5-10-1950

Hot-Dip Aluminizing of Low-Carbon Steels

Claude R. Barnes Jr.

Recommended Citation

Barnes, Claude R. Jr., "Hot-Dip Aluminizing of Low-Carbon Steels" (1950). *Bachelors Theses and Reports, 1928 - 1970.* Paper 302.

HOT-DIP ALUMINIZING

OF LOW-CARBON STEELS

By

Claude R. Barnes, Jr.

A Thesis

Submitted to the Department of Metallurgy

in Partial Fulfillment of the

Requirements for the Degree of

Bachelor of Science

in Metallurgical Engineering

MONTANA SCHOOL OF MINES

Butte, Montana

May 10, 1950

HOT-DIP ALUMINIZING

OF LOW-CARBON STEELS

By

Claude R. Barnes, Jr.

A Thesis

Submitted to the Department of Metallurgy

in Partial Fulfillment of the

Requirements for the Degree of

Bachelor of Science

in Metallurgical Engineering

MONTANA SCHOOL OF MINES

Butte, Montana

May 10, 1950

TABLE OF CONTENTS

TABLE OF ILLUSTRATIONS

"One of the most persistent problems which
confront the worker in iron and steel is the pre-
vention of corrosion. We cannot rid ourselves of
the agents which affect corrosion of iron without
at the same time ridding ourselves of the agents
which are essential to life itself."[1]

<div align="right">

Alfred Sang
"THE IRON AGE"

</div>

INTRODUCTION

Unlike iron, copper, lead, and zinc, aluminum was born in nobility and now serves the world as a base metal. It is said that Napoleon used aluminum cutlery, while guests with lower rank ate with gold and silver cutlery. In a relatively short period of sixty-five years, aluminum has grown to the rank of fifth in total weight of metals produced in the world. Throughout its short life, aluminum has been found to have excellent corrosion-resistant properties; yet only in recent years has aluminum been under consideration as a corrosion-resistant coating for iron and steel. Although there have been a number of processes for aluminum coatings patented and used, only a couple of these have either reached production or satisfactory results. In the hot dipping processes, the alloying of the aluminum and iron has formed a brittle interfacial layer of Al_3Fe which would prevent the coated metal from being formed. The problem under consideration here will be the elimination of the brittle interfacial layer and the production of a homogeneous and adherent coating.

Corrosion[*], or protection from corrosion, is

-1-

[*]Corrosion is defined by the Electrochemical Society as: "Destruction of metal by chemical or electrochemical reaction with its environment."

one of the most costly items in our present-day
world. The corrosion damage to metals and ma-
terials annually reaches a figure exceeding five
billion dollars. Of this monetary figure about
four billion dollars can be charged to the iron
and steel industry.[2] Some authors maintain that
this dollar value is only a small part of the total,
if the accidents, with their accompanying loss of
life and limb caused by corrosion are considered.

Of the many metallic coatings and alloying
elements being used today for adding corrosion
resistance to iron and steel; chromium, nickel,
and zinc are the most widely used. However, cad-
mium, aluminum, lead, tin, and copper, either alone
or in combination, are used to protect iron and
steel from corrosion. Each of these preceding
metals has its advantages in special applications.

ALUMINUM CORROSION PROTECTION

Corrosion resistance is a misnomer and more correctly it should be called corrosion protection of the base metal. It is found, if one studies all the so-called corrosion-resistant coatings that in effect they are readily corroded or corroded in preference to the base metal; e.g., aluminum derives its corrosion resistance from its immediate surface oxidation, zinc derives its corrosion resistance because it is preferentially corroded in the galvanic action set up between the zinc and the base metal (iron and steel).

These two preceding examples also serve as examples of what most chemists and authors consider to be the two types of corrosion, 1- direct chemical attack, 2- electrochemical action. In the direct chemical attack, the course and extent of the corrosion is determined by the physical properties of the product, viz., liquid, gas, or solid. Liquid or gaseous products will be removed and corrosion will continue umhampered; however, solid products will remain behind, at least temporarily, to either hinder or forbid further corrosion. The chemical basis

for direct chemical attack is through the change of free energy from the reactants to the products, the reaction must be spontaneous. Electrochemical corrosion is caused by the difference between the solution pressure of the metal and the osmotic pressure of the metal ions -- the result of which is to cause a metal in solution to be either positive or negative in electrical charge. If two dissimilar metals are immersed in an electrolyte and externally connected, an electric current can be obtained. The magnitude of this current increases as the distance between the two metals in the electromotive series increases. In solution the current flows from the negative to the positive electrode; therefore, the continual dissolution of the negatively charged metal protects or prohibits the solution of the positively charged metal.

