and damage to significance. Monitoring methods for tracking corrosion and deterioration of objects can be divided into four types:

- Sensual
- Visual
- Physical analysis
- Chemical analysis

The interpretation of these variables is often subjective. Typically an older more traditionally trained mechanic or engineer will use all of these methods to access the state of an object and its ability to perform its original function. Smell, taste, feel, sound and look are all critical in the engineers' decision-making. Rather than measure the pH of a fluid, the traditionalist will

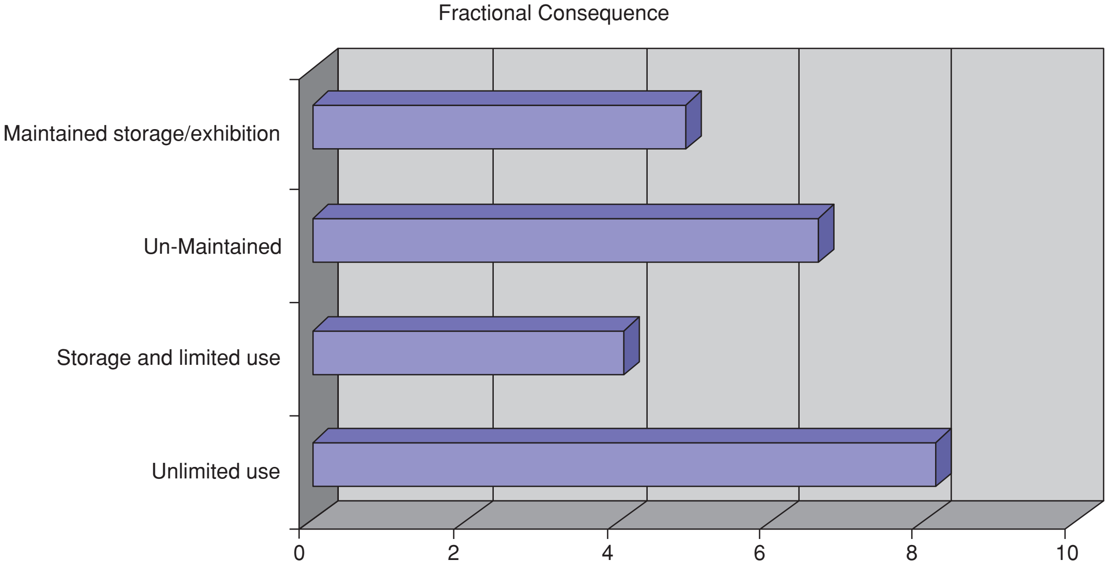

FIGURE 7. In this example several preventive scenarios are compared to find the best outcome (lowest consequence). Storage and limited use provides the best preventive outcome.

access the acidity much like a traditional winemaker would – smell and taste. Conservators do not necessarily have the skills (or desire) to emulate these methods and may have to rely on a quantitative approach for the assessment of condition or change in condition.

Fluid analysis has been used as a tool in the monitoring and failure analysis of operating LTOs for decades (Myshkin et al., 2003). This has mainly been with high-value installations or with LTOs that will cause a high loss of life should they fail (e.g. aircraft). Detection of changes in corrosion or wear before its effects can be seen or heard means that remedial action can avert tragedy and the high-value asset can be repaired and put back into service. Using a portable X-ray fluorescence (XRF) unit is useful for tracking alloying elements in oils, brake fluids and coolants. For thin films and crevices, however, XRF's bulk elemental analysis barely indicates what is happening, and the actual state is often visible only after substantial damage has been done. Measurement of changes in structural dimensions are one way of monitoring the state of large externally displayed objects and are currently being used with success in Hong Kong (Tse et al., 2011) and in Fremantle on dry docked ships and a submarine.

PREVENTIVE CONSERVATION OF ALUMINIUM OBJECTS CLEANLINESS

Cleanliness is critical with aluminium since defects in the protective oxide film will respond to differential aeration microenvironments created by grease, dirt and dust. In addition, the different porosity of coatings and permeability to oxygen migration will seriously affect the long term performance of the underlying metal. It is essential to avoid alkaline solutions since these will dissolve significant parts of the oxide film, which contain historical information about the object. Similarly, it is vital not to use mineral acids to clean the metal. The metals' finishing and inhibitor industries need to be consulted, and the most appropriate treatment to achieve the desired outcomes found. Detergents and surface cleaning methodologies are constantly being updated, so don't assume the product currently in use in a museum will be the most suitable. As Hinton showed in his presentation (this volume), surface-active products such as Zi400 are capable of changing the way we approach the conservation of aluminium, moving us from one-off treatments to maintenance approaches. For simple removal of dust and light grime, a microfiber cloth is very effective with minimal risk of scratching.

REDUCTION OF WATER ACCUMULATION AND TIME OF WETNESS

Reducing water accumulation and time of wetness on objects will reduce corrosion rates by several orders of magnitude (Vernon, 1927). In the simplest case it could mean making sure water does not pool in, on or around the object (Figure 8); moving the object into a covered area; or placing it in an appropriate storage area (Figure 9).

FIGURE 8. Reducing time of wetness by reducing pooling of water reduces corrosion.

