Effect of Iron-Containing Intermetallic Particles on Film Structure and Corrosion Resistance of Anodized AA2099 Alloy

H. Wu,1 Y. Ma,1,2 W. Huang,1,2 X. Zhou,2 K. Li,3 Y. Liao,4 Z. Wang,1 Z. Liang,1 and L. Liu1

1College of Materials Science and Engineering, Chongqing University of Technology, Chongqing 400054, People’s Republic of China
2Corrosion and Protection Centre, School of Materials, The University of Manchester, Manchester M13 9PL, United Kingdom
3Science and Technology on Power Beam Processes Laboratory, AVIC Manufacturing Technology Institute, Beijing 100024, People’s Republic of China
4Chongqing University of Education, Chongqing 400067, People’s Republic of China

The anodizing behavior of iron-containing intermetallic particles in AA2099 aluminum-lithium alloy and their effect on structure and corrosion resistance of the anodic film were investigated using electrochemical measurements and scanning electron microscopy. High-copper-containing Al-Fe-Mn-Cu particles (HCCPs) dissolved preferentially through dealloying at ~ 0 V (vs. saturated calomel electrode) in a tartaric-sulfuric acid solution, at 22, 37 and 42 °C, leading to formation of copper-rich nanoparticle of 50–200 nm diameters. They dissolved completely under normal anodizing conditions, resulting in cavity defects of micrometer dimensions in the anodic film and sunken regions in the alloy substrate immediately beneath the dissolved HCCPs. Immersion testing of the anodized alloy in 3.5% NaCl solution for 24 h indicated that localized corrosion of the anodized alloy predominantly developed at the site containing dissolved HCCPs at the film/alloy interface. It is suggested that HCCPs play a critical role in controlling the corrosion resistance of the anodic film formed on AA2099 aluminum-lithium alloy.

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The morphology and compositions of IMPs in the alloy were examined with EDX facilities, operated at an accelerating voltage of 20 kV. The morphology of the anodic film before and after the immersion test was examined using a Zeiss Sigma HD scanning electron microscope, fitted for tomography. Volumetric SEM images from a set of sequentially sectioned surfaces were acquired at accelerating voltage of 15 kV. Successively acquired 2D images were aligned to generate 3D volumetric reconstructions.

Results

Figure 1 shows backscattered electron micrographs of a mechanically ground alloy, showing the distribution of IMPs with different Cu/Fe ratios (spectra 8 and 9). After anodizing at 0 V (SC), at 25°C, for 300 s, the particle was transformed into nanoparticles of 50–200 nm diameters, despite of the composition variation (Figs. 3b, 3c, and 3f). Typical of the anodized alloy, showing distribution of intermetallic particles.

Table I. Chemical composition of selected A3209 alloy (wt%).

| Element | Cu | Li | Mg | Zn | Zr | Fe | Ti | Si | Al |
|---------|----|----|----|----|----|----|----|----|----|
| Content | 2.78 | 0.19 | 0.07 | 0.16 | 0.06 | 0.03 | 0.03 | 0.1 |

Specimens of 10 × 10 × 3 mm were prepared from an A3209 alloy ingot, with the nominal compositions (10% Cu | 12% Zn | 3% Mg | 1% Si | 1% Fe | 1% Al) and then solution treated (moderately treated at 500°C for 1 h and then quenched in ice water). The specimens after solution treatment were masked with indium to expose an area of 1 cm². The epoxy was allowed to cure for 1.5 h. The epoxy layers on selected specimens were removed by immersing the specimens in a mixed solution containing 20 g/L CrO3 and 35 mL/L H3PO4 at 60°C for 60 s to reduce the effect of carbon contamination.23-25