While it is true there are corrosion-resistant alloys and alloy steels which will probably suffice for todays needs, it would seem advantageous to add aluminum-coated, low-carbon steels to this list. A perusal of the literature indicates that the elements used for corrosion resistance in this country are either sadly lacking or require large quantities. Chromium and nickel production,

two of the common corrosion-resisting alloying elements, is practically negligable in this country. Chromium and nickel are also required in large quantities as shown by the following limits of the elements in stainless steels; ferritic stainless steels, 7 - 27% chromium; austenitic stainless steels, 7 - 26% chromium and 7 - 26% nickel; martensitic stainless steels, 10 - 18% chromium.[3] The argument that aluminum is scarce in this country is recognized; however, if aluminum were used to supplement nickel and chromium, our available supply of nickel and chromium could be made to last a much longer time.

Aluminum is desirable as a preventative of iron and steel corrosion in that it has a dual protection feature; aluminum will give protection to iron and steel from both the preceding discussed types of corrosion. Primarily, aluminum is not readily corroded because of the highly protective, impervious, and adherent oxide film which immediately forms on the aluminum surface. The oxide film on aluminum starts to form instantaneously on exposure of the aluminum to the atmosphere. This film, which is very thin (0.000001 cm)[4,5], is very resistant to a variety of corro-

osive conditions and the oxide film will also re-
generate itself if broken or removed. This film
gives to aluminum its high-temperature oxidation
resistance.

The second protective feature of aluminum is
electrochemical.[6] This protective feature of alu-
minum to the base metal is not very likely because
of the regenerative oxide film; however, in a chlo-
ride solution where the oxide would not form, the
electrochemical protection would still protect
the base metal. Since aluminum is higher in the
electromotive force series than zinc, it would
provide as great or greater cathodic protection
to the iron and steel than would zinc.[7]

Other metals are used for protection against
corrosion but it is known that aluminum would be
superior to them. (1) Zinc, the most commonly used
protective metal, is corroded away at the expense
of the base metal. Zinc also forms an oxide layer
but this oxide readily converts into the granular
zinc oxide which is easily removed from the metal.
(2) Magnesium is very similar to aluminum in its
formation of an oxide. However, magnesium oxide
readily converts to hydroxides, basic carbonates,

or basic sulfates which are readily soluble in water containing carbon dioxide.

APPLICATION

Aluminum in the recent years has come into prominence as one of the basic metals. Because of its availability, relatively low cost, and excellent corrosion resistance, aluminum has received much consideration as a metal for corrosion resistance. Aluminum may be more desirable than some of the other metals now in use as metallic coatings.

Before going further into the problem, it would be well to see to what uses the aluminum coated steel could be adapted. The main object of this research was in the line of corrosion resistance and workability of aluminum-coated steels; however, we cannot overlook the main advantage that aluminum coated steel would be applicable to the following conditions and would also have the strength and properties of the base metal steel.

1. Marine construction.
2. Sea coast atmospheric exposure.
3. Sea water immersion.
4. High temperature oxidation resistance without discoloration.

5. High heat reflectivity.

6. "Double seaming, arc welding, seam or
    spot welding, oxyacetylene welding or
    brazing."[8]

7. Food processing, storage, and handling.

8. Oil and gas industry.

This foregoing list is not the result of mere
speculation but it is derived from tests which have
been conducted from time to time by various com-
panies.

THE PROBLEM

Aluminum may be applied to iron and steel sur-
faces by any one of the following processes:[9,10]

1. Hot dipping.

2. Calorizing.

3. Electroplating.

4. Metal cladding.

5. Metal spraying.

6. Chemical reactions.

For the purpose of this problem, the hot-dip alu-
minizing process was chosen as it is reported, from
the operating standpoint to present the lowest -
cost process and to require the simplest equip-
ment.[11]

Of the previous processes mentioned, not all
have been successful. The cause for failure of
each process will not be described since this work
shall be concerned with only the hot-dip aluminiz-
ing process. In hot-dip aluminizing of steel, the
primary source of trouble is the formation of the
brittle interfacial layer of Al_3FE which will cause
the aluminum coating to peel or chip if the ob-
ject is subject to any bending, deformation, or
shock. However, one other source of trouble was

a contributing factor in the negative results in
this work. The aluminum bath oxidized so readily
that a homogeneous and adherent coating was very
difficult to obtain. This second difficulty,
which was a controlling factor in all the exper-
imental work, was not expected or forseen; how-
ever, when reference number 12 listed in the bib-
liography was obtained, this difficulty was con-
firmed as present in hot-dip aluminizing.

The original intent was to use an interme-
diate metal between the iron and aluminum and
thereby eliminate the brittle Al_3Fe as the source
of trouble. Copper was chosen for the interme-
diate metal since it would fill the following re-
quirements toward the molten aluminum.

