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Influence of 0.2% Fe addition on zirconium conversion coating on aluminium alloy

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Abstract

Conversion coating on aluminium/0.2%Fe alloy developed from a zirconium nitrate/fluoride solution has been examined with scanning electron (SEM) and transmission electron microscopes (TEM) with attached energy dispersive X-ray (EDX) facilities. Zirconium-rich islands of thicker sections were observed in the SEM. The thin sections from the transmission micrographs revealed undulating metal/coating and coating/solution interfaces. This is consistent with anode/cathode reactions in the formation and growth of conversion coatings on metals, especially aluminium alloys. The coating comprises of zirconium rich surface which is contaminated or otherwise with aluminium and other species from the coating solution.

Key words: Conversion coatings, corrosion, zirconium, aluminium alloy, chromate.

1. Introduction

Conversion coatings on aluminium and other alloys have been in usage for decades; however, those based on chromates have enjoyed pre-eminence during this period. It is now common knowledge that chromates have been implicated as environmental pollutants and carcinogens. With this background knowledge, various researchers [15] are intensively searching for chromate replacements in conversion coating baths. Such replacements have received attentions in reviews [6-8] and comparisons of chromates with other transition element compounds in conversion coating baths [5, 911]. The use of zirconium based conversion coatings in the vehicle manufacturing industries have gradually taken over from phosphate based coatings for environmental considerations. Phosphates, having been implicated in promotion of massive growth of sea plants which led to eutrophication as a result of over nourishment of aquatic plant life with the attendant reduction in biodiversity. Hence there have been major developments to address this and other health related issues. The introduction of Zr conversion coating into the auto coating industry commenced at about the year 2000 as reviewed by Milosev and Frankel [12], however, as concluded by Frankel and Khun [13] hexafluorozirconic acid based conversion coating is an effective surface treatment which promotes improvement of corrosion resistance, paint adhesion as well as to slow down organic coating delamination on treated surfaces.

The current study however, examines with electron microscopy techniques, the development of a zirconium conversion coating based on $Zr(NO_3)_4$ /fluoride solution on aluminium/0.2% wt iron alloy (Al/wt.0.2% Fe). Initial studies revealed that there are anodic/cathodic reactions [14, 15] which resulted in coating formation. This as it may be, with the introduction of cathodic Fe into the matrix of aluminium should result in



faster coating formation on Al/Fe alloy with respect to 99.99% aluminium. (super-pure aluminium). This formed the bases of this examination- a study in part elucidation of the mechanism for conversion coating formation on aluminium and its alloys as well as for the replacement of chromates in conversion coating baths.

2. MATERIALS AND METHODS

2.1 Materials

The materials employed were Al alloy with 0.2wt% Fe.; these were made into spadelike electrodes. The electrodes were electropolished prior to immersion for periods of time ranging from 30s to 900s in a conversion coating bath containing 4g/l Zr (NO₃)₄ and 1 g/l NaF. The pH of the solution was adjusted with HNO₃.

2.2 Methods

During the conversion coating procedures, the potentials of specimens were measured relative to saturated Calomel electrode, monitored by means of a high impedance voltmeter and a potentiometric chart recorder. Triplicate specimens were employed for the potential measurements and the final potential attained was taken to be their average. The coated specimens were examined in an ISIDS130 scanning electron microscope while elemental analyses of the coating were performed with the energy dispersive X-ray (EDX) facility attached to the SEM. A Vacuum Generator, Auger electron spectroscopy was employed to analyze the near surface regions of the coating. The equipment was operated on a 3 KeV primary electron beam using a beam current of 200μA. Ultramicrotomed sections of the specimens were obtained using an LKB Ultratome III 8800 ultramicrotome and examined in a Philips 301 transmission electron microscope. Elemental compositions of different regions of the coating were analyzed with EDX facility attached to Philips EM400T transmission electron microscope.

3. RESULT AND DISCUSSIONS

3.1 Surface/Cross section Morphologies and Composition

The SEM and TEM of electropolished aluminium has been described elsewhere [14, 15] as having occasional pits which occurred during electropolishing procedures as a result of the removal of intermetallic materials which intersected the surface of the alloy. The thickness of the electropolishing film was about 10nm [14]

The final open circuit potential (OCP) was -1.7V which is more negative than -1.4V for 99.99% aluminium in a similar conversion coating bath [14]. However, visual observation of specimens treated for various times in the conversion coating bath showed that the specimens remained reflective at 600 s of treatment time, similar to what obtained for the super-pure aluminium. Beyond 600 s, a dull grey colouration was observed over the macroscopic alloy surfaces. This implied that the initial coatings were thin and colourless whereas a protracted treatment time resulted in the development of a relatively thicker greyish coating. From scanning electron microscopy examination, discrete particles which progressively increased in population density were revealed on a generally dark background over the microscopic metal surface. A typical example is displayed in Fig 1, the micrograph for the specimen treated in the coating solution for 600 s. For all conversion coated specimens, EDX analysis showed the presence of Zr, Al, Fe and O containing compounds.

