



## Chromate conversion coating on Al–0.2 wt.% Fe alloy

M. Oki<sup>a,\*</sup>, E. Charles<sup>a,b</sup>

<sup>a</sup> School of Science and Technology, National Open University of Nigeria, Ahmadu Bello Way, Victoria Island, Lagos, Nigeria

<sup>b</sup> Department of Mechanical Engineering, Niger Delta University, Bayelsa State, Nigeria

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### ABSTRACT

SEM and TEM investigations revealed that the chromate coating developed rapidly over the macroscopic alloy surface. The coating thickness increased over the immersion period employed in this study and was about 50 nm and 200 nm for coatings formed after 30 s and 120 s respectively. The coating is composed of chromium compounds with aluminium compounds probably concentrated at the alloy/coating interface.

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### 1. Introduction

Chromate-containing conversion coatings on aluminium alloys have applications in many areas, such as automotive, aerospace, packaging etc. Environmental and toxicity problems are associated with these coating systems and as such, there are wide and intensive searches for their replacements in coating formulations [1,2]. However, the main attractions for their extensive application in industries are to improve paint adhesion and corrosion resistance of substrates treated in coating baths. These characteristic improvements have been subjects of discussion where the roles of surface features and coating composition may be jointly important [3,4].

Flaws are inevitable on electropolished aluminium surfaces and their behaviour during interactions with film-forming chemical environments has not been fully understood [2,5,6]. Some of these flaws are usually associated with intermetallics in which filmed surfaces constitute imperfections in the air-formed oxide films wherever they intersect the surface of the aluminium substrate. During surface preparation of alloys such as in etching and/or electropolishing procedures, the intermetallics on occasions may be completely removed into the solution thus, creating pits of various sizes and shapes [5]. The influence of these flaws on the morphology and composition of conversion coatings has received limited mention in the literature; hence, the aluminium substrate in the present investigation, which contains 0.2 wt.% Fe alloying component, was conversion-coated in a chromate bath prior to examination in the SEM and TEM. The Auger

electron spectroscopy analysis of the surface and EDX analysis of the coating have also been examined in this investigation.

### 2. Materials and methods

#### 2.1. Materials

Aluminium alloy, which contained 0.2 wt.% Fe, 0.002 wt.% Cu and 0.003 wt.% Si, was made out into spade-like electrodes of dimensions 10 mm × 5 mm × 0.5 mm. The electrodes were polished in a perchloric acid/ethanol mixture for 3 min, rinsed in distilled water and dried in air. These electrodes were immersed for various periods in a conversion coating bath containing 3.5 g/l Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 4 g/l CrO<sub>3</sub> and 1 g/l NaF.

#### 2.2. Methods

Conversion-coated specimens were examined directly in an ISI-DS130 scanning electron microscope with elemental analysis of the coating obtained in the energy dispersive X-ray (EDX) facility attached to the microscope. Ultramicrotomed sections of the specimens were obtained using an LKB Ultratome III 8800 ultramicrotome and examined in a Philips 301 transmission electron microscope. Using a probe size of 10 nm, elemental composition of the coating at different regions, ranging from the coating/solution interface to the alloy/coating interface, was obtained using the EDX facility attached to Philips EM400T transmission electron microscope. In addition, surface composition of the specimen was obtained using a Vacuum Generator, Auger electron spectroscopy with a 3 KeV primary electron beam and a beam current of 200 μA.

\* Corresponding author.

E-mail address: [m.oki11@yahoo.com](mailto:m.oki11@yahoo.com) (M. Oki).

### 3. Results and discussions

#### 3.1. Surface morphology

Apart from the light and dark coating materials, the scanning electron micrograph of the specimen treated for 30 s, displayed in Fig. 1 is characterised by mostly rounded materials about 500–2500 nm in diameter with a population density of about  $15 \times 10^9$  per  $m^2$ . The coating at this stage of development mapped and decorated the grain boundaries of the substrate. In addition, cracks of various sizes observable on the surface may have developed during drying out of the initial gel-like coating materials [7].

#### 3.2. Sectional morphology

For all treatment times, the transmission electron images of ultramicrotome sections of the coatings appeared similar albeit, with increases in thickness over the immersion periods employed. The coatings developed rapidly with a coating of 50 nm in thickness replacing the thin, electropolishing film on the substrate alloy after 30 s of treatment. The coating was 150 nm in thickness after 60 s and it increased to 200 nm for the coatings developed after 120 s of treatment. A typical section, displayed in Fig. 2, is the coating developed after 30 s of immersion in the coating solution, where the metal/coating interface is relatively flat with distinct light coating materials, marked C, running parallel to the surface of the substrate.

