Surface film characteristics of Al–Li–Cu–Mg alloys in 0.1 N NaOH

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Abstract. The nature of surface films that form under free corrosion conditions, and their effect on the subsequent polarization behaviour of an Al–1.90Li–1.80Cu–1.00Mg–0.09Zr alloy in 0.1 mol/l NaOH solution at 35°C have been studied. The variation of open circuit potential (OCP) as a function of time is characteristic for the alloy in the electrolyte. It initially changes in the noble direction with the surface of the specimen being enveloped by a black coating, and, later, when the black coating is punctured at some localized regions, the OCP shifts and stabilizes at an active value of -1450 mV vs saturated calomel electrode (SCE). X-ray diffraction analysis of the surface film layer indicates that it consists of essentially lithium aluminum hydroxide at shorter immersion time, and lithium aluminum hydroxide and copper hydroxide after longer immersion time in the electrolyte. The scale morphology as a function of immersion time has also been studied by scanning electron microscopy. Polarization experiments conducted after 2 and 15 h of immersion revealed that the alloy exhibited active–passive type polarization behaviour in both the cases. The polarization behaviour of the specimen immersed for longer times has been explained by considering Cu ennoblement on the surface. It was also observed that the hydride LiAlH₄ forms on the surface regions of the alloy under free corrosion conditions.

Keywords. Aluminum–lithium alloys; free corrosion potential; NaOH solution; surface film characteristics.

1. Introduction

Rising energy costs and the advent of tough composites have stimulated the development of advanced aluminum–lithium alloys for aircraft applications. The attractive combination of weight saving benefits and increased stiffness of Al–Li alloys has generated interest in these alloys (Sankaran and Grant 1980; Lavernia et al 1990). The substitution of Al–Li alloys in place of conventional 7XXX series Al alloys in aircraft components would entail a saving of 8–10% of the structural weight along with an increase of 15% in the elastic modulus, thereby providing an extra margin of safety for critical aerospace applications.

In addition to fuel efficiency, aircraft structures are also required to be corrosion resistant for safe and long service life. In this regard, several studies have shown that Al–Li alloys are susceptible to environmental degradation (Christodoulou et al 1983; Holroyd et al 1985; Binsfeld et al 1987; Meletis and Huang 1989; Wang et al 1992). The presence of the active element Li renders these alloys different in their corrosion behaviour compared to conventional Al alloys. These have been observed to be more susceptible to general corrosion by Niskanen et al (1981, 1982) and Ricker and Duquette (1983). Moreover, lithium-bearing precipitates in Al–Li alloys interact with hydrogen and renders the mechanism of hydrogen embrittlement (HE) complex in nature. In a detailed study of HE of aged and retrogressed-reaged Al–Li–Cu–Mg alloys, tensile specimens were precharged electrochemically with hydrogen at constant cathodic current density in an alkaline solution of 0.1 mol/l NaOH (Thakur and Balasubramaniam 1997b). Similarly, Kim et al (1988) and Chen et al (1993) have also used the same electrolyte for hydrogen precharging. It has also been observed by several investigators (Meletis and Huang 1989; Bandyopadhyay et al 1992; Thakur and Balasubramaniam 1997a) that the specimen surface turns black after cathodic hydrogen charging. Finally, it has been experimentally observed in Al–Li–Cu–Mg alloys that the pH of the electrolyte in pits is alkaline in nature, in contrast to the acidic pit environment in the case of conventional Al alloys (Craig et al 1987). Pits act as initiation sites for environment-induced cracking (EIC) of Al–Li alloys (Balasubramaniam et al 1991a), and therefore the surface film formation characteristics under alkaline conditions are also important in understanding the environmental degradation of Al–Li alloys by EIC. A thorough search of the literature revealed that polarization studies have not been conducted in pure NaOH solution as most of the investigators have used 3.5% NaCl electrolyte (Pizzo et al 1984; Tsao and Pizzo 1985; Craig et al 1987; Gui and Devine 1987; Lumsden and Allen 1988; Buchheit and Stoner 1989; Piascik and

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Gangloff 1989; Magnin and Rebiere 1987; Balasubramaniam et al 1991a; Ambat and Dwarakadasa 1992). Hence, there was a need to understand the film characteristics under open circuit, potentiodynamic, and cathodic hydrogen charging conditions. In the present study, the potentiodynamic polarization behaviour of Al-Li-Cu-Mg alloys has been studied in an alkaline solution of 0.1 mol/l NaOH and the surface film formed under free corrosion, and polarization conditions was characterized by X-ray diffraction (XRD), and scanning electron microscopy (SEM). The effect of temperature on the polarization behaviour has been addressed earlier (Thakur and Balasubramaniam 1997c).

