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An investigation of the corrosion inhibitive layers generated from lithium oxalate-containing organic coating on AA2024-T3 aluminium alloy

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The protective film formed in a defect by leaching of lithium oxalate from model organic coatings during neutral salt spray exposure has been investigated. A scribed area of about 1 mm width was introduced on the coated AA2024-T3 aluminium alloy. The scribed area was examined before and after exposure in neutral salt spray environment for 4, 8, 24 and 168 h by scanning and transmission electron microscopies. It was found that the lithium oxalate was able to leach from the organic coating during neutral salt spray exposure and it promoted the formation of a film that provided effective corrosion protection to the alloy. The typical film morphology consists of three different layers, including a relatively compact layer near the alloy substrate, a porous middle layer and a columnar outer layer. Variation of the film morphology was also observed at different locations of the scribed alloy surface, which may be related to the difference of local concentration of lithium species. Electron energy loss spectroscopy detected lithium, aluminium and oxygen in the film. Although the film showed the varied morphologies in different regions of the scribed area, the alloy substrate was protected from corrosion when the film was formed. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: AA2024 aluminium alloy; lithium; pigment; leaching; corrosion; inhibition

Introduction

Attempts to develop surface pretreatments and pigmented coatings that allow the replacement of carcinogenic and environmentally hazardous hexavalent chromium based processes and technologies used in aircraft and other coating systems have been carried out for decades. Various approaches have been attempted, but, to date, none has been able to demonstrate the same level of effectiveness as chromates.^[1–8]

For conversion coatings, alkaline lithium salt solutions have been proposed as a potential replacement of hexavalent chromium based chemical conversion coatings. Lithium salts, including lithium carbonate,^[9–15] lithium sulphate^[9] and lithium chloride,^[9] in aqueous alkaline environments have been found to form continuous surface conversion coatings on a range of substrates including superpure aluminium,^[10,11] AA6061,^[9] AA2024^[12,13] and AA7075^[12,13] aluminium alloys, and steel substrates^[14,15] by immersion or by combination of cathodic/anodic polarisation. Such conversion coatings significantly increased the corrosion resistance of the substrates through ennobling of the pitting potential of the alloys and reducing the overall corrosion current density. Conversion coatings formed with lithium carbonate on aluminium were analysed by X-ray diffraction, which suggested the presence of the layered hydroxalite lithium aluminium hydroxide carbonate hydrate $\text{Li}_2[\text{Al}_2(\text{OH})_6]_2 \cdot \text{CO}_3 \cdot n\text{H}_2\text{O}$.^[12] This was confirmed by electron diffraction using transmission electron microscopy (TEM) for the coating formed on AA1100 aluminium alloy.^[13]

For pigmented organic coatings, lithium salts also demonstrated their potential to replace chromate-containing pigments in recent studies.^[16–18] The lithium salts were leachable from the organic coating and promoted the formation of a protective film at the bare aluminium alloy substrate. It was found that a lithium-containing film with three distinct layers of barrier, porous, and columnar morphologies was developed during neutral salt spray testing in the scribed area of coated AA2024 aluminium alloy when the organic coating contained lithium salts. The morphology of the film showed similarity to the film formed by lithium conversion coatings^[12,13,16] in the top columnar layer, but with a thicker barrier

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layer formed beneath columnar and porous layer. The relatively thick film may be associated with the relatively low pH during salt spray testing compared with that for the formation of lithium conversion coating. The film protected AA2024 aluminium alloy from corrosion during neutral salt spray testing for 168 h.

Further to the investigation of the general filming behaviour in the scribed area of the bare alloy when coated with a lithium oxalate pigmented organic coating, a detailed investigation of the evolution of the film formed during neutral salt spray testing has been carried out. It was found that unlike the film formed by lithium-based conversion coatings with uniform morphology, the film formed in the scribe from a lithium oxalate pigmented coating during neutral salt spray testing shows variations in morphology. The mechanism of the formation of the film in different locations is explored, along with the corrosion protection of the film with varied morphologies.

