

Effect of equal-channel angular pressing on pitting corrosion resistance of anodized aluminum-copper alloy

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Abstract: The effect of equal-channel angular pressing (ECAP) on the pitting corrosion resistance of anodized Al-Cu alloy was investigated by electrochemical techniques in a solution containing 0.2 mol/L AlCl_3 and also by surface analysis. Anodizing was conducted for 20 min at 200 and 400 A/m^2 in a solution containing 1.53 mol/L H_2SO_4 and 0.0185 mol/L $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ at 20 °C. Anodized Al-Cu alloy was immediately dipped in boiling water for 20 min to seal the micro pores present in anodic oxide films. The time required before initiating pitting corrosion of anodized Al-Cu alloy is longer with ECAP than without, indicating that ECAP process improves the pitting corrosion resistance of anodized Al-Cu alloy. Second phase precipitates such as Si, Al-Cu-Mg and Al-Cu-Si-Fe-Mn intermetallic compounds are present in Al-Cu alloy and the size of these precipitates is greatly decreased by application of ECAP. Al-Cu-Mg intermetallic compounds are dissolved during anodization, whereas the precipitates composed of Si and Al-Cu-Si-Fe-Mn remain in anodic oxide films due to their more noble corrosion potential than Al. FE-SEM and EPMA observation reveal that the pitting corrosion of anodized Al-Cu alloy occurs preferentially around Al-Cu-Si-Fe-Mn intermetallic compounds, since the anodic oxide films are absent at the boundary between the normal oxide films and these impurity precipitates. The improvement of pitting corrosion resistance of anodized Al-Cu alloy processed by ECAP appears to be attributed to a decrease in the size of precipitates, which act as origins of pitting corrosion.

Key words: aluminum-copper alloy; equal-channel angular pressing; anodizing; pitting corrosion

1 Introduction

Since aluminum-copper alloys, called duralumin or super-duralumin, have excellent mechanical properties, they have been widely used as high-tension aluminum alloys for the aircraft applications[1]. However, copper, the alloying element added to improve the mechanical strength, forms intermetallic compound of Al_2Cu , which acts as the cathode in Al matrix. Al-Cu alloy is therefore vulnerable to localized corrosion such as pitting corrosion[2–3]. Al-Cu alloys are generally anodized by electrolysis to improve their poor corrosion resistance.

On the other hand, reducing the grain size of metallic material to the submicrometer range or even the nanometer range using the equal-channel angular

pressing (ECAP) is increasingly being studied with the aim of improving mechanical properties of aluminum such as strength and ductility[4–5]. However, the effect of ECAP on pitting corrosion resistance of anodized Al alloys has so far been reported rarely. Researches previously reported that the pitting corrosion resistance of Al and Al-Mg alloy was improved by ECAP, but the corrosion resistance of anodized Al-Mg alloy was worse with ECAP than without[6–8]. The pitting corrosion resistance of anodized Al alloys depends on the alloying elements, and the effect of ECAP on the pitting corrosion resistance also seems to change according to alloying elements.

In this study, copper was selected as alloying element, and the effect of ECAP on the pitting corrosion resistance of anodized Al-Cu alloy was investigated

using electrochemical techniques. The mechanism of change in the pitting corrosion resistance of anodized Al-Cu alloy with ECAP was also clarified by surface analysis.

2 Experimental

AA2024 (4.58% Cu, 0.10% Si, 0.24% Fe, 0.64% Mn, 1.38% Mg, 0.18% Zn, 0.02% Cr, and balance Al; mass fraction) was used as specimen of Al-Cu alloy. The Al-Cu alloy samples were subjected to solution treatment at 833 K for 1 h, water quenching and aging treatment at 683 K for 1 h. ECAP was conducted for 6 passes at room temperature using a die with a channel angle of 90°, which created an equivalent strain of about 1 during one passage through the die. And further details concerning ECAP facility were reported by IWAHASHI et al[9]. The sample was rotated by 90° about the longitudinal axis in the same sense between consecutive passes, generally designated as route Bc[10]. The pressing was performed at a rate of about 19 mm/s using MoS₂ as a lubricant. The initial grain size of Al-Cu alloy prior to ECAP was 30–50 μm. The average grain size of Al-Cu alloy after ECAP was confirmed by TEM observation to be 0.3–0.5 μm[11].