In order for any hot-dipping process to be
sucessful, there are five requirements that must
be fulfilled.[13,14]

    1. The base metal must be soluble and alloy
       with the molten metal. The base metal,
       regardless of its melting point, is sol-
       uble to some extent in the bath, this
       slight solubility and alloying effects
       the wetting of the base metal and pre-

vents coalescence. Copper, aluminum, and iron in any combination will pass this requirement.

2. The metal to be applied by dipping must have a relatively low melting point. A high temperature will increase the solubility of the base metal in the bath and also may alter the properties of the base metal considerably. Aluminum is thought to have about as high a melting point (1217°F) as is practical for hot dipping. The melting point of the copper (1981°F) is too high for hot dip application and would have to be applied in some other manner. This will be described later.

3. The metallic film must not coalesce but must wet and cover the entire surface. This tendency is counteracted by the alloying of the molten metal and the base metal if such alloying takes place.

4. The metals must alloy readily enough that a short immersion time may be used. The immersion time has a pronounced effect on

the thickness of the aluminum case. If
the time were too long, there would be a
needless waste of molten metal and the
coating may become so brittle that it
may be useless.

5. The object to be immersed must present
a clean surface to the molten metal.
Requirements one, three, and four are determined
by the physical characteristics of the metal and
requirements two and five are problems of this work.

A summary of the problem will reveal three
separate points of research which must be over-
come before a person could successfully attack
the intended problem of eliminating the brittle
Al_3Fe layer. A review of the three leading prob-
lems will be given again.

1. Applying the high melting point copper
and obtaining the desired thickness.
2. Cleaning the metal surface so that the
metal will be amenable.
3. Applying a homogeneous and adherent coat-
ing of aluminum to the copper plated base
metal.

LABORATORY EQUIPMENT AND MATERIALS

The laboratory equipment and materials used in this problem are as follows:

I. Low carbon steel. (Appendix Plate I)

The steel used in this problem was a commercial grade hot-rolled 1020 steel which would conform to the following analysis.

	Minimum	Maximum
Carbon	0.18%	0.23%
Manganese	0.30%	0.50%
Phosphorous		0.04%
Sulfur		0.05%

II. Metal cleaners.

    1. Degreasing solution.[15]

Potassium carbonate	60 gm/l.
Sodium hydroxide	15 gm/l.
Trisodium phosphate	10 gm/l.

    2. Pickling solution.[16]

Sulfuric acid	10 gm/l.

III. Copper plating. (Appendix Plate II)

    1. Copper cyanide plating solution.[17]

Copper cyanide	22 gm/l.
Sodium cyanide	34 gm/l.
Sodium carbonate	15 gm/l.
Sodium thiosulfate	2 gm/l.

2. Two volt, lead-acid batteries.

3. Rheostat.

4. D-C ammeter.

5. D-C voltmeter.

6. Solution agitator.

7. Plating cell.

8. Copper anodes.

(See Appendix Plate V for wiring diagram.)

IV. Preheating. (Appendix Plate III)

1. A-C supply.

2. Rheostat.

3. A-C ammeter.

4. Nitrogen.

5. Gas flow indicator.

6. Drying column and ascarite.

7. Pyrometer. The pyrometer was a Bristol Company standardized pyrometer head, leads, and temperature reading box.

8. Laboratory tube furnace. This furnace was a Leeds & Northrup Electric Laboratory Tube Furnace with a 1-3/8" x 10" refractory tube.

(See Appendix Plate V for wiring diagram.)

V. Aluminizing. (Appendix Plate IV)

1. A-C source.

2. Rheostat.

3. A-C ammeter.

4. Pyrometer. (Refer IV-7)

5. Commercial grade aluminum shot and bars.

6. Aluminizing furnace and crucibles. The basic furnace was an Electrical Heating Appliance Company pot furnace. A second furnace was built with the same type of heating elements as in the pot furnace. This furnace was put in series with the other furnace to give an over-all size of 3" x 10" to the heating pot. The crucibles used were made from fire clay, iron, and graphite. These crucibles will be discussed with its appropriate experiment.

(See Appendix Plate V for wiring diagram.)

VI. Metallography

1. Polishing and grinding equipment.

2. Microscope.

3. Etchants as noted.

4. Camera, photographic developing and printing equipment.

EXPERIMENTAL PROCEDURE

In each of the experiments the metal clean-
ing and copper plating followed the same proce-
dure, therefore, these two operations will be dis-
cussed first followed with a discussion of the re-
sults obtained in each of the separate hot dipping
experiments.