FIGURE 9. Moving objects indoors significantly reduces corrosion rates, as exemplified by this aircraft at the National Museum and Art Gallery of Papua New Guinea.

COATINGS

Waxes and acrylics are not effective as "maintenance" coatings on aluminium: they tend to be one shot treatments and are hard to reapply. For large objects in less than ideal storage conditions, such as commercial aircraft, the best approach is to use

Water Displacing Corrosion Preventatives (WDCP) (Wilson and Devereux, 1984). These coatings can be used in museums as part of a cyclical maintenance program (Hallam et al., 2004). Likewise they could also be used on internal void spaces of sculptures and other objects where condensation is a risk. We need to be aware that lacquered aluminium will undergo filiform corrosion without an inhibitor in high % RH environments and where pollution residues are present on the metal surface. Insufficient film thickness is also a critical factor in promoting this form of corrosion.

MOTHBALLING

Placing collections into long-term storage has been practiced by the military, and their techniques of outdoor storage can be emulated in museums with success (Mikesh 1989). Techniques involving dehumidification have been well documented (Munters, 1984) (Cargoaire, 1988) (Turner, 2005) and are useful in museums. Wrapping with plastic shrink wrap to create sealed environments, inhibitor coatings and washing (Gelner, 1998) (Miksic, Johnson, and Martin, 1984) are useful, but none of these strategies is a panacea. The objects still need to be accessed for periodic inspections and reapplication. Failure to inspect and reapply inhibitors can lead to catastrophic failures in museum storage.

MAINTENANCE STRATEGIES

Finding a successful preventive practice model or suite of options involves a critical assessment of the relevance of commercial products and trade practices. Once suitable practices have been rigorously assessed in conservation laboratories for their relevance and effectiveness, they can be implemented in a collaborative way to ensure the objects significance is preserved.

Experience at the National Museum of Australia (NMA) has led to the development of new procedures that assist the museum's collection managers in scheduling monitored maintenance and maintaining full functionality preservation as cost-effective approaches to the care of technology collections. This approach targets conservation for the most important, most used, and most vulnerable objects and demonstrates the consequences of no response. Details of the methodology can be found on the NMA website and in recent publications in the ICOM-CC, Metals Working Group conferences (Brunott et al, 2010).

Maintenance of operating functional objects in safe conditions is essential to avoid the serious consequences of incorrect storage. Objects with lubrication and hydraulic and cooling systems corrode and deteriorate if they are stored without maintenance and a monitoring program that circulates and changes inhibitors. This was exemplified by the studies carried out on a Lancaster Bombers coolant system (Heath et al., 2002). Objects with void spaces and lap joints fair a little better in static storage but will still corrode where moisture and debris can build up. The risk of corrosion detrimentally affecting the significance of the objects is very high.

When dealing with materials produced in the last century one has to assume the primers used were the best available but may be hazardous. We can assume that zinc chromates were used extensively in the construction of objects and that chromates were used in the anodizing processes. Cadmium may have been used in any associated ironwork. If we are dealing with aircraft, we can assume that radioactive luminous paints may have been part of the instruments and may have been redeposited throughout lower sections of the aircraft structure. PCBs will be present

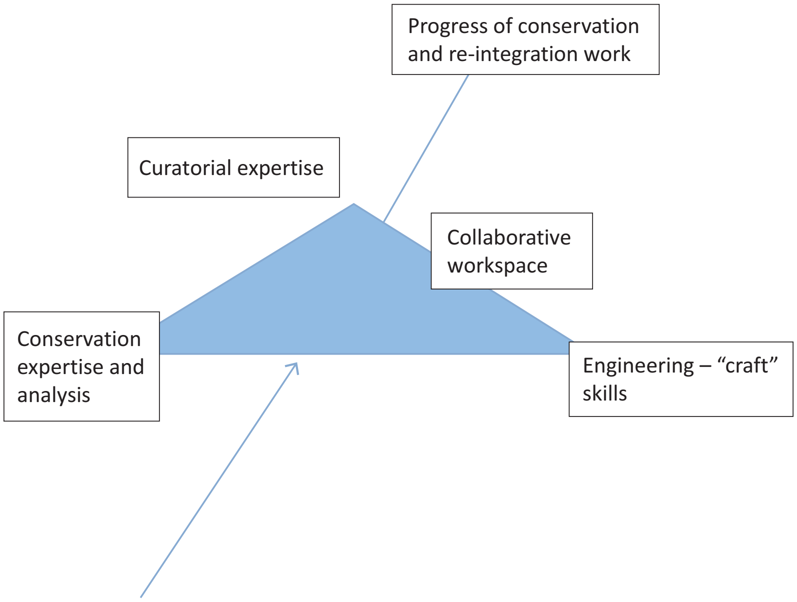

FIGURE 10. Schematic diagram of a collaborative workspace.

in electronics. It is essential to take a cautious approach to ensure we understand the hazards and how to deal with them within appropriate legislative backgrounds of your state or country.

