The propagation of localized corrosion in Al-Cu-Li alloy

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The mechanism of localized corrosion in 2A97 aluminium alloy has been investigated. Electron backscatter diffraction analysis was performed at the localized corrosion site to determine the grain-stored energy. The relationship between the grain-stored energy, namely the population density of crystallographic defects, and the corrosion susceptibility of the alloy has been established. It was revealed that the grain boundaries that surrounded grains of relatively high stored energy were preferentially attacked. Intergranular corrosion could occur at grain boundaries where second phase precipitate was absent. Non-uniform attack of the adjacent grain interior was also observed along the attacked grain boundary, with preferential dissolution of the grains with high stored energy. Copyright © 2015 The Authors Surface and Interface Analysis Published by John Wiley & Sons Ltd.

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Introduction

Aluminum-copper-lithium alloys are promising substitutes for conventional 2000 and 7000 series aluminium alloys in aircraft industry[1, 3] because of their reduced density and increased elastic modulus with lithium addition.[1, 3] Nowadays, Al-Cu-Li alloys have been used in the aircraft industry for fuselage and wing stringers.[2, 3] Although the new generation Al-Cu-Li alloys have overcome the major problem of mechanical anisotropy of the previous generation Al-Cu-Li alloys, the high corrosion susceptibility is still a major issue limiting the application of Al-Cu-Li alloys. Grain boundary attack, one of the most detrimental corrosion types, is commonly observed in Al-Cu-Li alloys.[8–12]

Previous work showed that T1 phase (Al2CuLi) precipitates significantly affected the localized corrosion behaviour in Al-Cu-Li alloys.[8, 10, 12–15] Buchheit suggested that the grain boundary T1 phase precipitates play a crucial role in the selective attack of grain/subgrain boundary in AA2090 Al-Cu-Li alloy. The preferential dissolution of T1 phase precipitates results in a local corrosive environment with low pH. Consequently, continuous dissolution develops along grain boundaries in the alloy.[12, 13] The intergranular corrosion associated with grain boundary T1 phase precipitates was further confirmed by Kertz, who revealed that high corrosion resistance to intergranular attack and inter-subgranular attack in Al-Cu-Li alloy could be obtained when T1 phase precipitate was absence at the grain boundaries.[15] Further, it was also found in other work that the intergranular corrosion susceptibility is related to the formation of precipitate free zone adjacent to the grain boundaries.[11, 16–18] With a 0.2-μm wide copper-depleted precipitate free zone developed along the grain boundary, the preferential dissolution of the precipitate free zone results in the attack along the grain boundary network in Al-Cu-Li alloy.[11] It was also found that intergranular corrosion susceptibility increased with the development of wider precipitate free zone with the coarsening of grain boundary precipitates.[17, 18]

More recent work indicated that the corrosion mechanism in Al-Cu-Li alloys was closely linked with the distribution of T1 phase precipitates.[8, 14, 19] The relatively high population density of grain boundary T1 phase precipitates in the AA2050 alloy without artificial ageing resulted in intergranular corrosion in the alloy. However, T1 phase precipitates were formed at the grain boundaries and interior in the alloy after ageing at 155 °C for 30 h. The alloy became susceptible to intragranular corrosion instead of intergranular corrosion as a consequence of the increased corrosion susceptibility of grain interior with a high volume fraction of T1 phase precipitate and the copper depletion in the matrix.[8] Detailed corrosion mechanism of T1 phase precipitate was proposed by Li,[20, 21] suggesting that T1 phase precipitate was anodic to aluminium matrix and the selective dissolution of Li resulted in copper-rich T1 phase remnant with a less negative potential with respect to aluminium matrix; consequently, micro-galvanic coupling between the T1 phase remnant and the aluminium matrix led to preferential dissolution of aluminium at the periphery.[20–22]
In the present work, the corrosion behaviour, particularly the propagation mechanism of localized corrosion, in an Al-Cu-Li alloy is investigated with the aim of correlating the corrosion behaviour with the microstructure of alloy in T4 condition where the precursors of the T1 phase precipitate are present in the alloy matrix, and the T1 phase precipitate is absent in the matrix and at the majority of the grain boundaries.