2. Experimental

The Al-Li alloy (designated as 1441) used in the present study was supplied by the Defence Metallurgical Research Laboratory, Hyderabad. The composition of the 1441 alloy was 1.90% Li, 1.80% Cu, 1.00% Mg, 0.09% Zr and balance Al. Incidentally, the film formation characteristics of another Al-Li alloy of composition 2.30% Li, 1.24% Cu, 0.80% Mg, 0.12% Zr and balance Al (designated as 1440) was also studied and its behaviour was similar to that reported in this communication for the 1441 alloy. Therefore, the 1440 alloy is not discussed here. Peak-aged (aged at 170°C for 18 h) coupons of 1 cm² cross-sectional area were sectioned from the sheet, and later all the surfaces were ground to 600 grit surface finish. Specimen coupons were connected with a conductive wire and this assembly was mounted on a cold-setting epoxy. Surfaces of the specimens were polished to 1 μm surface finish and were thoroughly cleaned with acetone prior to each polarization experiment.

Polarization experiments were conducted in a one litre electrochemical cell controlled by a potentiostat, interfaced with a personal computer. A platinum foil of 1 cm² area was used as a counter electrode. A 0.1 mol/l NaOH solution of pH 13 (not deaerated and not stirred) was the electrolyte used in the present study, as this was the solution in which cathodic hydrogen precharging was conducted for HE studies by Thakur and Balasubramaniam (1997b). For the polarization studies, the temperature of the electrolyte was that of the ambient temperature (25°C). The OCP from the time of immersion vs saturated calomel electrode (SCE) was monitored continuously. All the potentials mentioned in the text are with reference to SCE.

Before the start of each polarization experiment, the specimen was allowed to attain a stable potential. The data of potential vs time was recorded. After attaining a steady OCP, the potential was scanned at the rate of 1 mV/sec from −1800 mV to +1800 mV, which was then followed by reverse scan from +1800 mV to −1400 mV. Triplicate experiments were conducted and the experimental results were found to be reproducible.

X-ray diffraction (XRD) patterns were obtained before (for reference purposes) and after immersion for different time intervals (2 h, 15 h and 7 days) in the NaOH electrolyte in a Rich Siefert X-ray diffractometer 2002D using CuKα radiation. In some experiments, XRD patterns were also obtained after removing the surface scale by mechanical polishing with fine emery paper. In all the XRD experiments, the intensity of scaling, recorder chart speed, and sample rotation rate were maintained constant. Square (one cm on the side) specimen coupons were used for this purpose.

After obtaining the XRD patterns from the surface of the above specimens, the microstructural features of the surface film were observed in a JEOL 840A scanning electron microscope (SEM). Electrical charging of the surface film during observation in the SEM, was avoided by sputter coating the surface with a thin Ag layer prior to its insertion in the SEM.

3. Results and discussion

3.1 Corrosion potential vs time

The nature of variation of open circuit potential (OCP) with time of immersion in the alkaline solution, is presented in figure 1. The observed behaviour for the 1440 alloy was also similar. The OCP stabilizes after about 6 h. The OCP is at a very active value immediately upon immersion (−1550 mV) and then rapidly rises in the initial period to about −1400 mV. This initial steep
rise could be due to the polarization of anodic and cathodic reactions. The potential continues to rise even after attaining the value of $-1300 \, \text{mV}$, but the rate of further increase is much slower. The FCP reaches its maximum value ($-1250 \, \text{mV}$) after $\sim 5 \, \text{h}$.