STORAGE

Dinsmore and Lund (1962), Erickson (1954), and Killingray (1986) discuss the problems of the storage of functional objects in a military context for periods of non-operation. Dehumidification and periodic exercise are necessary to maintain functional objects in operable condition in long term storage. David Monthan at the Air Force Base uses natural dehumidification and yearly maintenance on its flying aircraft. Some aircraft have been stored for 20 years prior to being flown again (see Figure 1 in Alexander's paper, this volume). The Prototype 707 owned by Smithsonian's NASM was stored under this regime before being flown to Seattle for a rebuild in 1990 and finally to Dulles International Airport near Washington, D.C. on August 27, 2003.

Dehumidification has been used in museums for objects such as the optical equipment at the Australian War Memorial in Canberra or tanks in a maintenance storage cycle. A similar approach using the natural dry environments of Canberra has been used to store vehicles (Figure 11).

CONCLUSION

We need to be aware of what we are conserving and why, and for whom we are doing this job. It is important to understand what is significant and what are the risks of losing that significance due to degradation. We need to choose our preventive processes to minimize degradation with minimal intervention. We need to choose and execute our preventive processes in a collaborative manner. Aluminium alloy artefacts need to be kept clean, dry and maintained. During these processes it is vital to be alert to a wide range of health hazards associated with past technologies, for which the long-term exposure to toxic and radioactive materials was poorly understood.

FIGURE 11. Vehicles kept dust free and dry in storage by enclosure in a plastic bubble at the National Museum of Australia.

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The Boneyard: The World's Largest Military Aircraft Repository

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ABSTRACT. Davis-Monthan Air Force Base (AFB) in Tucson, Arizona, United States, is home to a unique and staggeringly vast collection of aerospace vehicles. The Aerospace Maintenance and Regeneration Center (AMARC) was originally created as a repository for the long-term storage of a growing number of surplus United States military and government aircraft after World War II. Over fifty years of preservation techniques and methodology development has recently drawn the attention of conservators interested in the facility's impressive results. Its location, geology and environment play key roles in the successful maintenance of thousands of aircraft. The AMARC serves as a large-scale preservation laboratory with implications and useful data for aerospace museums facing the challenge of conserving their collections, particularly those containing functional objects.

Keywords: Aluminum, Aircraft, David-Monthan Air Force Base, preventive conservation

INTRODUCTION

Following World War II, the need to store the fleet of surplus United States (U.S.) military aircraft resulted in the development of a facility near Tucson, Arizona, at Davis-Monthan Air Force Base (AFB). Currently, its official designation is the "Aerospace Maintenance and Regeneration Center" (AMARC); however, it is more commonly known as simply "The Boneyard". The primary function of the 309th Aerospace Maintenance and Regeneration Group (AMARG), the military and civilian personnel in charge of the AMARC, is the preservation and storage of the nation's surplus aircraft for programmed reclamation and the provision of spare parts for every branch of the military and government agencies. It should be noted that the terms "AMARG" (personnel) and "AMARC" (location), are often used interchangeably.

The site was originally selected for practical reasons, mainly the low humidity levels and sparse rainfall as well as the alkalinity and hardness of the soil. These attributes, along with the vast, open landscape, provide an ideal climate for the long-term storage of aircraft and aerospace vehicles, particularly those constructed using aluminum alloys, with minimal concern for degradation and corrosion. The natural climate and geology of the area make for such ideal preservation conditions that restoration facilities were added for stored aircraft to be returned to flight-capable status in 1985. As of December 2008, the facility housed more than four thousand aircraft as well as 13 Titan II rockets from all branches of the U.S. military, the National Aeronautics and Space Administration (NASA) and other federal agencies, with an original purchase total in excess of thirty-five billion dollars (*History Factsheet*, 2008).

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FIGURE 1. Aerial view of the AMARC at Davis-Monthan AFB. Photo credit: U.S. Navy.

Davis-Monthan AFB is located on the southern edge of Arizona tucked beneath the Santa Catalina Mountains just outside of Tucson, 70 miles from the Mexican border. At over 9,000 feet, Mount Lemmon dominates the landscape, providing the backdrop for the surreal image of over 4,000 aircraft neatly arranged over an area in excess of 2,000 acres (Figure 1). This paper will describe why this particular site was chosen for this repository, the basic principles of desert storage preservation and what lessons can be learned from this experience for the long-term preservation of aircraft and other functional aerospace vehicles.

HISTORICAL BACKGROUND

At the close of World War II, a need arose to find a viable and economical storage solution for the vast fleet of U.S. military aircraft that were no longer required for active service during peacetime. In April of 1946, the U.S. Army's San Antonio Air Technical Service Command selected Davis-Monthan Air Force Base to serve as a storage facility to house the numerous excess B-29 and C-47 aircraft remaining in the service's inventory (*History Factsheet*, 2008). With the creation of the Air Force as a separate U.S. military branch in 1947, the facility added support for active flying units and continued providing the nation with functional aircraft and spare parts through the Korean War, reverting to its storage role once hostilities ceased (AMARC Experience, n.d.).

In 1964, the Secretary of Defense instituted the consolidation of military aircraft storage to this singular location (*History Factsheet*, 2008), and by February 1965 the responsibilities of the Military Aircraft Storage and Disposition Center, as it was designated at the time, were expanded to include surplus aircraft from all the branches of the armed services (Air Force, Navy, Marines, Coast Guard and Army). This period also saw the escalation of fighting in Vietnam, and the Boneyard was called upon to quickly provide the needed aircraft and spare components, again reverting to storage following the end of the conflict. By 1973, the total number of stored aircraft peaked at over six thousand (AMARC Experience, n.d.).

