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XANES Study of Ce and Mo Containing Conversion Coatings on Aluminium

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Abstract: Ce-Mo conversion coatings on superpure aluminium have been examined using XANES and analytical TEM to study the coating development over the electropolished surface. Ce species are predominantly in the Ce^{3+} state in the coating, resulting from the various steps of the process, and Mo is in the Mo^{6+} state. After immersion in NaCl solution, Ce and Mo species leach from the coating. Conversion coating formation develops a hydrated film with cerium species incorporated; final anodic polarisation in MoO_4^{2-} solution results in Mo species in the hydrated film. Corrosion inhibition is attributed to the coating acting as a barrier layer to environmental access to the aluminium substrate and reduced cathodic activity.

1. INTRODUCTION

The Ce-Mo process has been developed to protect aluminium alloy substrates[1]. The improved behaviour of the coated substrate in NaCl solution, including high pitting potential, low passive current density and high pitting resistance, is revealed from anodic and cathodic polarisation, and electrochemical impedance spectroscopy. However understanding of the coating formation mechanism and the manner in which protection is afforded is limited due to lack of precise characterisation of the coating. Consequently the present study has investigated the valence states of incorporated cerium and molybdenum species in the coatings formed on superpure aluminium, together with morphological observations of the coatings and the electrochemical behaviour of the treated aluminium, enabling insight into the mechanism of coating formation from consideration of the individual steps in the process and the protection afforded.

2. EXPERIMENTAL

Electropolished 99.99% aluminium sheets were treated by the Ce-Mo process, which involved 2 hours immersion in boiling 10 mM $\text{Ce}(\text{NO}_3)_3$ solution followed by a further 2 hours immersion in boiling 5 mM CeCl_3 solution and, finally, potentiostatic anodic polarisation for 2 hours in 0.1 M Na_2MoO_4 solution at room temperature. The valence states of Mo and Ce species associated with the coating formed by the Ce-Mo process were evaluated by XANES analyses. Both Ce L_{III} and Mo K edge XANES spectra were measured for freshly treated specimens and others which had been immersed in 0.5 NaCl solution for 15 and 30 days. XANES measurements were made on beamline 7C at the Photon Factory, Japan, in the fluorescence mode in air using a harmonically rejecting Si(111) two-crystal monochromator. Two ionization chambers were used to measure incident photon (I_0) and fluorescence (I_f) intensities. Ultramicrotomy allowed TEM examination.

3. RESULTS AND INTERPRETATION

Ce L_{III} -edge standard spectra were determined for model compounds $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and CeO_2 , providing references for Ce^{3+} and Ce^{4+} species respectively (Fig.1, curves b and a); for the Mo K edge spectra, Mo metal foil, Na_2MoO_4 and MoO_2 compounds provided reference values for Mo^0 , Mo^{6+} and Mo^{4+} species respectively (Fig.2, curves a, b and c). Examination of the Ce L_{III} -edge XANES spectra of the standards reveals a single peak at the absorption edge for Ce^{3+} species, and a twin peak for Ce^{4+} , providing information for recognition and discrimination of the Ce^{3+} and Ce^{4+} valence states. Further, with increasing Ce^{4+} content, the height of the second peak increases proportionally, giving information on the constitution of the film from observation of the edge shape [2]. By comparison of the shape of the spectra with that of the standards, the valence states of molybdenum species can also be identified since, for MoO_4^{2-} , there is a small peak at the half height of the edge and, although the spectra of Mo foil and MoO_2 have a clear edge, different structures above the edge are evident. Further, the edge position for Mo foil (20003 eV) is 5 eV lower than that of MoO_2 .

Ce and Mo edge XANES spectra of the coatings, formed in each step of the Ce-Mo process, are shown in Figs.1 and 2 respectively, with the insets revealing sections of the corresponding coatings. The first hydrothermal treatment reveals a typical hydrated film, formed by reaction of aluminium with boiling water, comprising an inner textured region and an outer platelet layer (Fig.1a). The metal/film interface appears relatively flat. The second treatment gives a similar coating appearance. For the final coating from the Ce-Mo process, at selected areas, a thin layer, about 10-20 nm thick, of dark deposits of Ce rich species, is evident above an inner compact layer (Fig.1b). Mo species were found throughout the coating

by EDX. The metal/film interface is of scalloped appearance, resulting from the preferred dissolution of the aluminium during the treatment. Generally, the coating morphology is similar to that from the hydrothermal treatment (Fig.1c).