Metal cleaning is the first physical operation
required to make a metal amenable to hot dipping.
There are two steps in metal cleaning and here
again we have a precedence. The two metal-clean-
ing steps that must be carried out are; 1- de-
greasing, 2- descaling or pickling. The degreas-
ing of the metal must be done before pickling be-
cause the grease would protect the oxide scale
from the pickling solution and cause an uneven
attack on the metal. This investigation was not
concerned with any comparison and study of clean-
ing solutions or plating baths.

The procedures used for obtaining a clean
metal surface are contained in references 14 and 15.

The degreasing was carried out by immersing
the 1020 steel samples into the solutions noted

on page 14. The solution was heated to 40°C
(104°F) and held as near as possible to this temp-
erature for a period of five minutes. The solution
was stirred during the entire immersion time to in-
sure a uniform solution of the greases and fats.
The pickling of the steel employed the same pro-
cedure as that used for the degreasing with the
exception of the time and temperature: the temp-
erature used was 100°C and the time of immersion
was ten minutes. The method used to determine
whether the metal was clean was very simple al-
though satisfactory. If the metal, after wash-
ing, retained a thin uniform coating of water, it
was considered to be sufficiently clean.

The cleaned metal was plated with copper from
the copper cyanide solution using rolled copper
anodes. The cyanide solution was chosen for plat-
ing in preference to the sulfuric acid solution
since the action of the acid on the steel would
liberate hydrogen and cause further embrittlement
of the steel, also the copper would deposit on the
steel by cementation. A current density of five
amperes per square foot was used first with the
solution temperature at room temperature. With
a surface area of 0.066 square foot to be plated,

the current density converted to an ammeter read-
ing is 0.33 amperes. However, this amperage was
found to be too high as the anodes turned black
from the formation of the insoluble copper oxide.
As a result of this, the amperage was lowered to
0.20 amperes (3.03 amperes per square foot) with
a subsequent brightening of the anodes. The time
of plating was arbitrarily chosen as ten minutes.
The average case depth of the copper from a ten
minute plating time was 0.015 millimeter (See
Table I of the appendix).

Experiment 1.

Crucible - Twenty-five gram fire clay crucible.

Bath temperature - 1325°F.

Bath cover - None.

Time of dip - 15 seconds.

Results: This experiment was very unsatisfac-
tory as the bath was covered with a layer of alu-
minum oxide, and even though the oxide was removed
before dipping, the steel had a very uneven coat-
ing and in many spots no coating.

Conclusions: In order to obtain a satis-
factory coating, a cover would be required to eli-
minate the oxide layer. The oxide layer, regard-
less of how thin it was, was drawn under by the sur-

face tension of the bath and thereby prevented
the aluminum and copper from alloying.

Experiment 2.

Crucible - Twenty-five gram fire clay crucible.

Bath temperature - 1310°F.

Bath cover - Borax.

Time of dip - No dip.

Results: The borax cover did not melt but
formed a hard crust over the bath.

Conclusions: Since the top of the crucible
and the heating elements were at the same level it
was thought that a deeper furnace was necessary to
give a more uniform temperature throughout the
bath. The second furnace similar to the original
was built and placed on top of the original.

Experiment 3.

Crucible - Twenty-five gram fire clay crucible.

Bath temperature - 1275°F.

Bath cover - Cryolite.

Time of dip - No dip.

Results: The cryolite also formed a hard
crust over the bath which was almost impossible
to penetrate.

Conclusions: The cryolite also required too

high a temperature and therefore not be amenable
as a cover over the molten aluminum.

Experiment 4.

    Crucible - Twenty-five gram fire clay crucible.

    Bath temperature - 1290°F.

    Bath cover - Quenching salt (900 - 1400°F)

    Time of dip - 15 seconds.

    Results: The quenching salt eliminated the
oxide layer; however, the quenching salt formed a
layer between the copper and aluminum. During the
heating of the bath, enough of the salt volatil-
ized and corroded the heating elements causing
the elements to burn out.

    Conclusions: A taller pot would be required
so that the salt fumes would be kept away from the
heating elements.

Experiment 5.

    Crucible - 2½" diameter x 9" iron pot.

    Bath temperature - 1325°F.

    Bath cover - Quenching salt.

    Time of dip - No dip.

    Results: The aluminum bath was a spongy mass
of aluminum oxide and aluminum.

    Conclusions: The iron oxidized on its sur-

21993

-21-

face and the aluminum in turn deoxidized the iron. This cycle apparently continued.

Experiment 6.

Crucible - Graphite.

Bath temperature - 1325°F.

Bath cover - None.

Time of dip - 15 seconds.

Results: This experiment gave the first signs of a little success; however, the coating was quite rough with aluminum oxide inclusions. Plate VI, made from a selected cross-section, shows the bond produced between the steel, copper, and aluminum.