The 1980s saw the facility expand again to include the preservation of TITAN II, THOR and ATLAS rockets used for satellite launches by the Air Force's Space Division. In 1985, the facility was renamed the Aerospace Maintenance and Regeneration Center to more aptly convey its role of promoting the regeneration and reutilization of assets, depot-level maintenance for active units, and its historic storage functions (*History Factsheet*, 2008).

UNIQUE ENVIRONMENTAL ATTRIBUTES FOR PRESERVATION

The natural climate in Tucson, AZ is well-suited to the long-term storage of aerospace equipment, particularly for aluminum alloys. Over 300 days of sunshine per year and average lows of 39 degrees Fahrenheit in January and highs of 78 degrees Fahrenheit in July provide a relatively steady, temperate climate nearly void of extremes (*Monthly and Daily Normals (1981–2010) for Tucson, Arizona*, n.d.). The average temperature is 68 degrees Fahrenheit; the average relative humidity is between 8 and 15%, rarely exceeding 59%; and the annual rainfall is fewer than 12 inches.

Situated in a desert valley between five mountain ranges, Davis-Monthan AFB and the AMARC are sheltered from most forms of adverse weather. Summer monsoons, brought on by the weather trapping actions of the surrounding mountains, are short-lived (AMARC Experience, n.d.).The field elevation is listed as 2,704 feet above sea level, adding to the arid desert climate. Even in the presence of an afternoon downpour during July and August, the soil composition and convex shape of the area provides for excellent drainage. The soil itself is largely comprised of an approximately 40% calcium carbonate material known as *caliche* (Cooperative Extension, College of Agriculture, The University of Arizona, 1998). The caliche concretion has the added benefit of acting as a ready-made hardened tarmac capable of supporting many heavy airframes and the equipment necessary to work with such large aircraft, as shown in Figure 2 (History Factsheet, 2008). The high calcium carbonate content gives the soil a slightly alkaline pH of approximately 7.6 (Custom Soil Resource Report of Pima County, Arizona, Eastern Part, 2013). The pH level added to what is essentially a chloride free environment (electrical conductivity of the soil between 0.0 to 2.0 mmhos/cm) provide exceptional properties against corrosion (Soil Variables, n.d.).

FIGURE 2. Boeing VC-14 aircraft on caliche soil at AMARC.

309TH AEROSPACE MAINTENANCE AND REGENERATION GROUP (AMARG)

Highly-trained AMARG personnel carry out a nearly constant process of corrosion prevention and preservation work. Their tasks are carefully scheduled, applied and documented with emphasis on preserving the functionality of the aircraft. The entire process has been meticulously outlined in the form of Technical Order 1-1-686, *Desert Storage Preservation and Process Manual for Aircraft*. This 128-page manual details the procedures and materials used at the AMARG to such effectiveness that in August of 2013, a WB-57 F, like the one shown in Figure 3, was returned to flight status as a high altitude test-bed for NASA after forty-one years of storage at AMARG (Filmer, 2013).

Upon an aircraft's arrival to the AMARC, typically under its own power, a designation is given to denote the extent of preservation necessary based on the intended length of time it will be stored. The designation "Type 1000" refers to aircraft stored in near flyable condition that can remain so for up to four years without any preservation efforts. "Type 2000" is generally given to aircraft to be used for reclamation of spare parts as needed. "Type 3000" denotes an aircraft in flyable condition that is pending transfer, and "Type 4000" is for those aircraft that have reached the end of their usable life and are awaiting disposal with minimal preservation. For the purposes of this paper, only Type 1000 and 2000 will be discussed.

Each aircraft is "safed" (removal of hazardous components such as explosives-actuated devices like ejection seats) and thoroughly inspected for any damage or missing parts. Components are inventoried, and those deemed classified or prone to deterioration are removed and securely stored. Then, the airframe is moved to the "Flush Farm," where its fuel system is drained and flushed with NATO grade 1010 preservative oil (Technical Order 1-1-686, 1998). The oil is circulated through the entire system and engines, with any excess reclaimed and recycled. The next step is the "Wash Rack". At this stage, the aircraft is cleaned using water and a mild detergent, then evaluated for corrosion. Any issues are noted, and an appropriate treatment (replacement of panels, paint, etc.) is applied prior to the final stage: sealing the

FIGURE 3. B-57 on "Celebrity Row" at AMARC shown on the left and NASA WB-57 F shown on the right. Photo credit: NASA.

aircraft for storage. Desiccant material is then placed inside the engine intake and exhaust openings, other openings are sealed with a barrier material which varies based on aircraft type, and tape is used to seal access panels, doors and plates.