Prior to anodizing, mechanical polishing, etching and electropolishing were conducted as a pretreatment. Anodizing was conducted for 20 min in a solution containing 1.53 mol/L H₂SO₄ and 0.018 5 mol/L Al₂(SO₄)₃·16H₂O at 20 °C under galvanostatic conditions of 200 and 400 A/m². Anodized Al-Cu alloy was immediately dipped in boiling water for 20 min to seal the micro pores present in anodic oxide films. After the anodized Al-Cu alloy had been immersed in a solution containing 0.2 mol/L AlCl₃ at 25 °C for 30 min, the polarization curves were measured by polarizing the electrode from –0.7 V to 4.2 V vs NHE using the potential sweep method at 1 mV/s. In addition, the time-dependence of anodic current density was measured while being maintained at 1.2 V vs NHE after immersion for 30 min.

3 Results and discussion

Fig.1 shows the effect of ECAP on the polarization curves of Al-Cu alloy anodized at 200 A/m². The anodic current densities rapidly increased at the potential of about 0 V when the anode potential was shifted from corrosion potential to the more noble direction. This rapid increase in current density is caused by the initiation of pitting corrosion. The anodic current densities gradually increased when the anode potential was further shifted from pitting corrosion potential (ϕ_{pit}) to the more noble direction. This gradual increase in

current density is caused by growth of pitting corrosion. The corrosion potential of Al-Cu alloy was slightly shifted to the more noble direction by ECAP. The anodic current density of anodized Al-Cu alloy was smaller over the range of 0–4 V with ECAP, suggesting that ECAP process improved the pitting corrosion resistance.

The time-dependence of the anodic current density of Al-Cu alloy anodized at 200 and 400 A/m² is shown in Fig.2. Samples were held at 1.2 V in the solution containing 0.2 mol/L AlCl₃. The anodic current density of anodized Al-Cu alloy increased rapidly after a certain period of time due to the initiation of pitting corrosion. The time required for initiating pitting corrosion of anodized Al-Cu alloy was longer with ECAP than without, regardless of the anodizing current density, indicating that ECAP enhanced the pitting corrosion resistance.

Fig.3 shows SEM images of Al-Cu alloy with and without anodization. In Al-Cu alloy without anodizing, precipitates were present, irrespective of having undergone ECAP or not. It was found from EDX spectra

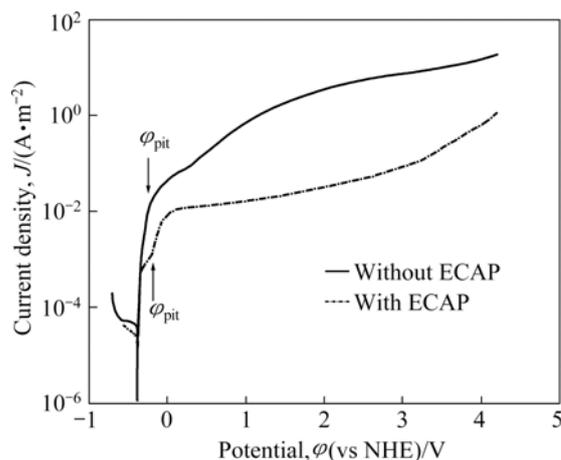


Fig.1 Effect of ECAP on polarization curves of anodized Al-Cu alloy in solution containing 0.2 mol/L AlCl₃ (Anodized at 200 A/m²)

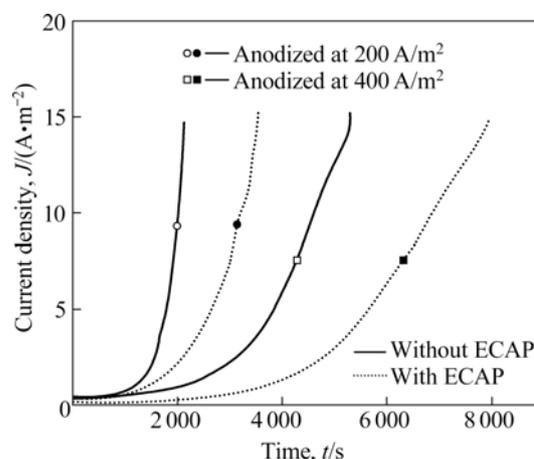


Fig.2 Time-dependence of anodic current densities of anodized Al-Cu alloy at constant potential of 1.2 V in 0.2 mol/L of AlCl₃