Conclusions: The metal should be preheated to prevent the shock chilling of the aluminum and thereby making it possible to eliminate some of the oxide drawn under with the dip.

Experiment 7.

Crucible - Graphite.

Bath temperature - 1300°F.

Bath cover - None.

Time of dip - 15 seconds.

Preheating temperature - 1325°F.

Preheating time - 30 seconds.

Preheating atmosphere - Nitrogen.

Results: The steel sample did not take a coating.

Conclusions: The sample oxidized in the pre-heating furnace.

CONCLUSIONS & RECOMMENDATIONS

The experiments in this problem did not give any favorable results that would aid in eliminating the brittle Al_3Fe layer. Little was learned as to the effectiveness of aluminum-coated steels for corrosion resistance; however, there are some conclusions to be drawn and recommendations to be made that would probably make the problem successful. These recommendations are given below:

1. The aluminizing and preheating furnaces should be one unit and it should be as air-tight as possible so that a controlled atmosphere could be used.

2. The steel should be preheated before aluminizing. Preheating would allow the aluminum coating to adhere to the copper by alloying rather than by freezing on the cold copper. With the temperature of the steel near the bath temperature, lower bath temperatures could be used and this would in turn affect the time of dipping and case depth.

3. In both the preheating and aluminizing furnaces, a mixture of hydrogen and nitrogen would be the cheapest atmosphere, yet give the

reducing effect of pure hydrogen.

4. The time and temperature of preheating
should be kept to a minimum to prevent a change
in the physical properties of the base metal.

5. The most positive way that the aluminum
case depth would be controlled would be by rolling
immediately after dipping.

6. Before the interfacial layer could be
studied, there must be a uniform adherent layer
of aluminum. This requires that the metal sur-
face be clean and that no oxides are present be-
tween the aluminum-copper interface.

"The aluminum coating of iron and steel pro-
duct(s) is feasible. However, some further effort
is required on the development of operating details
to enable aluminum coated steel to take its proper
position among coated metal products."[18]

APPENDIX

Table I   Depth of copper case.

Depth (mm)
0.01062
0.01336
0.01211
0.01376
0.01467
0.01805
0.01634
0.01629
0.01692
0.01260   Average 0.015307
0.01530
0.01805
0.01395
0.02426   Maximum
0.01628
0.01539
0.01575
0.02178
0.01490
0.01116
0.00991

Table II   Depth of aluminum case.

Depth (mm)
0.2965
0.2762
0.2985
0.3858   Maximum
0.3665
0.3077
0.2670
0.2220
0.1193
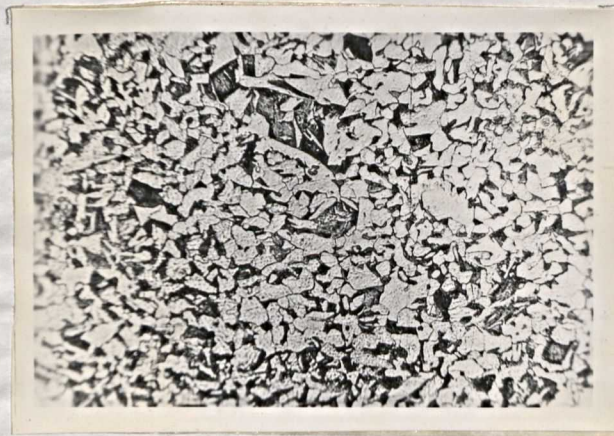0.2180   Average 0.2574
0.1311
0.1899
0.1422
0.0833   Minimum
0.2052
0.2858
0.3033
0.3642
0.3676
0.3171