The "sealing" process uses a multi-coat, strippable, vinyl compound called Spraylat (Spraylat Corporation was acquired by PPG Industries in December of 2012). At this time, the term "spraylat" is an eponym used amongst AMARG technicians to refer to any of the water-emulsion, strippable materials for protection of stored aircraft conforming to military specification MIL-C-6799. This two-part water based system is sprayed on to the aircraft following specific guidelines outlined in Technical Order 1-1-686 (AMARC Experience, 2008). The undercoat is black in color and seals the airframe's exposed cavities, such as the cockpit and engine inlets, and the exterior surfaces against moisture, dirt, wind abrasion, and animals or insects. This coat is applied to a wet film thickness of twelve to fourteen mils. The second coat is white in color due to the addition of ceramic particles. This results in a harder, more resilient surface and increases its ability to reflect sunlight and prevent heat build-up within the aircraft, thereby avoiding damage and rapid deterioration of materials and components. This second material is applied in two coats to a dry film thickness of at least five mils. In order to facilitate the removal of the strippable film at any point after application, nylon ripcords are positioned on the framework to aid this operation. After this is accomplished, a thorough examination is performed and necessary touch-ups applied.

Once the airframe is properly sealed, maintenance is recorded on the exterior of the aircraft, as shown in Figure 4, and periodic inspection and repair is necessary only every six months (Technical Order 1-1-686, 1998). This coating system is so effective that internal temperatures of the airframe are kept within ten to fifteen degrees of the ambient air, a feat that earlier attempts at "cocooning" failed to accomplish. Prior to the implementation of current procedures, the internal temperatures of stored aircraft could reach over 200 degrees Fahrenheit, and moisture trapped inside the aircraft caused significant damage (Seitz, 2014).

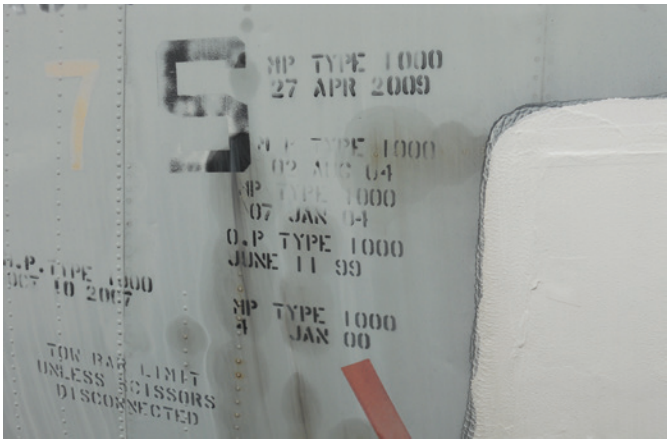

FIGURE 4. Stencils noting maintenance performed on stored aircraft.

The difficulty in providing adequate and environmentally friendly protection to large, composite and multi-metal objects has led to the development of new materials. In 2007, *R&D Magazine* presented an award to the Air Force Research Laboratory for its collaborative development of a non-chromate based aircraft primer. Produced by Deft Coatings (acquired by PPG Industries in 2013) and first used in an operational environment on F-15s, this product eliminates many of the risks to the environment and personnel associated with chromate-based paints. It was named as one of the "100 Most Technologically Significant Products" by the magazine (Cooper, 2008). As technologies and techniques continue to advance, conservators have sites such as AMARC at their disposal, filled with myriad examples of real-world applications across a spectrum of materials.

PIMA AIR AND SPACE MUSEUM

Situated directly adjacent to the AMARG facility is the Pima Air & Space Museum (Figure 5). This huge collection of over three hundred aircraft is the result of collaboration between Air Force leadership at Davis-Monthan and the local government. In an effort to preserve the historical significance of the aircraft stored there, AMARG officials set aside examples of the many types of aircraft on an unofficial "Celebrity Row" (Marchand, 2014).

In 1966, the idea was formed to create a separate museum to house the collection and make it more readily available for the public's viewing. It would take 10 years of fundraising, site reparation to meet the Air Force Museum's standards, and transporting the initial collection of approximately fifty aircraft before the doors opened to the public on May 8, 1976. What began as "little more than a fenced-in field with airplanes parked on it and a small, white trailer to serve as [a] ticket booth" today boasts over 189,000 square feet of indoor displays and the massive outdoor park, in which objects range from WWII to modern air and space craft (Pima Air & Space Museum, n.d.).

CONCLUSION

The Air Force and the AMARG have inadvertently provided a large-scale, long-term experiment to evaluate the effectiveness of specifically developed preservation techniques. Several decades of development have resulted in an accumulation of knowledge on modern materials preservation. Most museums may not have a need to preserve the functionality of their collections; however, AMARC has demonstrated how to utilize the environment combined with corrosion control and prevention methods to achieve this goal. While the same environment may

FIGURE 5. Aerial view of Pima Air and Space Museum. Photo credit: PASM.

be difficult to duplicate in a museum setting, the results underscore the importance and effectiveness of a conservation and maintenance program aimed at maintaining moisture and temperature control. Finally, a new generation of environmentally friendly corrosion inhibitors has shown great potential for application to aluminum.

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About the Contributors

Jerrad Alexander was the lead conservation technician on the Apollo F-1 Engine Conservation project for the Cosmosphere International SciEd Center and Space Museum. He served in the United States Air Force as an Aircraft Armament Systems Specialist and Combat Search and Rescue Flight Engineer. He earned an Associate degree in Aircraft Systems Technologies from the Community College of the Air Force, a Bachelor of Arts degree in Organizational Management from Ashford University, and his Master of Cultural Materials Conservation graduate degree from the University of Melbourne, Australia. His training, experience and research focus on the care of large technology, aerospace and military museum collections. E-mail: jalexanderconsult@gmail.com

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James Ashby is an architect specializing in the conservation of the built heritage of the modern era. Based in Ottawa, Canada, he has advised on numerous architectural conservation projects, has participated in the development and delivery of a national training program on modern built heritage and has advised on several nominations of twentieth century heritage to the UNESCO World Heritage List. Ashby was recently a guest scholar at the Getty Conservation Institute, pursuing his research on the legacy of the megastructure movement.