Experimental

Polyurethane-based binder was used for the formulation of a model primer coating, and lithium oxalate was used as pigment.^[16] The binder contained a polyester resin (Desmophen® MPA) and an aliphatic polyisocyanate (Tolonate® HDB 75 MX) with a NCO/OH ratio of 0.75 and a pigment volume concentration (PVC) of 30%. AA2024-T3 aluminium alloy anodized in a mixed tartaric-sulphuric acid electrolyte was used as the substrate. A mechanical milling device was used to artificially damage the coating with a U-shaped scribe. The panels of the coated alloy, with dimensions of 7 × 7 cm, were scribed from corner to corner, leaving a 1-mm wide scribe that penetrated to a depth of 100–150 μm into the metal. After scribing, the primer coated alloy samples were exposed to neutral salt spray conditions (ASTM-B117) for varying periods up to 168 h. After exposure, the specimens were rinsed for 2 min with flowing deionized water to remove any residual chlorides and the panels were air dried.

The scribed areas were examined by scanning electron microscopy (SEM) using a ZEISS Ultra 55 instrument with an acceleration voltage of 0.5 kV. The cross sections of the scribed region were also examined by TEM using a JEOL FX 2000 II instrument operated at 120 kV, with a nominal sample thickness of 15 nm prepared by a Leica EM UC6 ultra-microtome with a diamond knife. Electron energy loss spectroscopy (EELS) was conducted on a TECNAI F30 TEM fitted with a Gif2001 detector, operated at 300 kV.

Results

Appearance of the scribed area before and after salt spray testing

The effectiveness of lithium oxalate as pigment in the coating on the corrosion protection of AA2024 aluminium alloy has been assessed by examining the scribed regions of the coated alloy in SEM (Fig. 1). The surface of the scribed alloy before exposure to the salt spray showed a mixture of shingling, cracking and parallel scribe lines as a result of the high levels of shear strain imposed during scribing (Fig. 1a), as observed previously.^[5] Metal debris can also be observed (Fig. 1a). After the salt spray exposure for 168 h, in the case that the lithium-containing pigment was absent in the coating, the initial scribing lines and shingles had disappeared, with corrosion product deposited over the exposed surface (Fig. 1b). In contrast to the un-pigmented specimen, when lithium