PLATE I

SAE 1020

Transverse section

Etch: 4% Nital

200X

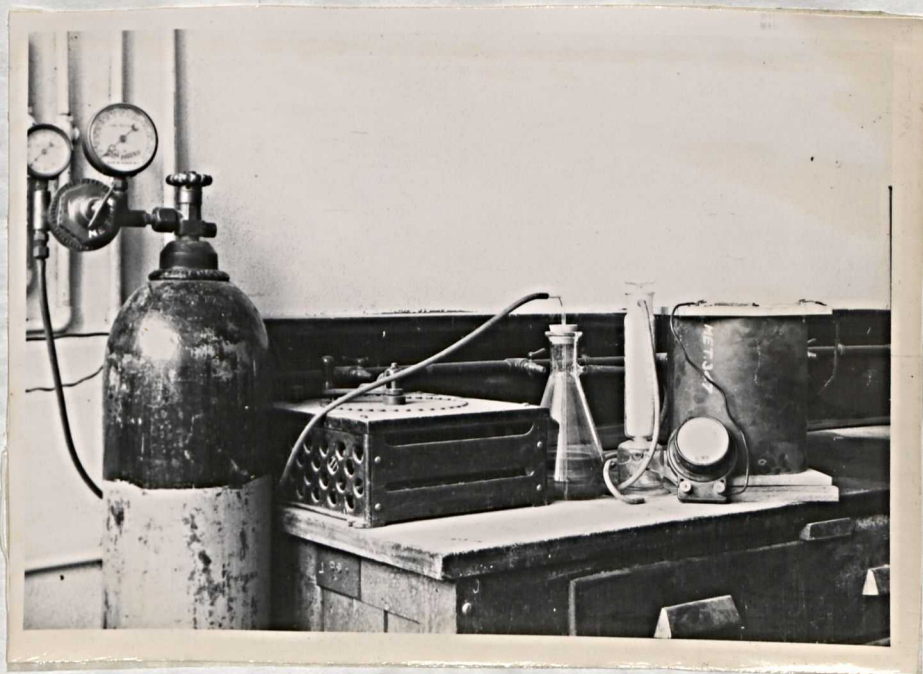SAE 1020

Longitudinal Section
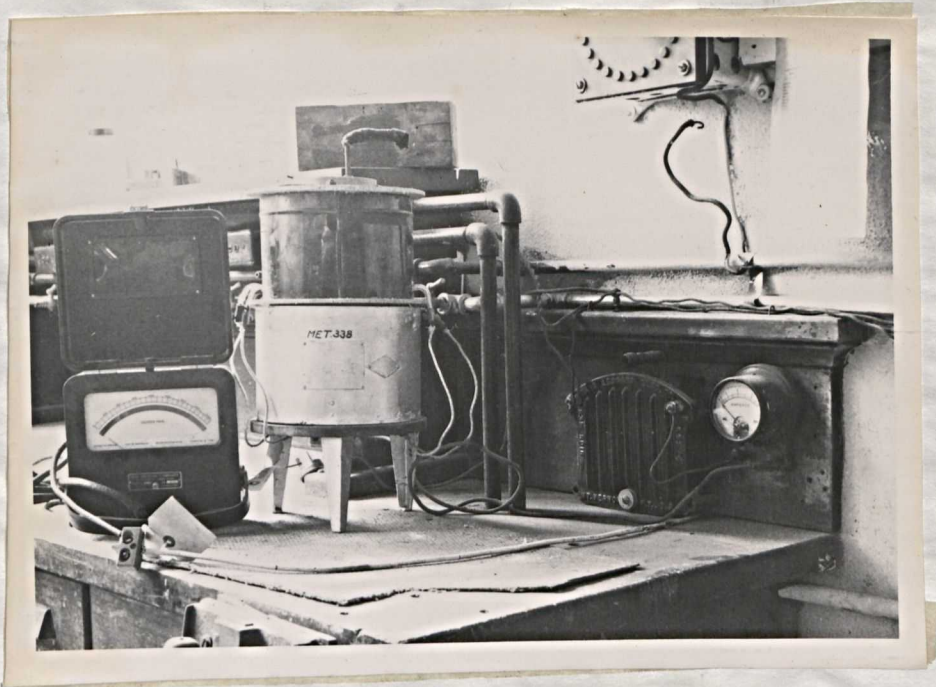
Etch: 4% Nital

200X

PLATE II
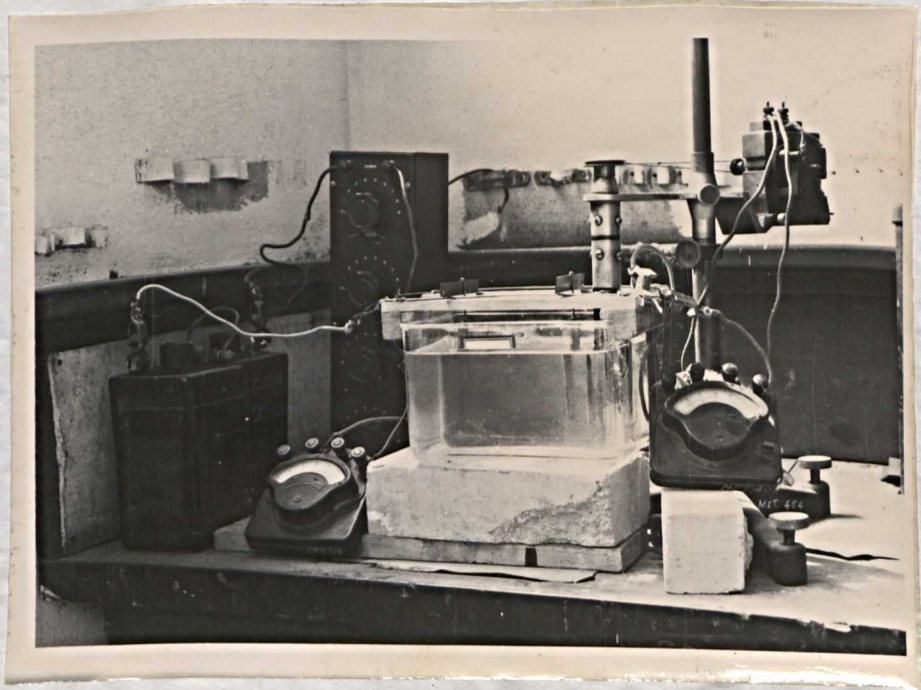
Copper Plating Equipment
showing batteries, rheostat, agitator,
cell, ammeter, voltmeter, and anodes.