For potentiostatic anodizing, the specimen was anodized at a constant voltage of 14 V vs. the counter electrode, at 37°C, for 300 s, the particle was transformed into nanoparticles of 50–200 nm diameters, despite of the composition variation. The current densities generally increased with increasing voltages and temperatures. Particularly, a current density surge appeared at 0.25 V (SC) and 25°C, for 300 s, the particle was transformed into nanoparticles of 50–200 nm diameters, despite of the composition variation.
nanoparticles were revealed more clearly, probably due to reduced residual corrosion products. This suggests that increasing temperature accelerated the dealloying and dissolution process of HCCPs. The suggestion is also supported by the relatively stronger current density surge and its shift to lower voltage end at higher temperatures. Figure 4 compares the morphology of a multiphase particle consisting of LCCP (Particle 6) and HCCP (Particle 11) before (Fig. 4a) and after (Fig. 4b) anodizing at 0 V (SCE), at 37 °C, for 300 s. Note that in Fig. 4a the HCCP parts are relatively brighter than the LCCP parts, in the backscattered SEM image, due to much higher level of copper contents in HCCPs than LCCPs. However, in Fig. 4b the HCCP parts are revealed darker compared with the LCCP parts after anodizing under the selected conditions, confirming preferential dissolution of HCCPs. The alloy was then anodized at 14 V, at 37 °C, for 1500 to generate a relatively thick anodic film. The recorded current density-time response curve (Fig. 5) agrees with that of the AA2099-T8 alloy anodized under the same conditions,21 suggesting that the selected alloy conditions (casted, homogenized and then solution treated) does not evidently change the general anodizing behavior of the alloy. Figs. 6a and 6b show secondary electron micrographs of the alloy after anodizing, in two typical areas. With the determination of IMP compositions and 6b show secondary electron micrographs of the alloy after anodizing (Fig. 6d). Similar phenomena were observed in other regions and the results were not included to avoid repetition. Figure 7 shows the cross sections of the alloy after anodizing, revealing a partially anodized particle (Fig. 7a) and a cavity (Fig. 7b) surrounded by an anodic film (∼4.6 μm thickness). As expected, the partially anodized particle corresponds to LCCP (75.0% Al-14.8% Fe-5.4% Mn-4.8% Cu) and the anodic film formed from the particle is indicated by the arrow in Fig. 7a. The cavity is about 5.4 μm long and 1.6 μm thick. Nanoparticles (∼100 nm in diameter), similar to those shown in Figs. 3d and 3f, are revealed on the bottom of the cavity (see inset of Fig. 7b). It is suggested that the cavity was caused by dissolution of a HCCP as a consequence of anodizing. Due to rapid dissolution of the HCCP and consequent formation of the cavity, a sunken region developed in the anodic film in these regions. As discussed later, additional defects might be introduced in the anodic, deteriorating corrosion resistance of the anodic film in these regions.

In order to investigate the effect of anodized IMPs on corrosion resistance of the anodized alloy, the specimen after anodizing at 14 V (SCE), at 37 °C, for 1500 was immersed in 3.5% NaCl solution for up to 84 h. Figure 9 shows open circuit potential-time curves of the bare LCCP (Particle 6) and HCCP (Particle 11) before (Fig. 4a) and after (Fig. 4b) anodizing at 0 V (SCE), at 37 °C, for 300 s. Note that in Fig. 4a the HCCP parts are relatively brighter than the LCCP parts, in the backscattered SEM image, due to much higher level of copper contents in HCCPs than LCCPs. However, in Fig. 4b the HCCP parts are revealed darker compared with the LCCP parts after anodizing under the selected conditions, confirming preferential dissolution of HCCPs.

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### Table II. EDX analysis of intermetallic particles and alloy substrate in solution-treated AA2099 aluminum alloy before anodizing and corrosion test (wt%)*