The valence states of Ce and Mo species, obtained from XANES, for the coatings are summarised as follows: (a) after immersion in boiling $\text{Ce}(\text{NO}_3)_3$ solution for 2 hours, the Ce species are present as a mixture of mainly Ce^{3+} with a small contribution from Ce^{4+} species (Fig.1, curve c); (b) after the second step, 2 h immersion in boiling 5 mM CeCl_3 solution, the Ce edge height is 6 times that of the first step, suggesting increased Ce species in the film, with similar proportions of Ce^{3+} and Ce^{4+} species to that from the first step (Fig.1, curve d); (c) the final step of the Ce-Mo process, i.e. anodic polarisation in Na_2MoO_4 for 2 hours results in an overall decrease of Ce species, by about 50%, with no Ce^{4+} contribution to the spectrum (Fig.1, curve e); (d) compared with the standard Mo K edge spectra, the Mo species associated with the film are in the Mo^{6+} valence state (Fig.2, c); (e) immersion of the treated specimens in 0.5 M NaCl solution for 15 and 30 days dramatically decreases both Ce and Mo species, i.e. up to 95% for Ce and 70% for Mo. The Mo species remaining in the Mo^{6+} state (Figs.2, d and e). The XANES result thus suggests leaching of Ce and Mo species into NaCl solution during immersion.

Coating development during hydrothermal treatment is similar to hydrated film growth on aluminium in boiling water, with transformation of the original air-formed film to variously hydrated alumina including pseudoboehmite. Oxygen reduction occurs at cathodic sites with local increase of pH. With Ce ions, $\text{Ce}(\text{OH})_3$ precipitates locally, with small amounts oxidized to $\text{Ce}(\text{OH})_4$. Thus, a hydrated oxide layer (with probably trapped Ce species) forms over the macroscopic surface, with Ce hydroxide deposited at cathodic sites. Anodic polarization of the previously hydrothermally treated aluminium substrate in molybdate solution heals flaw sites in the hydrated film by anodic alumina formation, where the substrate anodizes, generating acidic conditions and leading to dissolution of some $\text{Ce}(\text{OH})_3$ and precipitation of MoO_3 gel-like material. $\text{Ce}(\text{OH})_4$ may also dissolve or be reduced due to the strong oxidizing properties of Ce^{4+} ions in acid environment. Elsewhere, where there are no flaws in the hydrated film from the hydrothermal treatments, the hydrated layer is little affected by the final anodic polarization.

Electrochemical measurements reveal that the Ce-Mo treated aluminium has an increased pitting potential and reduced anodic and cathodic current densities. This arises from (i) the film developed by the anodic treatment in the presence of a hydrated oxide acts as an insulating barrier, limiting exposure of aluminium to the environment; (ii) incorporated molybdenum species provide a potential self-healing ability when the film is damaged and (iii) cathodic activity is restricted due to deposited cerium compounds.

4. CONCLUSIONS

XANES has been shown to be a powerful tool in chemical states recognition, allowing mechanisms of protective coating formation on aluminium to be advanced.

References

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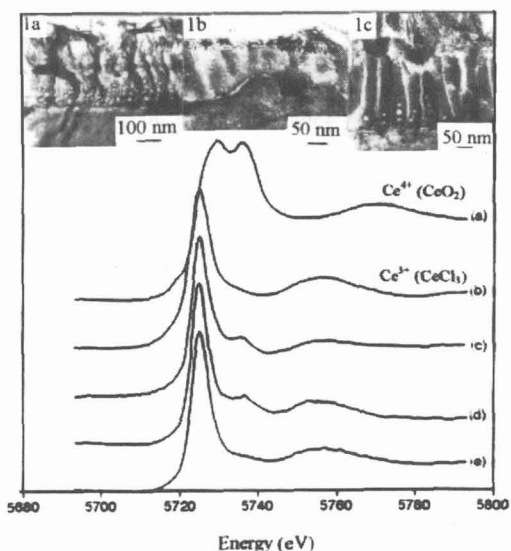


Fig.1 Ce L_{III} edge XANES spectra of standards and coated Al.

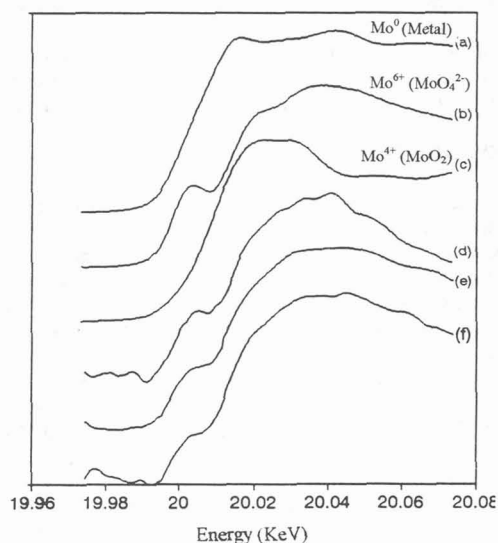


Fig.2 Mo K edge XANES spectra of standards and coated Al.