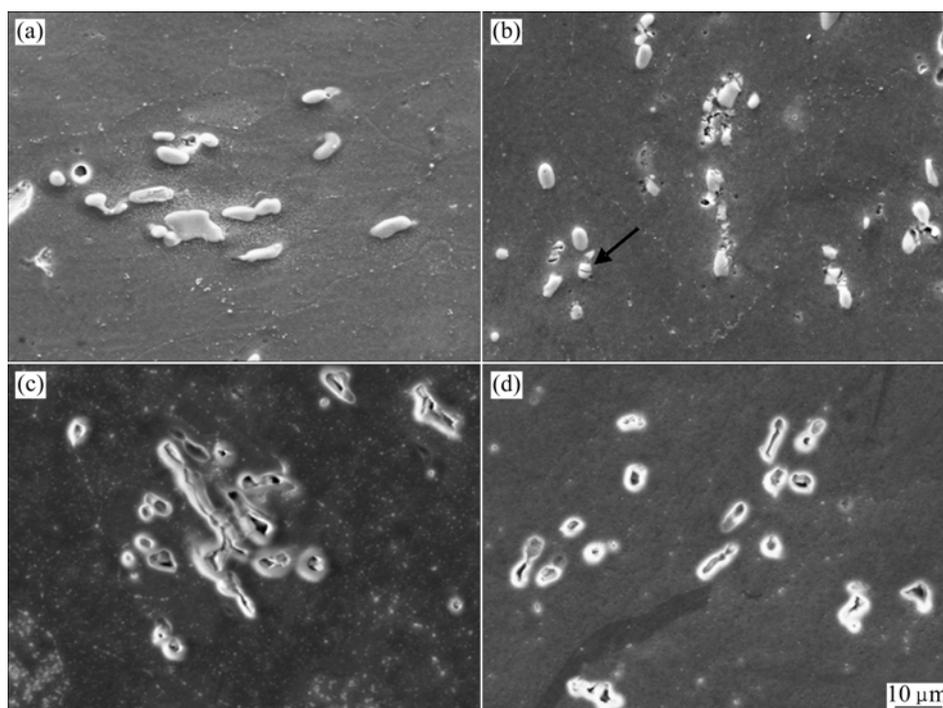


Fig.3 Effect of ECAP on morphology of Al-Cu alloy (a, b) and anodized Al-Cu alloy (c, d): (a) and (c) Without ECAP; (b) and (d) With ECAP

that these precipitates were Si, Al-Cu-Mg or Al-Cu-Si-Fe-Mn intermetallic compounds. It was reported that Al-Cu-Mg and Al-Cu-Si-Fe-Mn intermetallic compounds in Al-Cu alloy existed as Al_2CuMg and $(\text{Fe, Mn})_x\text{Si}(\text{Al, Cu})_y$, respectively[12]. However, the size of the precipitates in Al-Cu alloy was decreased due to ECAP, as shown by the arrow in Fig.3(b). The average size of precipitates in Al-Cu alloy was decreased from 10–12 μm to 5–6 μm by application of ECAP. It is known that second-phase precipitates can be broken up during the ECAP process[13], as was also found in this study. In anodized Al-Cu alloy, small pits were formed in the oxide films where the precipitates were present; and the size was smaller with ECAP than without. EDX spectra in small pit areas revealed that Si and Al-Cu-Si-Fe-Mn compounds were present in oxide films, indicating that these precipitates remained in anodic oxide films without being oxidized. On the other hand, Al-Cu-Mg intermetallic compounds were not detected after anodization, suggesting that these intermetallic compounds were dissolved during anodization.

Fig.4 shows the FE-SEM image of anodized Al-Cu alloy without ECAP. And the high magnification images of local positions are shown in Fig.5. Normal areas (Fig.5(a)) and defect areas (Figs.5(b), (c) and (d)) were observed in anodized Al-Cu alloy. Hydrated alumina ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) with a network structure was formed in normal areas (Fig.5(a)) of anodized Al-Cu. Hydrated alumina of the same network structure as normal areas was also formed in small pits areas (Figs.5(b) and (c))