George T. Bailey graduated from the University of Canberra in 1991, with a Bachelor of Applied Science degree in the Conservation of Cultural Materials (Objects and Metals). George has worked at the Australian War Memorial since October 1990, and is currently acting Manager, Preventive, Objects and Large Technology Conservation. In 1993 he undertook a three month sojourn at the Imperial War Museum, Duxford, UK, and in 1997 he was seconded to the Auckland Institute and Museum, NZ, preparing aircraft for display. George has lectured in conservation at the University of Canberra, University of Melbourne and Canberra Institute of Technology.

Justine P. Bello is Architectural Conservator for the National Park Service, where she oversees the ongoing preservation of major memorials and works of public art across the National Mall and Memorial Parks. She maintains expertise in all aspects of conservation including condition assessments, conservation treatments, materials testing and analysis, and construction management. Prior to joining NPS, Justine was Senior Conservator and Vice-President of Operations at Conservation Solutions, Inc. Justine holds a MS in Historic Preservation from Columbia's Graduate School of Architecture, Planning and Preservation, a BA in Historic Preservation from the University of Mary Washington and has been a Professional Associate of the American Institute for Conservation since 2010.

Sylvie Bergès after studying law and information-communication, she discovered in the mid-80s the Seaplane History Museum of Biscarrosse in the Landes (France), created and directed by Marie-Paule Vie-Klaze. The latter transmitted to her a passion for the fantastic history of Biscarrosse aviation heritage. She took over the management of the Museum in 1999. She now strives with her team, to maintain the "memory" of Biscarrosse Lake, to enrich the museum's collections, ensuring the preservation of the technical and industrial heritage, and to share the history of aviation.

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Clara Deck is Senior Conservator at The Henry Ford. She has designed and supervised conservation treatments for thousands of objects from a carousel, steam engines and automobiles to furniture, decorative arts and toys. She has work on dozens of exhibitions including the newly opened Driving America, numerous loans and ongoing storage upgrades. A member of the American Institute for Conservation, she has served as a grant reviewer for IMLS, NEH and Save America's Treasures. She has a particular interest in industrial artifacts, modern materials and mechanical musical contraptions.

Christian Degrigny received a PhD in analytical chemistry from the University of Paris IV in 1990. As an engineer in electrochemistry, he specialized in electrochemical diagnosis and treatment of historical and archaeological metallic objects. From 1991 to 2000 he worked as a conservation scientist in Valectra of Electricité de France laboratory and Art-Métal and at Arc'Antique private workshop. From 2000 to 2003 he continued his work at the EVTEK in Finland and the Centre for Restoration in Malta. In 2006, Degrigny became a part-time lecturer and researcher at the Haute Ecole Arc Conservation-restauration (HE-Arc CR) in Neuchâtel, Switzerland.

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David Hallam has been involved in the conservation of cultural heritage since the mid 1970's, specializing in metallic and technological objects conservation. For over 20 years, Hallam headed the metallic objects conservation program at the Australian War Memorial. Hallam was Head of Conservation at Queensland Museum and established the Objects Conservation Program at the National Museum of Australia. Hallam's practical approach to preventive conservation lead to appointment as Woodrow Wilson Fellow of the National Air and Space Museum of the Smithsonian Institution in 1989 and to appointments as Visiting Fellow at the Research School of Chemistry at ANU.

Bruce Hinton has an honours degree from the University of Queensland, Department of Mining and Metallurgical Engineering, Brisbane Australia, and a PhD in Corrosion Engineering from the University of Manchester UK. Bruce was involved for over 40 years in research at the Defence Science and Technology Organisation in Melbourne in the areas of atmospheric corrosion, corrosion inhibition, metal finishing, stress corrosion cracking, corrosion sensors, corrosion fatigue and hydrogen embrittlement. During that period he acted extensively as a consultant to the Australian Air Force, Navy and Army, in the field of corrosion prevention and control in aircraft structures. In 2010, he was appointed an honorary Adjunct Professor in Corrosion Science and Engineering at both Monash and Deakin Universities in Melbourne. He also acts as a consultant to Australian companies working in the aerospace, gas pipeline and water treatment fields.

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Rosa Lowinger holds a 1982 M.A. and conservation certificate from NYU's Institute of Fine Arts. A Fellow of the American Institute for Conservation and the American Academy in Rome, she has been in private practice for over 30 years, serving dozens of municipal and contemporary private art collections. In 2013 she co-chaired the Association for Preservation Technology's workshop on modern metal finishes and curated *Concrete Paradise: Miami Marine Stadium* for the Coral Gables Museum. She is the author of *Tropicana Nights: The Life and Times of the Legendary Cuban Nightclub* and numerous articles on art, architecture and contemporary culture.