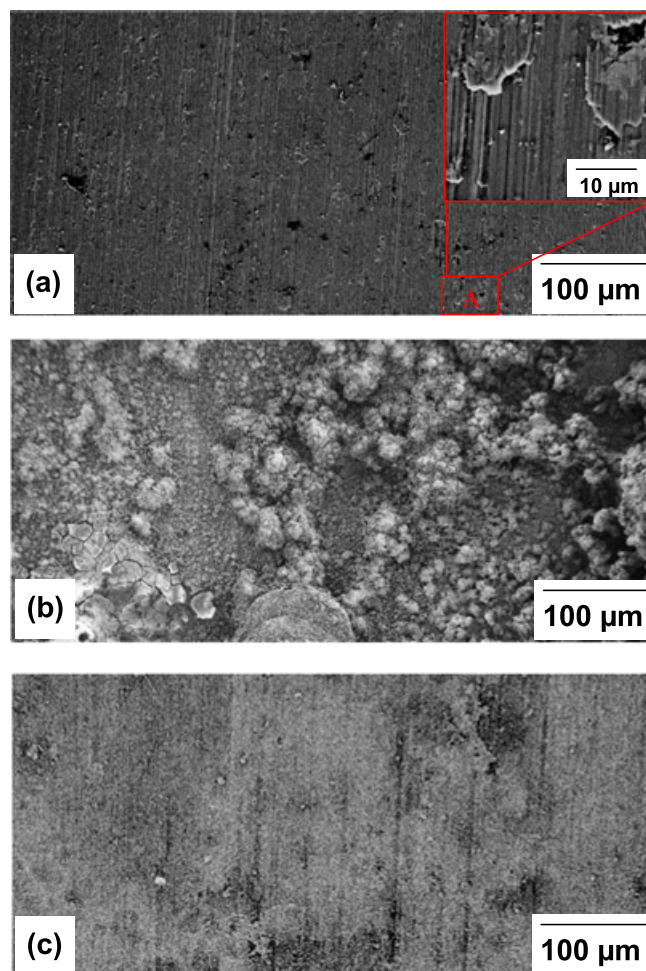


Figure 1. Scanning electron micrographs of the scribed area on coated AA2024-T3 alloy before and after 168 h neutral salt spray exposure: (a) before exposure; (b) coating without inhibitor after 168 h exposure; (c) coating pigmented with lithium oxalate after 168 h exposure.

oxalate was introduced in the organic primer, the original shingling and parallel scribe lines were still visible on the scribed surface of the alloy after salt spray testing for 168 h, as shown in Fig. 1c.

The planar view and cross sectional view of the scribed areas of the samples coated with the primer coatings without and with lithium oxalate are shown in Figs 2 and 3. Figures 2a and 2b are the planar view and cross-sectional view of the scribed area of

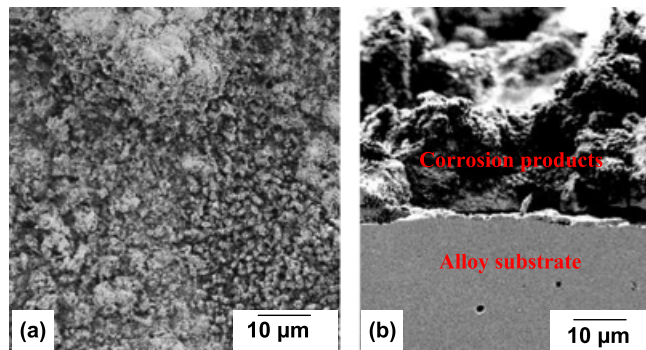


Figure 2. Planar and cross-sectional views of the scribed area after 168 h neutral salt spray exposure when the coating contained no lithium oxalate: (a) planar view; (b) cross-sectional view.