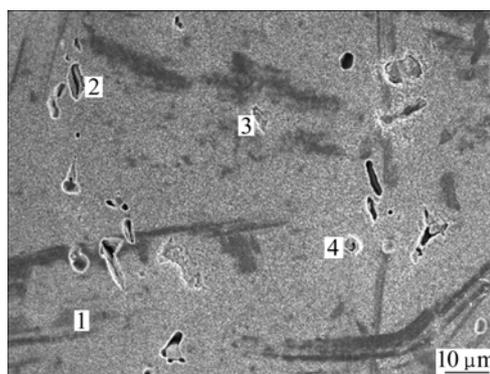


Fig.4 FE-SEM image of oxide film formed on Al-Cu alloy without ECAP (anodized at 200 A/m^2 for 20 min)

where Al-Cu-Mg compounds appear to be dissolved during anodization. The impurity precipitates such as Al-Cu-Si-Fe-Mn compounds in Al-Cu alloy (Fig.5(d)) remained in oxide films without being oxidized. The anodic oxide films were absent at the boundary between the normal oxide films and these impurity precipitates, as shown by the arrow in Fig.5(d). Anodized Al-Cu alloy with ECAP showed the same trend as those without ECAP. It is reported that the immersion potentials of Al-Cu-Mg intermetallic compounds in the solution containing NaCl were less noble than Al matrix, whereas those of Si and Al-Cu-Si-Fe-Mn precipitates were more noble than Al matrix[14]. It is assumed that Al-Cu-Mg intermetallic compounds were preferentially dissolved during anodization due to their less noble corrosion potential than Al matrix, whereas the precipitates composed of Si and Al-Cu-Si-Fe-Mn remained in anodic

oxide films without being oxidized.

Pitting corrosion of anodized Al-Cu alloy with ECAP occurred while being held at 1.2 V in 0.2 mol/L AlCl_3

solution. Fig.6 shows SEM images and EDX spectra of the pitting area at the initial stage. A pitting area of 15 μm in size was observed at the center in Fig.6(a).

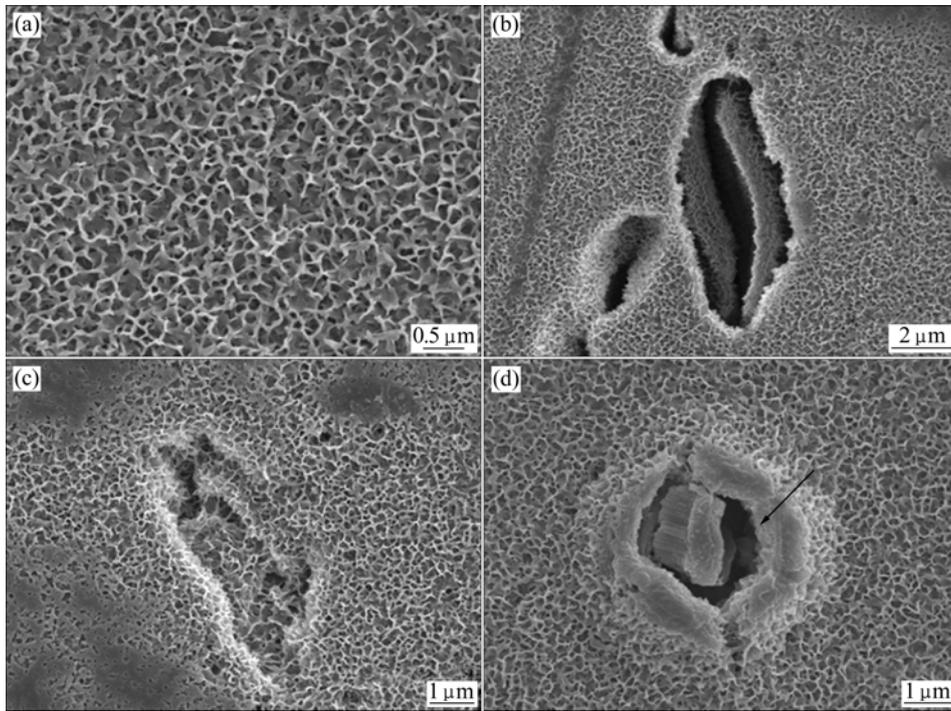


Fig.5 High magnification images of local positions in Fig.4: (a) Area 1 (Normal area); (b) and (c) Areas 2 and 3 (Dissolution areas of Al-Cu-Mg intermetallic compound); (d) Area 4 (Al-Cu-Si-Fe-Mn intermetallic compound)