PLATE III

Preheating Equipment
showing Nitrogen source, rheostat,
gas flow indicator, drying column,
ammeter, and tube furnace.

PLATE IV

Aluminizing Equipment
showing rheostat, ammeter,
pyrometer, and furnace.

PLATE V

Rheostat

Batteries

Anodes

Ammeter

Cathode

Voltmeter

COPPER PLATING

110 V
A-C Supply

Rheostat

Ammeter

Heating Elements

PREHEATING

Ammeter
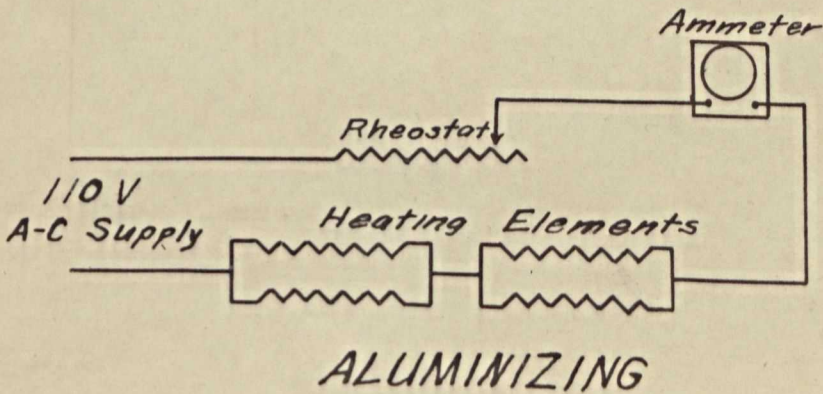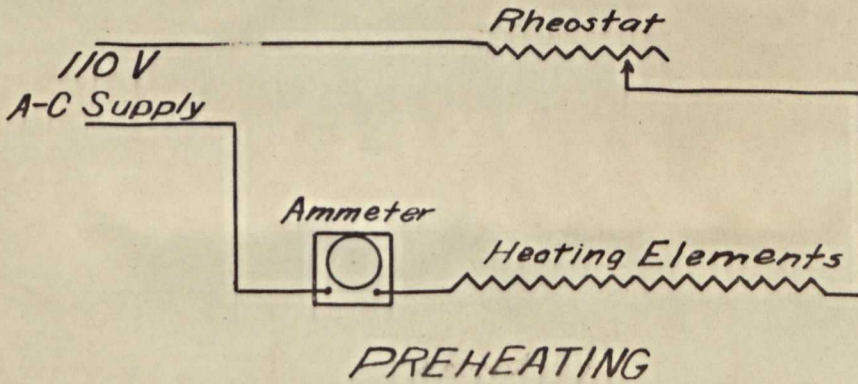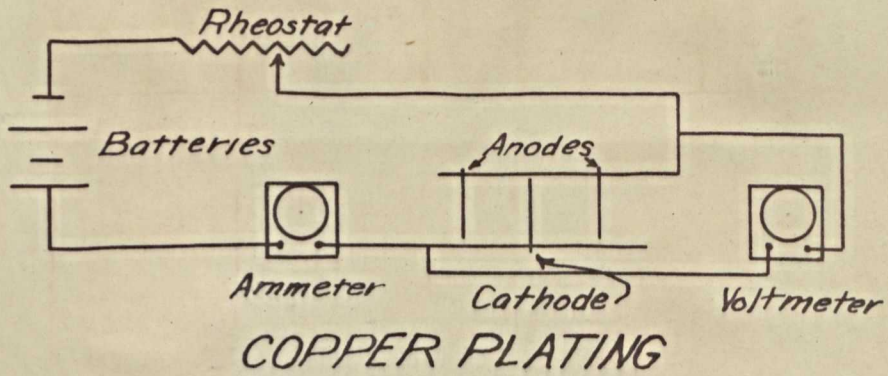
Rheostat