This may be related to the layer described by Brown et al. [8] as thin alumina passive film which is present on aluminium surface through which electron tunneling occurs for deposition of conversion coating to occur. Within the coating, there are micro and macro linear features which represent cracks sandwiched among open textured coating materials that run through the section from the coating/solution interface to the metal/coating interface. These features have their outer regions decorate the surface of the coating, where they are likely anchor sites, providing keying facilities for subsequently applied organic paints [5,6].

#### 3.3. Chemical composition

From general analysis, using the EDX attachment in the SEM, X-rays corresponding to chromium and aluminium were detected, while spot analysis indicated that the discrete features are mainly compounds rich in iron, chromium and aluminium. Apparently, the aluminium and iron X-rays identified may have originated mainly from the substrate which is an aluminium alloy. Strikingly, EDX analysis of a 30 s coating stripped from the substrate, using mercuric chloride solution, indicated that, X-rays detected were those of chromium, indicating that the coating is mainly composed of chromium compounds. Other elements, if

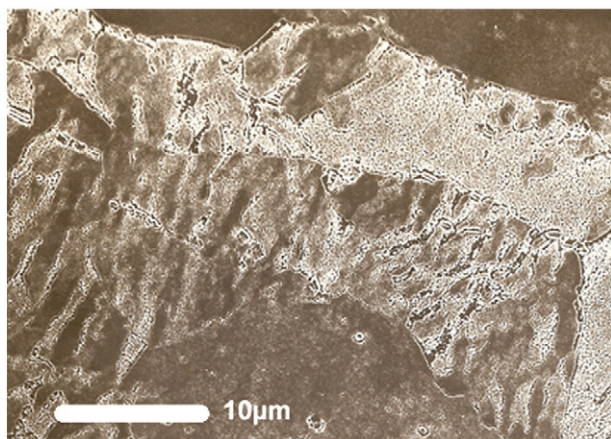


Fig. 1. SEM micrograph of Al-0.2 wt.% Fe treated for 30 s in a chromate bath.

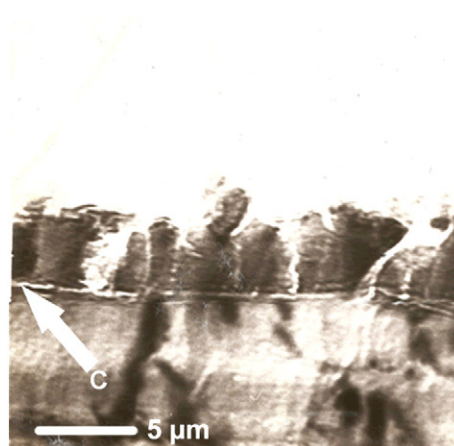


Fig. 2. TEM micrograph of ultramicrotomed section through a 30 s coating developed on Al-0.2 wt.% Fe (the substrate is at the bottom of the micrograph).

present within the coating, were below the detection limit of the EDX, approximately 0.2 at. wt.%. Information regarding elemental composition gathered during spot analysis of ultramicrotomed sections of the coating developed for 120 s, using a probe size of 10 nm in TEM 400 T indicated that at the coating solution interface and within the middle of the coating only chromium X-rays were detected. However, analysis at regions nearer the metal/coating interface indicated some aluminium X-rays as well as those of chromium. It is most likely that the bulk of Al X-rays observed were generated from the substrate as the analysis moved closer to the alloy/coating interface.

Further information on the surface composition from AES analysis of a coating developed after 120 s of pretreatment, indicated Auger peaks for chromium at 526 eV, oxygen at 511 eV and fluorine at 652 eV. The carbon peak, which was indicated at 272 eV, is a contaminant from the decomposition product of oil in the vacuum system. Thus, the surface coating material is composed of chromium and oxygen compounds, probably, hydrated chromium oxide. Understandably, iron was not detected in the coating during EDX as well as AES surface analyses which may be as a result of the limited spatial areas analysed.

### 4. Conclusion

The surface of the coating is characterised with micro and macro features which can provide anchors for subsequently applied paints. The coating is predominantly composed of chromium oxide.

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