| Particle/Spectrum | Al  | Fe  | Mn  | Cu  | Zn  | Mg  | Cu/Fe |
|-------------------|-----|-----|-----|-----|-----|-----|-------|
| Low-copper- containing Particle (LCCP) | 1   | 72.2| 15.0| 8.1 | 4.7 | -   | 0.3    |
|                   | 2   | 73.2| 15.1| 7.1 | 4.7 | -   | 0.3    |
|                   | 3   | 74.4| 14.8| 6.1 | 4.7 | -   | 0.3    |
|                   | 4   | 72.1| 15.7| 6.5 | 5.8 | -   | 0.4    |
|                   | 5   | 71.7| 15.7| 7.5 | 5.1 | -   | 0.3    |
|                   | 6   | 72.1| 15.6| 7.4 | 4.9 | -   | 0.3    |
|                   | 7   | 71.1| 16.3| 7.7 | 4.9 | -   | 0.3    |
| High-copper- containing Particle (HCCP) | 8   | 56.6| 15.7| 5.9 | 21.8| -   | 1.4    |
|                   | 9   | 54.2| 12.3| 1.1 | 32.4| -   | 2.6    |
|                   | 10  | 59.2| 10.6| 2.7 | 27.4| -   | 2.6    |
|                   | 11  | 53.2| 11.9| 2.8 | 32.1| -   | 2.7    |
|                   | 12  | 68.5| 7.6 | 2.4 | 21.5| -   | 2.8    |
|                   | 13  | 56.6| 12.6| 1.7 | 29.1| -   | 2.3    |
|                   | 14  | 55.4| 12.0| 2.8 | 29.8| -   | 2.5    |
|                   | 15  | 55.4| 11.9| 2.7 | 29.9| -   | 2.5    |
|                   | 16  | 64.2| 9.0 | 1.9 | 24.9| -   | 2.8    |
|                   | 17  | 59.4| 11.9| 2.4 | 26.3| -   | 2.2    |
|                   | 18  | 55.8| 11.9| 2.1 | 30.2| -   | 2.5    |
|                   | 19  | 57.6| 11.4| 2.6 | 28.4| -   | 2.5    |
|                   | 20  | 56.2| 11.6| 2.4 | 29.9| -   | 2.6    |
| Alloy matrix      | 21  | 95.8| -   | 0.2 | 2.7 | 0.8 | 0.5    |
|                   | 22  | 95.8| -   | 0.2 | 2.8 | 0.7 | 0.5    |

* Lithium cannot be detected by the EDX employed in the present work.

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**Figure 2.** Current density-voltage curves recorded during potentiodynamic polarization of solution-treated AA2099 alloy from 0 V (OCP) to 10 V (SCE) in tartaric-sulfuric acid (TSA) solution, at a sweep rate of 0.1 mV/min, at different temperatures.
and anodized AA2099 Al alloy recorded during the immersing test. The OCP of the bare alloy increased from $-1.05 \, \text{V}$ to $-0.59 \, \text{V}$ in the first several seconds, then it decreased slightly to $-0.63 \, \text{V}$ in the next 4 hours; thereafter, it dropped twice before finally stabilizing at $-0.82 \, \text{V}$. It is believed that the OCP-time response of the bare alloy suggests passivation, initiation of localized corrosion and propagation of localized corrosion during the immersion test. The OCP of the anodized alloy fluctuated mildly between $-0.63$ and $-0.67$ during the immersion process. Compared with the bare alloy, there is no sharp increase of OCP at the commencement of immersion for the anodized alloy because a porous anodic film has already existed on the alloy surface. The relatively stable OCP of the anodized alloy suggests that the anodic film delays the corrosion process of the anodized alloy.

Figure 10 shows secondary electron micrographs of the anodized alloy after immersion for 24 h. Petal-like cracks varying from several to tens micrometers are revealed on the specimen surface (Figs. 10a and 10b). Scrutiny of the specimen surface indicates that the petal-like cracks are absent in the surface regions containing dissolved HCCPs (Fig. 10c) or anodized LCCPs (Fig. 10d, the part as labeled). This suggests that the petal-like cracks are related to structures which are within or below the anodic film. Figure 11a shows the same area as shown in Fig. 10d, however, after removal of the anodic film, revealing remained LCCPs and sunken regions left by HCCPs. A circular region (as indicated by the dashed-line arrow in Fig. 11a) is revealed in the periphery of the sunken region. Figure 11b shows the framed area K at increased magnification, revealing different morphology in the bulk surface and the circular regions, with the boundary being schematically indicated by the dashed line. The regular scallop feature on the bulk surface corresponds to the pore base and is generated by normal growth of the anodic film. The presence of such feature suggests integrity of the film and intact of the alloy substrate in this region after the immersion test. The irregular feature in the circular region,
which is also found in the sunken region, suggests that the electrolyte penetrated the anodic film and reached the alloy substrate in this region, resulting in localized corrosion of the anodized alloy. Figure 11c shows the framed area L at increased magnification, revealing regular scallop feature in the surrounding regions of the LCCP. This indicates that the partially anodized LCCP did not lead to localized corrosion of the anodized alloy under the selected conditions. Another region after film removal is shown in Fig. 11d. Note that all attacked sites (as suggested by the circular region and indicated by solid-line arrows) are associated with sunken regions (i.e. dissolved HCCPs). However, the circular region is not found in the periphery of the sunken regions indicated by dashed-line arrows, suggesting that not all dissolved HCCPs led to localized corrosion of the anodized alloy after immersion in 3.5% NaCl solution for 24 h.