110 V
A-C Supply

Heating Elements

ALUMINIZING

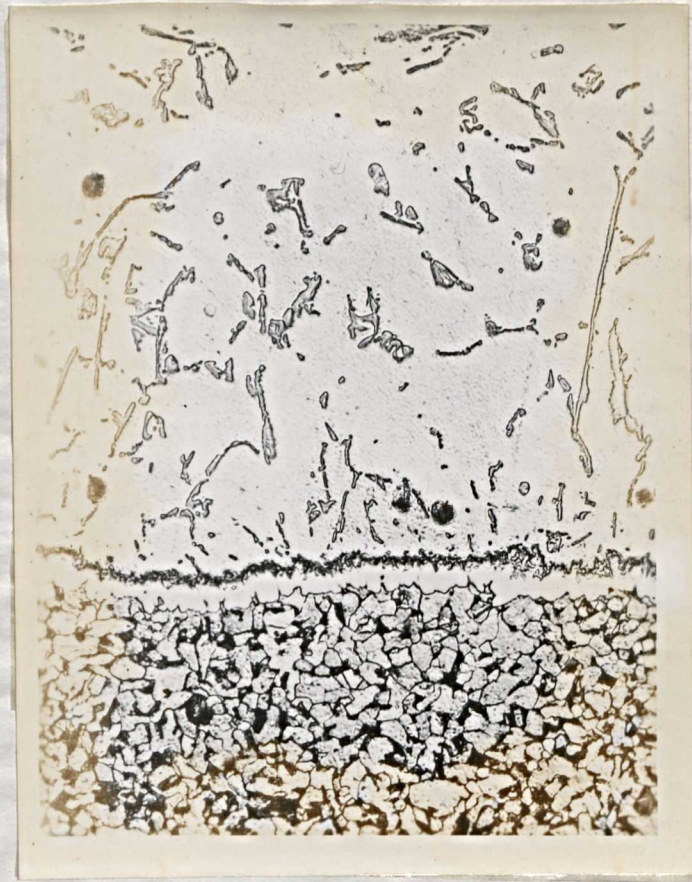PLATE VI

Coated sample

showing steel, copper,

and aluminum

Etch: Ammonium persulfate

189X

BIBLIOGRAPHY

1. Flanders, W. T., *Galvanizing and Tinning*, pp 9,
    Williams Company, New York, 1916.

2. Heussner, C. E., Protection of Base Metals by
    use of Metallic Coatings, pp 6, American Society
    for Testing Materials "*Symposium on Protecting
    Metals against Corrosion*", 1938.

3. *Metals Handbook*, American Society for Metals,
    pp 581 - 582, 1948 Ediction.

4. McKay, R. J., Worthington, R., *Corrosion Resist-
    ance of Metals and Alloys*, pp 113, Reinhold Pub-
    lishing Corporation, 1936.

5. Hedges, E. S., *Protective Film on Metals*, pp 86,
    Chapman & Hall Ltd, 1932.

6. Dix, E. H., Jr., Corrosion of Light Metals, pp 131,
    Corrosion of Metals, 1946.

7. McKay., ibid, pp 33.

8. Metals Handbook., ibid, pp 704 - 705.

9. Burns, R. M., Schuh, A. E., *Protective Coatings
    for Metals*, pp 35 - 56, Reinhold Publishing Corp-
    oration, 1939.

10. Stroup, P. T., Purdy, G. A., Aluminum Coating
    of Steel, A Comparison of Various Processes,
    Metals Progress, pp 59, January 1950, Vol 57 No 1.

11. Stroup., ibid, pp 61.

12. Guillet, Leon, The Alferieff Hot Dip Aluminizing
     Process, (Condensed translation from Le Genie
     Civil, Vol 64, (1944) No 13 (3136) -- 101 - 103
     by Henry Brutcher)

13. Rawdon, H. S., Protective Metallic Coatings,
     pp 26 - 30, Chemical Catalog Company, 1928.

14. Hedges., ibid, pp 198 - 200.

15. Blum, W., Hogaboom, G. B., Principles of Electro-
     plating and Electroforming, pp 145, McGraw-Hill
     Book Company, 1930.

16. Blum., ibid, pp 150.

17. Blum., ibid, pp 228.

18. Stroup., ibid, pp 63.

ACKNOWLEDGEMENTS

I wish to express my gratitude to the faculty members of the Metallurgy Department for their assistance and guidance during this problem; and specifically to Mr. Curtis L. Graverson, Assistant Professor of Metallurgy, who read and made suggestions during the writing of this thesis. Thanks are also due to Mrs. Loretta Buss Peck, Librarian, for facilities made available in the Library for a review of the literature; and to Mrs. Stephen W. Nile for expediting the obtaining of the foreign translation.