The following observations were made visually regarding the changes in the surface of the specimen after its immersion in the electrolyte. The specimen surface was very clean and appeared bright before immersion. With increasing immersion time, the surface tarnished and acquired a black layer. This black layer completely covered the surface, and it was tenacious. The black layer coverage was uniform (i.e. did not show any ruptures) till the maximum in the OCP was attained. Then, an interesting feature was observed in all the experiments. The black layer was attacked at a few locations, which appeared as pin-holes, coupled with vigorous bubble evolution from these locations. When such a state was observed on the surface, the OCP decreased rapidly from $-1250 \, \text{mV}$ until it reached a value of about $-1450 \, \text{mV}$. The number of ruptured pin-holes (or localized reaction sites), interestingly, remained the same while the potential fell rapidly towards active potentials. After the fall of potential, the OCP stabilized and did not change despite longer duration of immersion time ($> 14 \, \text{h}$). The number of pits still remained the same when the OCP stabilized and bubble evolution was observed from these localized rupture sites. Moreover, the colour of the film turned greenish or greenish-yellow after attaining the stable OCP. It is important to note that the above behaviour was observed in a large number of independently conducted experiments. Interestingly, Craig et al (1987) in their study of the local chemistry of pits in Al-Li-Cu-Mg alloys, noted that, after longer duration of immersion, the pits were packed with greenish hydrous deposits with both metallic Cu and oxidized Cu particles in and around the pits.

In summary, the FCP did not stabilize immediately after immersion, but exhibited a characteristic behaviour described above. It had been earlier observed by Colvin et al (1986) that a ternary Al-Li-Ge alloy took a fairly long time (18–36 h) for stabilization in deaerated 3.5% NaCl solution. Apart from this reference source, there has been no mention of the nature of stabilization of the OCP of Al-Li alloys, as most of the investigators have stated that the OCP stabilized in a fairly short time in NaCl solutions (Pizzo et al 1984; Tsao and Pizzo 1985; Craig et al 1987; Gui and Devine 1987; Lumsden and Allen 1988; Buchheit and Stoner 1989; Piascik and Gangloff 1989; Magnin and Rebiere 1987; Balasubramaniam et al 1991a; Ambat and Dwarakadasa 1992).

3.2 Potentiodynamic polarization

To understand the effect of the surface film on the corrosion behaviour of the alloy, potentiodynamic polarization experiments were conducted for the conditions when the OCP attained a value of (i) $-1300 \, \text{mV}$ after 2 h immersion, and (ii) $-1450 \, \text{mV}$ after 15 h immersion.

![Figure 2](image1.png)  
Figure 2. Cyclic potentiodynamic polarization curves for 1441 alloy in 0.1 mol/l NaOH solution after 2 h immersion at 25°C.

![Figure 3](image2.png)  
Figure 3. Cyclic potentiodynamic polarization curves for 1441 alloy in 0.1 mol/l NaOH solution after 15 h immersion at 25°C.
immersion. The polarization curves for these two conditions are presented in figures 2 and 3, respectively. The potentiodynamic polarization curves for the two conditions exhibit pseudo active–passive transition or active–passive type polarization behaviour, but true passivity is not obtained, as the current density does not change by several orders of magnitude in the passive region compared to $i_{\text{crit}}$ (after the formation of the passive film).

The exact nature of the passive film that forms is not known. The passive region could also be a region of mass-transport-limited corrosion, with the characteristic nose resulting due to transition from a slightly more porous oxide/corrosion product to slightly less porous one. However, it must be appreciated that the presence of such a film on the surface does result in lower corrosion rates compared to the active state, although only to a lesser degree. Therefore, the polarization behaviour of the alloy has been termed as the pseudo active–passive behaviour. Interestingly, the nature of the passive film for the 1440 Al–Li–Cu–Mg alloy as well as for different heat treatment conditions (i.e. under aged, peak aged and over aged). Further, in both the cases the cathodic reduction line intersects the anodic polarization curve of the alloy, in the active region, thereby leading to the experimental polarization curves that exhibit active–passive transition.

While the active–passive transition is clearly seen in figure 3, it is not very clear in figure 2 because the critical current density and passive current density are relatively high, and moreover nearly equal. Nevertheless, figure 2 does show the transition from active to passive state. It is also seen that the critical current density and the passive current density after 15 h immersion is lower than after 2 h immersion indicating that the surface layer that has formed on immersion in the electrolyte does affect these parameters. However, in the case of 15 h immersion, there could be some pits which tend to passivate, but this effect cannot be clearly separated from the surface film formed during polarization.