With the consideration that the petal-like cracks are associated with localized corrosion of the anodized alloy, a cross section of the anodic film containing petal-like cracks was prepared using ultramicrotomy (Fig. 12a). The anodic film in the cracked area detached from the alloy substrate. Additionally, a cavity and a remained particle were detected below the detached anodic film, in the central region of the petal-like cracks. EDX analysis of the remained particle gives 74.0% Al, 1.9% Fe, 0.6%Mn, 2.8% Cu, 1.9% Zn, 0.7% Si, 0.5% S, 13.5% O and 4.1% C, confirming that it belongs to a partially anodized LCCP. The co-existence of the cavity and remained particle suggests that the cavity is at the film/substrate interface because the remained particle should be attached to the alloy substrate. Little anodic film is found at the side wall of the cavity, suggesting that the cavity was formed just before the termination of anodizing. Scrutiny of the attacked region reveals corroded alloy substrate below the detached anodic film and different film morphology above the corroded alloy substrate (Fig. 12b). It is believed that corrosion products arising from the corroded alloy substrate modified the surrounding anodic film, probably through a diffusion process. Figure 12c shows the cross section of another film region, again, revealing cracked anodic film, cavity at the film/substrate interface, corroded alloy substrate below the cracked anodic film and modified anodic film. There are no evident petal-like cracks revealed on the surface of the anodic film in this region, suggesting that the corrosion event shown in Fig. 11c is still in earlier stages compared with that shown in Fig. 11a. Figs. 11d and 11e show the cross sections of the anodic film region containing cavities several hundred nanometers above the film/substrate interface. Neither corrosion attack of the alloy substrate nor modified anodic film is revealed in these regions. Thus, it is suggested that the location of the cavities (or dissolved HCCPs) affects the corrosion behavior of the anodized alloy. Figure 11f shows the cross section of the anodic film region containing a partially anodized LCCP. As expected, no evident corrosion phenomenon is revealed in the alloy substrate below the partially anodized LCCP.

**Discussion**

It is demonstrated that HCCPs dissolved preferentially at $\sim$0 V (SCE) in tartaric-sulfuric acid solution at 22, 37 and 42 C (Fig. 2).
The potential is comparable to that of S (Al₂CuMg) phase in AA2024-T3 and AA7075-T6 alloys anodized under similar conditions. The preferential dissolution of HCCPs proceeded through a dealloying mechanism, leading to formation of copper-rich nanoparticles of 50–200 nm diameters. Theoretically, the remained copper-rich nanoparticles might be anodized when the anodizing voltage is above 3 V if they are electrochemically connected to the alloy substrate. However, a continuous and stable anodic film is unlikely to be formed on copper-rich nanoparticles because large amount of oxygen gas will be generated during anodizing of copper. Thus, it is deduced that HCCPs would dissolve, completely and rapidly, during normal anodizing upon exposure to the electrolyte and electric filed.