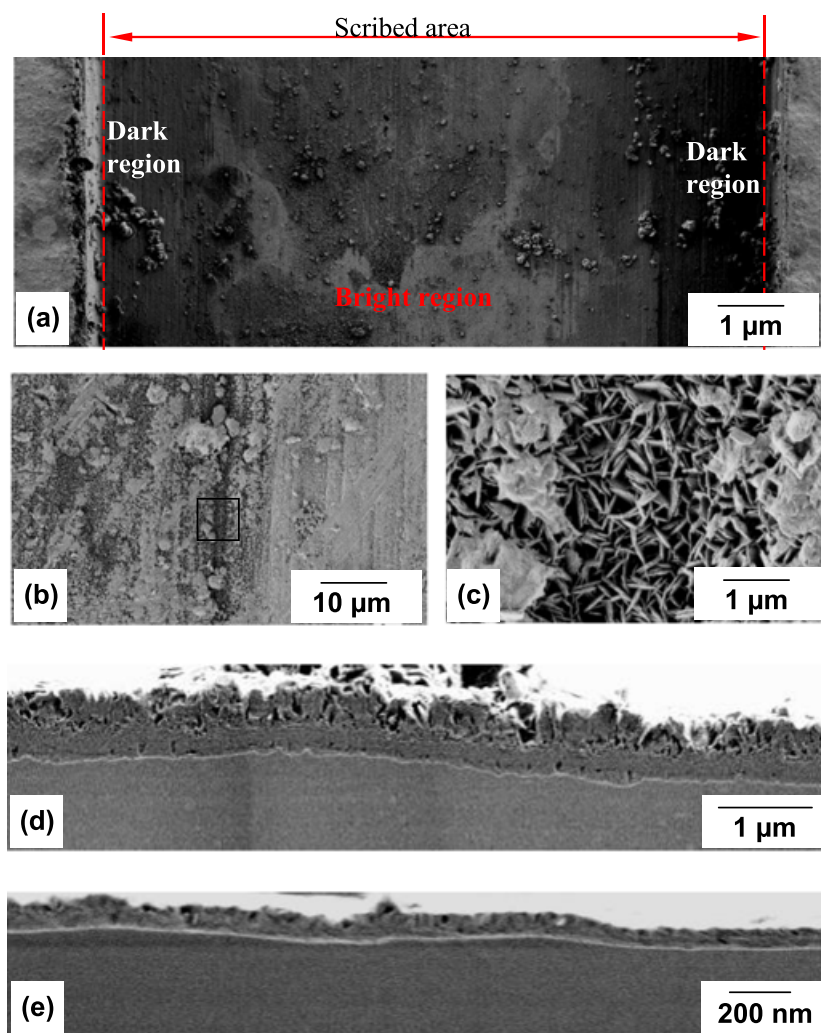


Figure 3. Scanning electron micrographs of protective layers formed in scribed area after 168 h neutral salt spray testing when the primer coating pigmented with lithium oxalate: (a)–(c): planar views; and (d)–(e): cross-sectional views.

the specimen coated with the primer coating without lithium oxalate. A large amount of corrosion product had developed within the scribed area (Fig. 2a) with a thickness between 20–40 μm (Fig. 2b). In the case when lithium oxalate pigmented coating was applied, the surface of the scribed area appeared as dark and bright regions with little corrosion product (Figs. 3a). The dark appearance is more prominent in the regions close to the primer coating. The higher magnification image of the square region indicated in Fig. 3b showed that fine textures had developed in the dark region (Fig. 3c). Cross-sectional view of the scribed area revealed that a protective film had been formed above the alloy surface within the scribed area. The protective film showed varying thicknesses (about 0.1–0.7 μm) and morphologies, as illustrated in Figs 3d and 3e. Some areas of the film comprised a barrier layer close to the metal/film interface, a porous layer above the barrier layer and a columnar-shaped layer in the outer region (Fig. 3d). Other areas of the film comprised a porous layer above the barrier layer with insignificant columnar layer (Fig. 3e). Comparing the planar view and cross-sectional view, it is evident that when the columnar-shaped layer was present in the outer region, the film was relatively thick and the appearance was dark in planar view; when the columnar-shaped layer was absent, the film was relatively thin and the planar view showed a relatively bright appearance (Fig. 3b).

Development of protective layer during neutral salt spray exposure

From Figs 1 and 3 it is evident that after the salt spray testing, a protective layer had developed at the surface of the scribed areas when a lithium oxalate containing model coating was applied on an AA2024 sample. The early stages of film development have been investigated by cross sectional examination of the scribed area after salt spray exposure for 4, 8 and 24 h, as shown in Fig. 4. After salt spray exposure for 4 h, the edge region of the scribed area had developed a very fine columnar morphology on top of the barrier film (Fig. 4a), while the film in the centre of the scribed area was relatively flat (Fig. 4b). The barrier film had also developed on an AlFeMnCu particle without disrupting the continuity of the film in the central region (Fig. 4c). After 8 h salt spray exposure, centre region of the resultant film was similar to that after 4 h testing, with a barrier film developed (Fig. 4d), while edge regions showed significant columnar-shaped films (Fig. 4e). After 24 h testing, a three-layered morphology had been developed in edge region and near centre region of the scribed area, with typical morphologies displayed in Figs 4g and 4h. In centre region, the barrier type film without the columnar-shaped morphologies was still present (Fig. 4f). Energy-dispersive X-ray analysis showed that the film contained