The curves did reveal some changes for the specimens immersed for different times. Table 1 presents the various parameters obtained from the polarization curves for the specimens after (i) 2 h, and (ii) 15 h immersions. The zero current potential in the forward scan ($ZCP_f$) was nobler for condition (i). However, the potentials for primary passivation ($E_{pp}$) and complete passivation ($E_{cp}$) for the condition (ii) were lower compared to the condition (i), thereby implying the enhanced pseudo–passive behaviour of the specimen immersed in the solution for 15 h, which is also reflected by the nature of the polarization curves obtained for the two conditions (figures 2 and 3). The enhanced pseudo-passivity is also reflected in the lower critical ($i_{\text{crit}}$) and passive ($i_{\text{pass}}$) current densities obtained for condition (ii) compared to condition (i) (table 1). This could be due to the larger exposure time that resulted in the formation of a more uniform film on the surface, and possibly a thicker corrosion product. Incidentally, the $i_{\text{crit}}$ and $i_{\text{pass}}$ are comparable to that obtained by Ambat and Dwarakadasa (1992) for a number of Al–Li alloys in alkaline pH. Upon further increasing the potential, the current density does not vary with the potential and this is indicative of the pseudo-passive region. The passive film is stable up to the breakdown potential after which the specimen pits at a few localized locations. The breakdown potentials for the condition (i) is higher than for the condition (ii). Ambat and Dwarakadasa (1992) observed that the breakdown potential of several Al–Li alloys to be about −500 mV in alkaline pH 12 NaCl solution, and this is understandable as the presence of chloride ions leads to earlier destabilization of the passive film on the surface of Al–Li alloys (Schnuriger et al 1987). Moreover, the passive range obtained for the specimen immersed in the solution for 15 h is comparable to that obtained for the specimen immersed in the solution for 2 h, although the $i_{\text{crit}}$ is higher for the latter. Upon reversal of scan after reaching +1800 mV, it was observed that the reverse scan closely follows the path of the forward scan, thereby indicating the good re-passivation behaviour of these alloys in the alkaline pH electrolyte.

The reverse scan intersects the forward scan and zero current potential is obtained at the potential $ZCP_p$. Further, on reversal of scan, the $ZCP_p$ is obtained at a much more noble potential compared to $ZCP_f$ on the forward scan. This can be explained due to corrosion occurring under free corrosion conditions, and after the attainment of breakdown potential (during polarization) it causes the surface to be enriched with Cu as a result of dealloying of Al and Li (Buchheit and Stoner 1989). The specimen that had been immersed for 15 h has a higher amount of enriched Cu on the surface, which is probably due to longer immersion under free corrosion condition rather than due to corrosion occurring during polarization. It

Table 1. Electrochemical polarization characteristics of the 1441 alloy in 0·1 mol/l NaOH solution after 2 h and 15 h immersion at 25°C.

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>OCP (mV vs SCE)</th>
<th>ZCPf (mV vs SCE)</th>
<th>ZCPp (mV vs SCE)</th>
<th>$E_{pp}$ (mV vs SCE)</th>
<th>$E_{cp}$ (mV vs SCE)</th>
<th>$i_{\text{crit}}$ (mA cm$^{-2}$)</th>
<th>$i_{\text{pass}}$ (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>−1300</td>
<td>−1250</td>
<td>−1050</td>
<td>−950</td>
<td>−200</td>
<td>15.9</td>
<td>10.0</td>
</tr>
<tr>
<td>15</td>
<td>−1458</td>
<td>−1350</td>
<td>−720</td>
<td>−1200</td>
<td>−900</td>
<td>6.3</td>
<td>1.6</td>
</tr>
</tbody>
</table>
was observed that the specimen immersed for 2 h has a lower amount of surface Cu enrichment (reflected by its ZCP), although it corrodes faster according to the polarization characteristics (table 1). The presence of a Cu corrosion product in the film, for longer immersion time, has been observed with SEM and this is discussed later. Moreover, Craig et al. (1987) have also observed Cu enrichment on the surface of Al-Li-Cu-Mg alloys exposed to alkaline environments. Therefore, during the reverse scan, the exchange current density for hydrogen reduction reaction is increased. This is due to the surface being richer in Cu, since the exchange current density for hydrogen evolution reaction is higher on Cu than on Al (Kortum and Bockris 1951). Therefore, the zero current potential is shifted to positive potentials. A similar explanation was evoked by Buchheit and Stoner (1989) to explain the cyclic polarization behaviour of Al2CuLi in NaCl solution.