**Experimental methods**

Cold rolled 2A97-T4 Al-Cu-Li alloy (Li 0.8–2.3 wt.%, Fe 0.15 wt.%, Si 0.15 wt.%, Cu 2.0–3.2 wt.%, Mn 0.20–0.6 wt.%, Zn 0.17–1.0 wt.%, Mg 0.25–0.50 wt.%, Al rem.) was investigated in this study. The specimens with the dimensions of 20 × 15 mm were prepared from the cold rolled thin sheet of 2 mm thickness. The specimens were successively ground with 800, 1200, 2500 and 4000 grit silicon carbide paper and polished sequentially using 3 and 1 μm diamond pastes. After the mechanically polishing, the specimens were cleaned ultrasonically in an acetone bath and dried in a cool air stream. Corrosion immersion testing was carried out in a 3.5 wt.% NaCl solution at the ambient temperature. Ultramicrotomy was employed to obtain the cross sections at the stable localized corrosion site for scanning electron microscopy and the corresponding thin foils for transmission electron microscopy (TEM). The TEM specimen of the as-received alloy was also prepared with twin-jet electropolishing using a mixture of 700-ml methanol and 300-ml nitric acid at the temperature of –35 °C. Electron backscatter diffraction (EBSD) was employed to further characterize the stable localized corrosion site of the alloy. Argon plasma cleaning of the specimens was conducted to obtain a stress-free surface for EBSD analysis.

**Results**

Because localized corrosion behaviour of Al-Cu-Li alloy is closely linked with T1 phase precipitates,[8,10,15,19] the distribution of T1 phase precipitates in the 2A97-T4 aluminium alloy was characterized using a high resolution scanning electron microscopy. Figure 1(a) exhibits a scanning electron micrograph of a triple grain boundary junction. It is evident that the grain boundaries A-A and B-B are relatively clean with little grain boundary decoration by precipitate in contrast to the bright feature along grain boundary C-C. The framed area in Fig. 1(a) at increased magnification is shown in Fig. 1(b), revealing a high population density of needle-shaped precipitates along the boundary. High resolution TEM lattice image indicates that the precipitates at the grain boundaries are T1 phase. Further, a sufficient number of the grain boundaries have been examined, confirming that only a small portion of the grain boundaries in the 2A97-T4 aluminium alloy is decorated by the T1 phase precipitate.

Figure 2 shows the scanning electron micrographs of typical localized corrosion sites in the 2A97-T4 alloy after immersion in a 3.5 wt.% NaCl-testing solution for 5 h. Figure 2(a) displays the plan view of a localized corrosion site, exhibiting a corrosion product ring around 120 μm in diameter along with attacked grain boundaries and a corrosion pit within the ring. The cross section of the localized corrosion site along the red line in Fig. 2(a) was obtained by ultramicrotomy. Figure 2(b) shows the backscattered electron micrograph of the cross section, indicating that localized corrosion propagates into subsurface region of the alloy along grain boundary network. The width of corroded volume along the grain boundaries is in the range of 200–400 nm. The uniform width of the corroded volumes at the corrosion front and at the regions near the alloy surface suggests that corrosion propagation was confined within the narrow region immediately adjacent to the grain boundaries. Interestingly, selective matrix dissolution beneath the alloy surface was revealed from the cross section of another localized corrosion site, as shown in Fig. 2(c). The matrix dissolution was developed into the interior of selected grain while other grains remained intact, suggesting perhaps different corrosion susceptibility of grains in the alloy. Figure 2(d) shows the framed area in Fig. 2(c) at increased magnification, indicating clearly that the selective corrosion of the grain interior propagated in the form of crystallographic dissolution.

Previous work[23,24] suggested that intergranular corrosion in Al-Cu-Mg alloy may occur at the grain boundaries that surround grains of relatively high stored energy in the form of alloy matrix dissolution within the region immediately adjacent to the grain boundaries. Therefore, similar EBSD analysis was also conducted on the localized corrosion site in the 2A97-T4 alloy after immersion in a 3.5 wt.% NaCl solution for 20 h. Argon plasma was employed to remove the corrosion product from the surface of the tested alloy and to produce a stress-free surface for EBSD analysis. As shown in Fig. 3(a), attacked grain boundary is the dominant corrosion morphology developed on the alloy surface while selective matrix dissolution characterized with crystallographic pits within grain interior is also evident in the framed areas in Fig. 3(b). The corresponding grain-stored energy map of the area shown in Fig. 3(a) was determined from the EBSD analysis, as shown in Fig. 3(c), with the yellow lines indicating high angle grain boundaries and the black colour representing the non-indexed areas (For the yellow color mentioned in Fig. 3(c), the reader is referred to the web version of the article.). Because of the low intensity of diffraction from the cavities and the corroded grain boundaries, these regions could...
not be indexed. The different crystallographic structure of intermetallic particle also resulted in the non-indexed areas in the EBSD map. The grain-stored energy map is a grey-scale map, in which areas with relatively low stored energy appear relatively dark and high brightness representing high level of grain-stored energy. Comparing with morphology of the localized corrosion site shown

Figure 2. Scanning electron micrographs of typical localized corrosion site in 2A97-T4 alloy after immersion in a 3.5 wt.% NaCl solution for 5 h: (a) plan view; (b)–(d) cross section.