Ian MacLeod was Executive Director of Fremantle Museums and Collections at the Western Australian Museum from 1978 until 2016. With Neil North, he pioneered the use of in-situ corrosion surveys and in-situ treatment of metallic artifacts on historic shipwreck sites. He led the conservation team that restored the historic *Xantho* (1872) steam engine during a 25 year treatment program. MacLeod has demonstrated that the application of corrosion science to the interpretation of events in the life of artifacts provides a powerful tool for heritage management programs. On his 2016 retirement from the museum, Ian was made a Fellow of the Western Australian Museum in recognition of his remarkable contribution to conservation of cultural heritage. He is now in private practice and consulting on collection management, rock art and metals conservation.

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Emmanuel Rocca is a researcher at the Institut Jean Lamour at the University of Lorraine and CNRS in Nancy, France, where he has worked since 2000. His research topics are focused on the electrochemistry of materials devoted to the study of corrosion mechanisms and corrosion protection of metals. His research includes the development of corrosion inhibitor formulations, chemical conversion coatings, and some electrochemical coatings such as anodizing for several applicants and industries. For metallic artefacts, he is working on corrosion mechanisms of complex materials such as corroded iron or aluminum in order to propose new strategies for corrosion protection. He has a PhD from The University of Lorraine, France.

Richard W. Russell is the manager of the Materials and Processes Engineering Branch within the Materials Science Division at Kennedy Space Center. This branch supports design and processing activities for flight programs and ground systems at KSC. Rick has over 25 years of experience in the field of Materials and Processes with NASA, the DoD and private industry. Rick has Master's degree in Materials Science and Engineering from the University of Florida, a Bachelor's degree in Metallurgical Engineering from the University of Illinois and has extensive experience in all aspects of materials and processes covering design, manufacturing, processing and nondestructive evaluation.

D. Saha is Senior Scientist at the Central Pollution Control Board (CPCB) in Delhi, India since 1988. CPCB is the apex body for prevention & control of pollution in India. He has been involved with river water quality profile study, survey of polluted areas, preparation of environmental management plan, and establishment of Laboratories in CPCB. He also established an air pollution monitoring Laboratory at Tajmahal, India and been involved in various prevention and control programs in and around the Taj-Trapezium Zone. Since 2009, Dr. Saha serves as the Head of Air Laboratory at the CPCB.

Malgorzata Sawicki is the Head, Frames Conservation, at the Art Gallery of New South Wales, Australia since 1986. Malgorzata trained in gilded/ polychrome objects conservation at the State Enterprise for the Heritage Preservation, Warsaw, Poland, and studied Preservation of Architectural Heritage at the University of Nicholas Copernicus, Poland, prior to her migration to Australia. She has a Master of Applied Science in Materials Conservation, with Distinction, (2000), and PhD (2009) for research on non-traditional gilding techniques, from the Western Sydney University, Australia. Malgorzata was honoured by AICCM with the *Conservator of the Year* award (1999), and *Certificate of Appreciation for Outstanding Research in the Field of Materials Conservation* (2009). She was Coordinator of the ICOM-CC Wood, Furniture and Lacquer Working Group (2008–2014); she is Fellow of IIC, and professional member of AICCM.

Lyndsie Selwyn graduated in 1985 from the University of California at San Diego in California with a PhD in physical chemistry, followed by post-doctoral research at the National Research Council of Canada in Ottawa. In 1987 she joined the Canadian Conservation Institute and is presently a senior conservation scientist. Her research focuses on the corrosion and conservation problems associated with metals.

Joseph Sembrat is Vice President and Principal Conservator at Conservation Solutions, a Division of EverGreene Architectural Arts, Inc. with over 25 years of experience in art, artifact, and architecture conservation. Some projects of note that he has worked on include the US Capitol and Supreme Court, the West Block of Parliament in Ottawa, Canada, the Ca' d'Zan Mansion at the Ringling Museum of Art, Vizcaya Museum and Gardens, Columbia University outdoor sculpture collection, three Saturn V rockets and numerous other aerospace artifacts. Joe holds an MS in Historic Preservation from Columbia School of Architecture, Planning and Preservation (1993), and a BA in Art History from the University of Pennsylvania (1990). Joe has been a Fellow of the American Institute for Conservation (AIC) since 2007.

Aaron Shugar is currently the Andrew W. Mellon Associate Professor of Conservation Science in the Art Conservation Department, SUNY - Buffalo State. Dr. Shugar earned a M.Sc. at Sheffield University and awarded a Ph.D. from University College, London. He served as Co- Director of the Archaeometallurgical Laboratory at Lehigh University in Bethlehem, PA, was a visiting research scientist at the Smithsonian Museum Conservation Institute, served as the President of the Society for Archaeological Sciences and is currently an editor for Studies in Conservation, and associate editor for STAR. His research focuses on the analysis of inorganic archaeological and art materials.

Christina L. Simms is the Conservator of Objects and Sculpture at McKay Lodge Art Conservation Laboratory in Oberlin, Ohio. She recently completed research positions at the Smithsonian National Air and Space Museum and J. Paul Getty Museum. She is a graduate of the Buffalo State Art Conservation program.