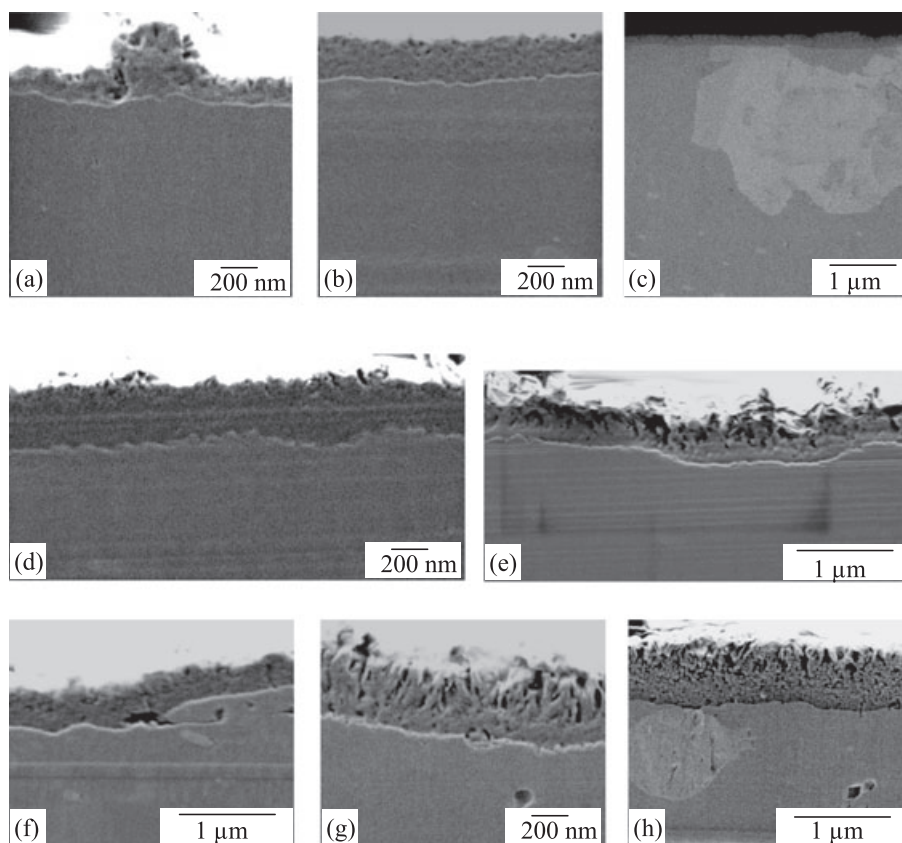


Figure 4. Development of the protective film within the scribed area on the alloy coated with the primer coating pigmented with lithium oxalate during neutral salt spray exposure: (a)–(c) 4 h; (d)–(e) 8 h; (f)–(h) 24 h.

aluminium and oxygen. Further, residual chlorine species were also detected locally.

TEM observation and EELS analysis

Transmission electron microscopy and EELS were used for further observation and analysis because EELS is able to detect the lithium species in the coating, while other techniques, i.e. energy-dispersive X-ray analysis, cannot detect lithium species in the film.

Fig. 5 displays transmission electron micrographs of cross sections of the thin film formed on the central and edge regions of scribed area on AA2024 aluminium alloy coated with organic primer pigmented with lithium oxalate after salt spray exposure for 168 h. The TEM images clearly showed the barrier layer immediately above the alloy substrate (Figs 5a and 5b). The columnar-

shaped outer layer was present at edge regions (Fig. 5b). Interestingly, fine grains, approximately 20–100 nm diameter, are evident in the alloy immediately beneath film, suggesting that a near-surface deformed layer could be generated by the scribing. The deformed layer was observed previously when thermomechanical processing or mechanical polishing was carried out in aluminium alloys.^[5,19–23] The composition of the film was analysed by EELS mapping (Fig. 6) in a location near the centre region, which detected aluminium, lithium and oxygen in the film. High-resolution TEM lattice images of the film is displayed in Fig. 7, revealing a mixture of amorphous and polycrystalline structures, similar to the film formed when lithium carbonate was used as corrosion inhibitive pigment in the organic coating.^[24] The interplanar spacings and the angles between the planes are measured, as indicated in the inset in Fig. 7. However, the lattice images of the crystalline