3.3 Characterization of surface film

Figures 4a and b present the XRD patterns for 1441 samples immersed for 0 (reference) and 7 days in NaOH solution at 25°C. The extra peaks observed in figure 4b were compared with the theoretical peaks of the hydrides, oxides and hydroxides of Al, Li, Cu and Mg. The extra peaks matched with the reported peaks of Cu(OH)2 and LiAl2(OH)7·12H2O (JCPDS Powder Diffraction Files 1974) and the peaks in figure 4b have been indexed accordingly. It has been hypothesized that the black film that forms under cathodic charging conditions is of Al(OH)3 + LiOH (Piascik and Gangloff 1989), and the present study reveals the exact nature of the scale. It has been reported that Cu(OH)2 is bluish green. The bluish green colour of the surface film layer indirectly confirms the presence of copper hydroxide in the film. A greenish surface deposit in the pits of Al-Li-Cu-Mg alloys was also reported by Craig et al. (1987). It was also noticed that the intensities of the peaks from the Cu(OH)2 phase is higher after 15 h immersion than after 2 h immersion. The XRD patterns obtained from the surface of the alloy after cathodic hydrogen charging at 10 mA/cm2 also revealed the presence of these two phases. In most of the polarization experiments conducted, it was noticed that as soon as the cathodic polarization began, severe hydrogen evolution was observed over the green-filmed specimen surface. As the potential approached the ZCP, the green layer generally peeled off from certain locations on the surface. As the potential was scanned beyond the ZCP into the anodic polarization region, the colour of the specimen further changed to dark green and remained the same till the end of the experiment. The green layer that had peeled off from the specimen during the polarization experiment was carefully filtered out from the test electrolyte, dried and analyzed by XRD.

The analysis of the film revealed that it essentially consisted of Cu(OH)2 and LiAl2(OH)7·12H2O, as observed earlier for the scales formed under immersion conditions.

Interestingly, some of the peaks obtained from the immersed specimens (figure 4b) corresponded unambiguously to the hydride phase, LiAlH4. In order to verify the presence of LiAlH4, the surface film, which had formed under immersion condition, was completely removed by careful mechanical polishing with fine emery paper till the surface again appeared bright and shiny. Care was taken to remove the film completely from the surface, especially from the pits. Though it is quite
likely that some oxide might still have been left behind, as it is quite impossible to completely remove the scales by mechanical polishing. However, it must be borne in mind that a certain minimum volume fraction of the phase is required to obtain significant XRD signal from this phase and it is unlikely that the oxide would have been present in significant amounts after the polishing procedure.

XRD patterns were obtained from the cleaned specimens and one such pattern obtained from the clean surface of the specimen immersed for 7 days is given in figure 4c. Detailed analysis of the diffraction lines of the oxide Cu(OH)$_2$ and LiAlH$_4$ indicates that the 100% major peak of the former occurs at a slightly higher 20 angle compared to the latter, which could be always clearly distinguished in the XRD patterns (figure 4). The diffraction patterns that were obtained at the slow scan speed (in the region 20 = 15°-30°) clearly showed this difference in the position of the peak after the oxide scale was removed from the surface. Therefore there is no ambiguity in the identification of the hydride. The maximum intensity (210) peak of the LiAlH$_4$ phase was observed in all the cases, thus indicating that this hydride forms under free corrosion conditions in the sub-surface regions of Al–Li alloys. The presence of this hydride phase was also noticed in the 2 h and 15 h immersion specimens after their surface films had been removed; however, the intensity of the peak was much weaker compared to the 7-day immersion specimen. The presence of this phase in Al–Li alloys after cathodic hydrogen charging had earlier been confirmed by transmission electron microscopy in the presence of stress (Balasubramaniam et al 1991b), and by XRD in the absence of stress (Thakur and Balasubramaniam 1997a; Velez and Sundaram 1998). Moreover, the presence of hydrides has also been indicated by laser-Raman spectroscopy of freshly-fractured surface of Al–Li alloys (Lewandowski and Holroyd 1990). The present study further reveals that this hydride can also form under free corrosion conditions owing to the availability of hydrogen which results from the reduction reactions that occur on the specimen surface during immersion in the electrolyte. An interesting observation, in connection with hydrogen evolution, was that when few shavings of the Al–Li alloy were placed in the NaOH electrolyte kept in a petri dish, the shavings moved on their own due to buoyancy created by vigorous hydrogen evolution. The present identification of the hydride under free corrosion conditions is important as regards EIC of Al–Li alloys, since the presence of hydrides in the near-surface regions of the alloys would have deleterious consequences by serving as potential crack initiation sites during EIC (Balasubramaniam et al 1991a; Thakur and Balasubramaniam 1997b).