Figure 3. (a) Scanning electron micrograph of a typical localized corrosion site in the 2A97-T4 alloy after immersion in a 3.5 wt.% NaCl solution for 20 h; (b) the framed area in (a) at increased magnifications; and (c) the corresponding grain-stored energy map in grey scale.
in Fig. 3(a), it is evident that the attacked grain boundaries are those that surround the grains with relatively high grain-stored energy. Further, the crystallographic dissolution of the grain interior also occurred within the grains of relatively high stored energy. However, the correlation between the corrosion sites and the grain-stored energy shown in Fig. 3 is not as obvious as that observed previously in the cold worked Al-Cu-Mg and Al-Cu-Li alloys in T3 and T8 tempers.

Figure 4 shows the transmission electron micrograph of the corrosion front at a localized corrosion site developed after immersion in a 3.5 wt.% NaCl solution for 5 h, exhibiting the corrosion morphology generated by selective attack of grain boundary and the neighbouring grains. It is evident that corrosion was developed unevenly across the grain boundaries, for example, the interior of grain B was preferentially attacked compared with grain C. Interestingly, the grain boundary A-A, which was decorated with a high population of precipitates, suffered little attack, whereas the grain boundary B-B with no evident compositional difference was preferentially attacked.

Discussion

As stated in the Introduction, previous work suggested that the corrosion susceptibility in Al-Cu-Li alloy highly depends on the distribution of T1 phase precipitates. However, as shown in Fig. 4, the grain boundary without any precipitates could also be attacked. The present study indicates that the grain-stored energy, namely the crystallographic defects density, along with the distribution of T1 phase precipitates affects the corrosion behaviour in the 2A97-T4 alloy.

The density of misorientations within a grain reflects the density of dislocations in that grain. The energy associated with misorientation above a selected threshold value (0.8°) can be calculated using the Read-Shockley equation as follows:

\[ \gamma_0 = \gamma_0 \theta (A - \ln \theta) \]

where \( \theta \) is the misorientation angle and \( \gamma_0 \) and A are constants. The stored energy of an individual grain is determined by averaging the sum of the mean energies of pixels over the area of the individual grain.\(^{[23,24]}\) Then, the spatial distribution of the grain-stored energy is represented as a map, which reflects the average population density of dislocations in the individual grains. The heterogeneous distribution of grain-stored energy is associated with the fabrication history of the alloy. T4 temper involves solution heat treatment and nature ageing. However, the material was produced using a coil process, which involves also sheet deformation in addition to cold rolling. Plastic deformation is grain-orientation dependent because the number of available slip systems is determined by the grain orientation with respect to the fabrication direction. Therefore, higher level of plastic deformation could be introduced to the grains with more active slip systems, leading to the high population density of dislocation within the grains. As a result, heterogeneous distribution of crystallographic defects was generated in the alloy.

Two factors might contribute to the increased corrosion susceptibility of the grains with high stored energy. First, the higher population density of dislocation leads to the higher level of thermodynamic instability, which results in the higher corrosion susceptibility. Previous research revealed that with dislocation density difference, electrochemical potential difference around 20 mV can be generated.\(^{[25]}\) Therefore, the boundary and interior of the grain with higher level of defects have higher corrosion susceptibility than those of the grains with lower stored energy. Second, the dislocations provide the preferential site for the nucleation of T1 phase precipitates in Al-Cu-Li alloy, especially along the grain boundary because of the higher dislocation density along the grain boundary than average level of the grain interior.\(^{[27,28]}\) The preferential development of the T1 phase precipitate along the grain boundaries provided local sites that are susceptible to corrosion because of the relatively negative potential of the T1 phase precipitates.

Conclusions

Localized corrosion in the 2A97-T4 Al-Cu-Li alloy during immersion in NaCl solution was propagated in the forms of intergranular corrosion and crystallographic pitting. The grain boundaries that surrounded grains of relatively high stored energy were preferentially attacked. Intergranular corrosion could occur at grain boundaries where second phase precipitate was absent. The crystallographic dissolution of the alloy matrix also occurred within the grains of relatively high stored energy. However, the correlation between the preferential attack and the grain-stored energy for the T4 temper is not as obvious as that observed previously in the significantly cold worked Al-Cu-Mg and Al-Cu-Li alloys in T3 and T8 tempers.
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