D. D. N. Singh is former Chief Scientist of CSIR the National Metallurgical Laboratory in Jamshedpur India. Currently Dr. Singh is Adjunct Professor of Corrosion and Surface Engineering, National Institute of Technology, Jamshedpur, India.

J. K. Singh is working as project assistant at CSIR the National Metallurgical Laboratory in Jamshedpur, India in corrosion and coatings of metals and materials. He has a master's degree in chemistry.

Christina Tengnér is a metal conservator at the Army Museum at The National Swedish Museums of Military History part of the Swedish Air Force Museum since 2003, following a move from the Royal Academy of Science and their collection of scientific instruments. She has degrees in Art History from Uppsala University, and in Metal Conservation from The Department of Conservation at Gothenburg University, Sweden. Her main focus of interest is modern metals/alloys, and in recent years the addition of polymers and synthetic materials in composite objects.

Virginie Ternisien was a conservator for the Warren Lasch Conservation Center (WLCC) from 2013–2016, after working for the Maryland Archaeological Conservation Laboratory. She graduated with a Bachelor's and two Master's degrees in Conservation, both from Paris 1 Panthéon-Sorbonne University, specializing in the conservation of archaeological objects. During her tenure at the WLCC she dedicated her efforts to the *H.L. Hunley* project and to the development of subcritical fluid technology for stabilizing metal artifacts. She is currently taking a hiatus from cultural heritage conservation to focus on wildlife conservation with the U.S. Fish and Wildlife Service at Midway Atoll National Wildlife Refuge, Hawaii.

Yolaine Tissier graduated as an engineer from Polytech'Nantes, France in 2013. She supplemented her knowledge in heritage materials with a complementary Master's degree "MAPE" from Créteil University. She recently received her Ph.D. in physical chemistry of materials from the University of "Paris Est", France. She is currently employed with SITES – Société Instrumentation et Traitement Essais sur Site in Aix-en-Provence.

William G. Tompkins, director, National Collections Program, Smithsonian Institution, serves as an advisor to Smithsonian leadership and staff on matters relating to collections management. With 35 years' experience at the Smithsonian, he strives to improve the stewardship of collections by providing central leadership, policy oversight, strategic planning, and support of Institution-wide collections initiatives. He is responsible for the development and implementation of Institutional and unit collections management standards to ensure collections are acquired, maintained, and used according to Smithsonian policy, professional standards, and legal obligations. Previously, he served as assistant director of the Smithsonian's Office of the Registrar and as collections manager of the National Numismatic Collection at the National Museum of American History.

F. Robert van der Linden is the current Chair of the Aeronautics Department of the Smithsonian National Air and Space Museum. He is the Curator of Air Transportation and Special Purpose Aircraft and the author and editor of seven books. He has a B.A from the University of Denver, and an M.A. and Ph.D. from the George Washington University. Dr. van der Linden joined the museum in 1975 and currently resides with his wife and daughter in Washington, D.C.

Delphine Vantelon is a researcher in geochemistry, specializing in X-ray matter interactions in natural complex systems. She obtained her PhD in 2001 from the University of Lorraine and in 2003 joined the LUCIA beamline staff (synchrotron SOLEIL) which is one of the only beamlines worldwide dedicated to X-ray absorption spectroscopy (XAS). She is currently the manager of the beamline, since 2012. Within this respect, she is member of the Steering Committee of the joint research program IFPEN-SOLEIL. She co-coordinates the working group on perspectives in "Energy, Environment and Sustainable Development" for a SOLEIL upgrade.

John Weitz joined the Aluminum Association in July, 2012, coming from Wise Alloys, where he had served as Metallurgy Manager since 2007. In that role, he was responsible for developing and improving manufacturing methods for Wise's products. Weritz received his in Metallurgical Engineering from the University of Illinois at Chicago Circle and brings over 30 years of experience in the production of aluminum sheet, plate, foil, and extrusion products. He began his career at Reynolds Metals Company, earning roles of increasing responsibility in 25 years with the company, including Metallurgical, Quality Assurance and Production Management positions. Subsequently, he moved to McCook Metals LLC, where he was Senior Vice President and responsible for additional plants acquired by Michigan Avenue Partners.

Dr. Richard Whurer is the Research Manager of the Advanced Materials Characterisation Facility at the University of Western Sydney. Richard has extensive experience variable pressure and environmental scanning electron microscopes, microanalysis systems, X-ray mapping and with electron microprobe analysis and wavelength dispersive spectroscopy, X-ray diffraction and electron back scattered diffraction. Richard has a PhD in Applied Science from UTS and is the President of the Australian Microbeam Analysis Society. He has over 70 reviewed publications ranging from art works to gunshot residue analysis; however his main focus remains characterisation techniques development and aiding the analysis of materials and biological materials.

Lisa Young has served as objects conservator at the National Air and Space Museum since 2009. She earned her B.Sc. in Conservation at the University of Wales, Cardiff. She has worked at NASM since 1997, where she researched the preservation of spacesuits. From 1999–2006 she was the conservator to Save America's Treasures Project where she consulted on the Saturn V rocket assembly and performed research on the National collection of spacesuits. She has published articles and given numerous presentations on the conservation of spacesuits, served as President of the Washington Conservation Guild (2005–2007) and is a Fellow of the American Institute for Conservation (AIC).

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