SEM of the surface topology of samples that were immersed for 2 h, 15 h and 7 days showed clear evidence of the kind of mud-cake cracking that is observed on Al-base alloys (figure 5). The cracked appearance suggests dehydration upon removal from immersion. The sample that had been immersed for 2 h revealed a relatively thin scale that did not completely cover the entire surface of the specimen. The composition of the scale was analyzed by the energy dispersive analysis by X-rays (EDAX) facility of the SEM, and it consisted essentially of Al. On the other hand the specimen that had been immersed for 15 h, revealed that a thicker surface film completely covered the surface. Spot analysis obtained by EDAX revealed that Cu was also significantly present in addition to Al and Mg in the scale. The surface film on the 7-day immersion specimen was uniformly present on the surface. The scale consisted of essentially Al and Cu, as analyzed by EDAX. Although the quantitative accuracy of the EDAX technique is low, the study, nevertheless, provided that there was enrichment of Cu in the surface film for longer immersion times, which has also been corroborated by XRD studies. It must be mentioned that the EDAX cannot detect the presence of Li as it analyzes elements only beyond the atomic number.

![Figure 5](image-url)
10 (i.e. Na onwards). However, the presence of Li in the scale, as hydrated lithium aluminum hydroxide, can be concluded on the basis of the XRD analysis which clearly provided the composition of the scale.

The results of SEM and XRD studies can be explained as follows. Initially the composition of the scale formed on the surface is rich in Al and Li, mostly due to the formation of the LiAl₆(OH)₁₂·12H₂O phase formed as a result of dissolution of Al and Li from the surface. Lithium has been shown to be incorporated in the oxide film of Al–Li alloys. The source of Li enhancement in the film is the leaching out of Li from the alloys and, under suitable condition, it becomes incorporated in the film (Moran et al. 1986; Gui and Devine 1987). The enrichment has been experimentally verified by testing in Li-containing solution, and characterizing the passive film by secondary ion mass spectroscopy (Gui and Devine 1987). Moreover, the oxides of Al are generally grey and this compares well with the observation that the initial scale formed on the surface is greyish. This implies that there is enrichment of Cu at the metal/surface layer interface. With increasing time, the scale is also enriched in Cu, which could either be due to the corrosion of Cu from the specimen or due to the re-precipitation of Cu that was dissolved initially from the alloy on to the surface. In this regard, dealloying of Cu from Al–Li–Cu alloys has been observed. It has been suggested that the dissolved Cu ions are transported from the dissolution sites and re-deposited on the surface where they can possibly form a corrosion product (Buchheit and Stoner 1989). Therefore, the visual greenish appearance of the scale only after longer period of immersion, suggests that a process similar to that outlined above perhaps occurs as well in the present Al–Li alloy. Further, this is in conformity with the findings of the presence of metallic Cu and green deposits in the pits of Al–Li alloys by Craig et al. (1987).

4. Conclusions

A characteristic nature of stabilization of the free corrosion potential as a function of time in 0.1 mol/l NaOH solution was observed for the Al–1.90Li–1.80Cu–1.00Mg–0.09Zr alloy. The OCP stabilizes after a fairly long time. Potentiodynamic polarization study indicated that the alloy exhibited active–passive type behaviour after 2 h and 15 h immersion, with the latter condition showing enhanced pseudo-passivity. The composition of the scales has been analyzed by XRD and the nature of the scale morphology has been studied by SEM. The surface of the alloy is covered by a hydrated hydroxide film of Al and Li at short times of immersion. Copper hydroxide is also observed in the surface scale after longer times of immersion. It was also observed that the hydrate LiAlH₄ forms in the near-surface regions of the alloy under free corrosion conditions.

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