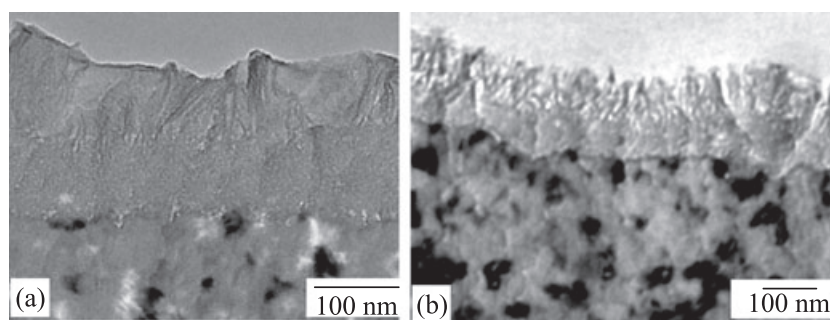


Figure 5. Transmission electron micrographs of the protective film formed within the scribed area on the alloy after neutral salt spray testing for 168 h: (a) barrier film formation; (b) film with barrier layer and columnar-shaped layer.

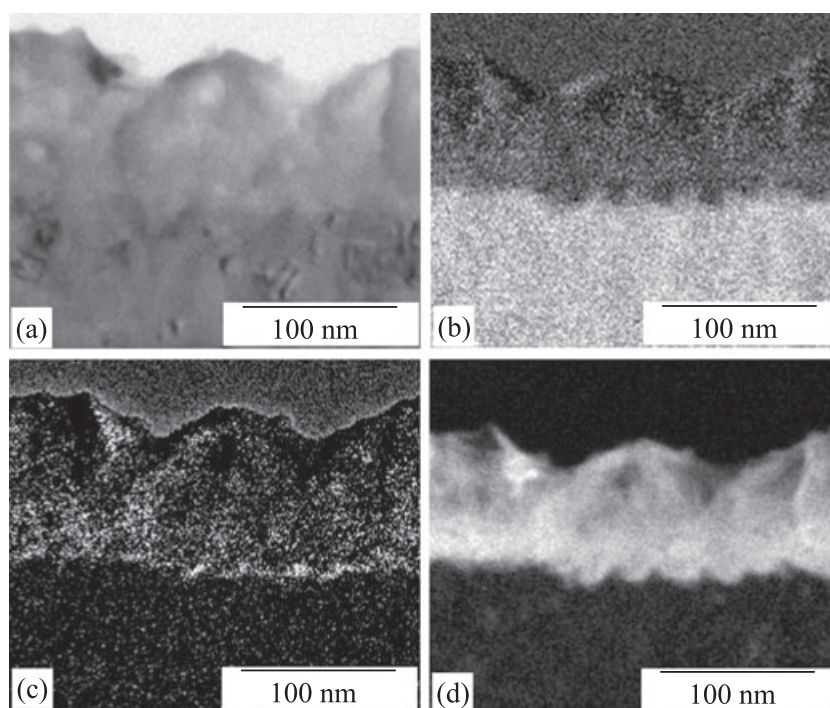


Figure 6. EELS mapping of the protective film: (a) TEM image; (b) aluminium map; (c) lithium map; and (d) oxygen map.

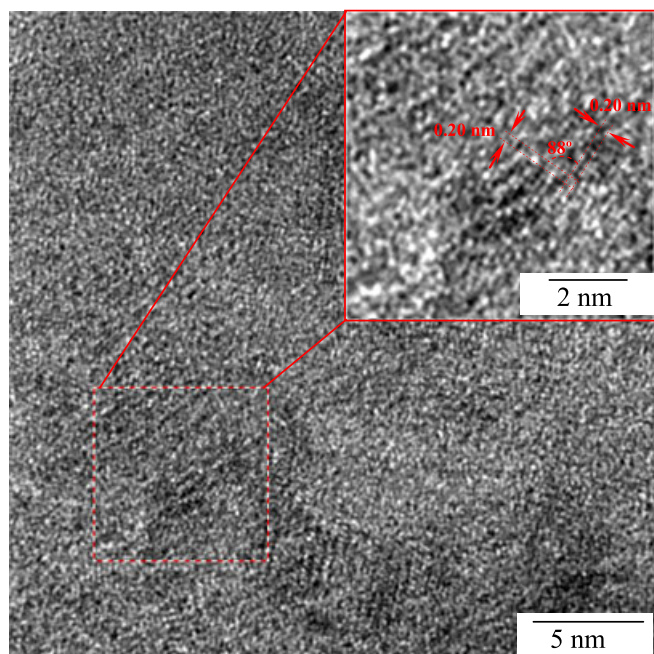


Figure 7. High-resolution TEM lattice images of the film formed in the scribed area of the alloy coated with lithium oxalate pigmented coating.