Plan view of the alloy after normal anodizing and subsequent immersion in 3.5% NaCl solutions for 24 h reveals petal-like cracks in the anodic film (Figs. 10a, 10b and 10d). After film removal, a sunken region is shown in the alloy substrate beneath the petal-like cracks (Fig. 11a), suggesting that the petal-like cracks are related to dissolved HCCPs. The corrosion attack of the alloy substrate in the sunken and its surrounding regions (Fig. 11b) indicates that the dissolved HCCP is responsible for the penetration of the electrolyte through the anodic film in the localized region. It is noted that there were always sunken regions in the corrosion sites (Sites 1 in Fig. 11a and Sites 2 and 3 in Fig. 11d); while no evident corrosion phenomena were detected at the sunken regions indicated by dashed-line arrows in Fig. 11d. Such observation indicates that the dissolution of HCCP is the necessary but not sufficient condition for the development of localized corrosion in the anodized alloy under the selected conditions. Figure 11d indicates that the corroded sunken regions are not necessarily larger or deeper than the intact sunken regions, suggesting that the size of the HCCP is not the decisive factor for initiating corrosion.

Figure 7. Cross-sectional view of solution-treated AA2099 alloy after anodizing: (a) a partially anodized LCCP embedded in bulk anodic film; and (b) a cavity within bulk anodic film due to dissolution of HCCP. The cross-sections were made by mechanical bending.

Figure 8. 3D volumetric reconstruction of solution-treated AA2099 alloy after anodizing, revealing (a) cavities in the anodic film and (b) hemispherical film/alloy interface below the cavities. Three intersected planes are shown in (a); selective transparency is applied to the aluminum matrix in (b).

Figure 9. Open circuit potential-time curves of the bare and anodized AA2099 aluminum alloy recorded during immersing in 3.5 wt% NaCl solution at room temperature for 84 h.
localized corrosion. Remained LCCP is only occasionally observed at the corrosion sites (Figs. 11d and 12a), suggesting that co-existence of HCCP and LCCP is not the decisive factor either. Cross-sectional view of the alloy after anodizing for 1500 s and subsequent immersion in 3.5% NaCl solution for 24 h indicates that dissolved HCCPs (or cavities) at the film/alloy interface (Figs. 12a and 12c) are more likely to cause localized corrosion than those away from the film/alloy interface (Figs. 12d and 12e). Therefore, it is deduced that the location of the dissolved HCCPs (or cavities) plays a critical role in initiating localized corrosion. As suggested in Fig. 8b, there should be a sudden change of film growth direction in the sunken regions, probably from the normal direction of the bulk surface to the normal direction of the cavity surface. Such localized film growth might introduce defects in the anodic film, deteriorating the corrosion resistance of the anodic film. However, full understanding of the corrosion mechanism is still not clear and will be the subject of future work.

Remained LCCPs are frequently observed at the film/alloy interface because of the relatively smaller anodizing rate of LCCPs relative...
to Al matrix. As a consequence, local film thickness should be slightly reduced at the sites of remained LCCPs. However, no evident corrosion phenomena were detected at the sites of partially oxidized LCCPs under the selected conditions (Figs. 11c and 12f). This indicates that LCCPs have less detrimental effect than HCCPs on the corrosion susceptibility of the anodized alloy. Therefore, it might be interesting for metallurgists to develop a procedure to transform HCCPs into LCCPs if it is technically or economically not possible to further reduce iron-containing IMPs in the alloy.

Conclusions

1) High-copper-containing Al-Fe-Mn-Cu particles (HCCPs) dissolved preferentially at $\sim 0$ V (SCE) in tartaric-sulfuric acid solution through dealloying, forming copper-rich nanoparticles of 50–200 nm diameters at the sites of the dissolved particles; such electrochemical activity of HCCPs explains the dissolution of them and formation of cavity defects of micrometer dimensions in the anodic film under normal anodizing conditions.

2) Not all dissolved HCCPs led to localized corrosion of the anodized alloy after immersion in 3.5% NaCl solution for 24 h; the corrosion resistance of the anodic film is associated with the location of dissolved HCCPs, with those at the film/alloy interface being more likely to cause localized corrosion.

3) Although a thinner and more flawed anodic film would be formed on low-copper-containing Al-Fe-Mn-Cu particles (LCCPs) compared with the bulk alloy substrate, it seems that LCCPs have much less detrimental effect on corrosion resistance of the anodic film. Therefore, it is possible to improve the corrosion resistance of AA2099 Al-Li alloy by transforming HCCPs into LCCPs.

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ORCID

Y. Ma https://orcid.org/0000-0001-5427-9295

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