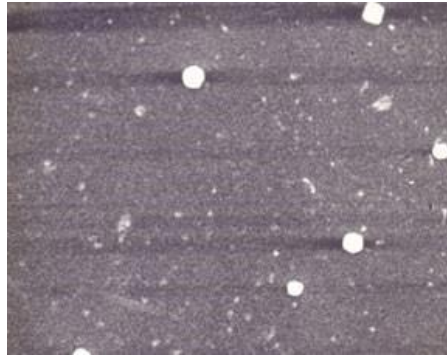
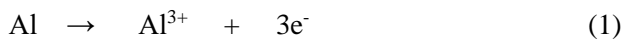


Figure 1. Scanning electron micrograph of aluminium alloy treated for 600 s in I-Zr conversion coating bath.

These coating components were derived from the electrochemical reactions which proceeded on the metal surface after the activation of the substrate by fluoride species $5\mu\text{m}$ in the coating solution [15]. Thus, a pH driven deposition of metal oxides which is preceded by cathodic hydrogen evolution [16], naturally deposits zirconium oxides at local cathodic sites such as iron inclusions in the alloy. These reactions are:

F-



A parallel anodic reaction suggested by Thompson [17] was that the thinning of the oxide skin on aluminium occurred with formation of aluminium ions which were further reoxidized to Al_2O_3 formed the basic anodic reaction. The oxide layer allowed electron tunneling for subsequent cathodic reactions to take place. Hence, Al as indicated from the EDX analysis may be derived from such sources as well as from the substrate. The transmission electron microscopic studies on Ultramicrotomed sections of the specimens treated for various times displayed relatively uneven metal/coating and coating solution interfaces as discussed elsewhere [15].



Fig2 Transmission electron microscopy of Al/0.2Fe wt.% aluminium treated for 600 s in

Zirconium conversion coating solution.

The non-uniformity in the thicknesses of the coatings may be as a result of disruptions of the coating materials during ultramicrotomy however, at the metal/coating interface, the local penetration of coating materials into the substrate, Fig. 2, suggest preferential coating development in such regions. The undulating textured nature of the coating may as well indicate local cathodic and anodic regions at the interface as indicated by the electrochemical reactions in equations (1), (2) and (3). Such textured regions are likely the discrete particles revealed in the SEM micrographs of similarly treated specimens. In general as observed in the TEM, the thin electropolishing film was replaced by a coating material of 45 nm in thickness after 60 s of treatment of the alloy specimen in the conversion coating bath. Further growth in thickness was observed on treatment for various times up to 900 s. However, at 1800 s, the coating diminished in thickness to about 50 nm in thickness. This showed that during protracted treatment, the initially formed coating was probably partly dissolved in the outer regions by the relatively aggressive coating solution. This is in agreement with the findings of Mohammadzade and Ghanbari [18] who concluded that the ZrO_2 filming process consisted of precipitation, growth, and finally a growth self-limiting stage. In addition however, removal of the friable coating material during ultramicrotomy may partly account for the observed decrease in coating thickness after such a protracted immersion period. The coating thickness versus time of aluminium alloy treatment in the zirconium coating solution is displayed in Fig.3 where it can be observed that at 60 s, the thin electropolishing film had been replaced by a relatively thicker coating as a result of the initial deposition of conversion coating materials as discussed with electrochemical equations in (1), (2) and (3). However, between 60 s to about 300 s the coating growth

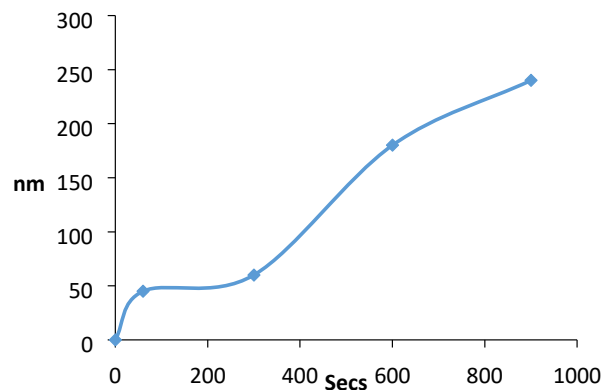


Figure 3. Coating thickness versus time of treatment in the conversion coating solution.

was stunted while the electrochemical reactions established themselves on the microscopic alloy surface with further opening up of reaction sites by penetrating the initially formed coating in one manner or the other for growth to commence at the metal/coating interface [19-22].

In a similar study on 99.99% aluminium (super-pure aluminium) [14], the authors established that the coating thickness at 900 s of treatment of the super-pure aluminium

in a similar treatment bath was 50 nm whereas; the coating thickness in the present study was 240 nm. In addition, textured coating materials were observed within the coating sections in the present study while in the contrary, only crystallites, probably less than 2.5 nm in sizes were observed in the sections of the coatings developed on 99.99% aluminium. These observations as well as the open circuit potential of about 1.7 V as against -1.4V observed for super-pure aluminium further indicated that the alloy is electrochemically more active hence a faster rate of coating development and improved thickness were observed for the Al/0.2%Fe alloy.

Further, AES analyses revealed that the outer regions of the coating are principally composed of zirconium and aluminium oxides/hydroxides.

4. CONCLUSIONS

The electrochemical nature of conversion coating formation and development on aluminium and its alloys from a bath containing fluoride species was partially established with the addition of iron in aluminium matrix.

The coating thickness obtained after 900secs of immersion in the coating bath was 240nm. Further protracted treatment resulted in coating dissolution which may be detrimental to improved corrosion and adhesion properties of zirconium conversion coating on aluminium.

The keying facilities afforded for subsequently applied organic finishes as a result of the micro- roughness of the treated surface will be important features for improved paint adhesion on treated alloy surfaces.

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