regions could not distinguish between the hydrotalcite,^[12,13,25] α - LiAlO_2 ^[26–28] and $\text{Al}(\text{OH})_3$.^[29,30] Further study is currently being carried out to characterize the structure of the crystal.

Discussion

The scribed area on the AA2024 aluminium alloy clearly exhibited shingles, cracks and scribing lines before salt spray testing. After salt

spray exposure, these features had disappeared in the case when the coating was not pigmented with lithium oxalate. Instead, a thick layer of corrosion products was formed; in some areas this layer was more than 20- μm thick, as revealed in Fig. 2b. This indicates that the scribed area suffered from significant corrosion during the 168 h salt spray exposure. In contrast, when the coating was pigmented with lithium oxalate, the scribed areas were relatively pristine, as shown in Fig. 1c. This suggests that the presence of lithium oxalate in the organic coating provided fast and effective corrosion protection to the scribed area of the coated alloy. EELS analysis showed that lithium species were present in the protective film, demonstrating that lithium species are able to be released from the primer coating and react with hydrated aluminium oxide to form a transparent protective film. Although the film is relatively thin, less than 1- μm thick, the neutral salt spray testing results suggest that the film is sufficiently stable to provide long-term protection.

Through the observation of the evolution of protective film with time during salt spray testing in different locations of the scribed area, it is evident that the film formed in scribed area revealed significant variation in morphology. In some locations, a significant presence of the columnar and a porous morphology above the barrier film is evident. This morphology may form with high lithium concentration, which consequently results in relatively high local pH. In other locations, significant barrier layer is present, with insignificant columnar morphology. These regions may correlate to lower lithium concentrations and or milder pH. Significant columnar morphology was developed close to the side wall, which is closer to the organic coating with leachable lithium oxalate.

Observation of the evolution of the film during salt spray exposure showed that after 4 h, the protective film has been developed. Comparing the thickness of the film formed during salt spray from 4, 8, 24 and 168 h, a slight increase of the film thickness was observed with time for the overall scribed area, although local thickness may also vary by the initial morphology of the scribed surface and local cathodic/anodic activities in the alloy.

Conclusions

- (1) When lithium oxalate was added to the organic model coating, lithium species were able to leach out from the organic coating and migrate to the damaged area, which promoted the formation of a film, of about 0.1 to 0.7 μm thickness, on the alloy within the damaged area.
- (2) The film formed by leaching of lithium oxalate contains mainly aluminium, lithium and oxygen, which is able to protect the AA2024 aluminium alloy from corrosion during neutral salt spray test.
- (3) The film evolved during the salt spray testing. After 4 h, precursors of columnar morphology developed locally. After 8 and 24 h salt spray testing, significant columnar layer developed in local regions. However, the film showed variations in morphology, with regions closer to the organic coating developed significant columnar outer layer, and centre regions showed a smooth barrier region with little columnar outer layer even after 168 h salt spray testing.
- (4) The film developed in the regions close to the organic coating showed significant columnar outer layer, perhaps because of the high concentration of lithium species in the region. Away from the organic coating, at the central region of the scribed area, barrier layer with little columnar out layer developed, perhaps because of relatively low lithium concentrations and milder pH.
- (5) The film showed a mixture of amorphous and nano-sized crystalline materials. The lattice fringe images of the nano-crystals suggest that hydroxalite and/or $\alpha\text{-LiAlO}_2$ and/or $\text{Al}(\text{OH})_3$ are present in the film.

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