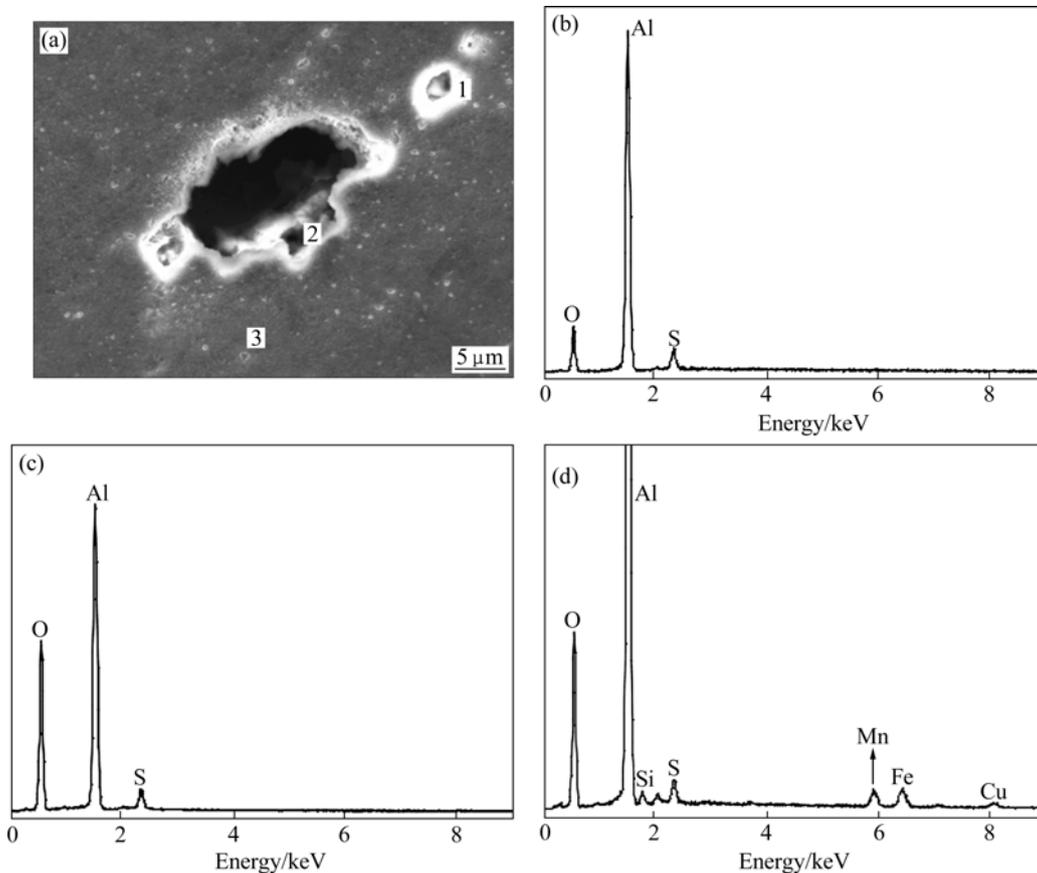


Fig.6 SEM image and EDS spectra of anodized Al-Cu alloy with ECAP after kept at 1.2 V in 0.2 mol/L AlCl_3 solution (Anodized at 400 A/m^2 for 20 min): (a) Morphology; (b) EDS spectrum of Area 1; (c) EDS spectrum of Area 2; (d) EDS spectrum of Area 3

Components of oxide films such as Al, O and S were detected in normal area of anodic oxide films, as shown in EDX spectra (Fig.6(c)). EDX spectrum (Fig.6(b)) in the defect area like small pits also shows the presence of Al, O and S, revealing that these small pits are dissolution areas of Al-Cu-Mg intermetallic compounds. Since EDX spectrum (Fig.6(d)) inside pitting area shows the presence of Cu, Si, Mn and Fe, revealing that these precipitates are Al-Cu-Si-Fe-Mn intermetallic compounds, pitting corrosion of anodized Al-Cu alloy appears to occur around the precipitates of Al-Cu-Si-Fe-Mn intermetallic compounds. Anodized Al-Cu alloy without ECAP showed the almost same trend as the surface morphology of the pitting areas as anodized Al with ECAP.

The pitting corrosion resistance of anodized Al-Cu alloy was improved by ECAP, as shown in Fig.1. Since the size of Al-Cu-Si-Fe-Mn precipitates remaining in anodic oxide films was decreased by ECAP (Figs.3(c) and (d)) and the pitting corrosion occurred preferentially around these precipitates, the improvement of pitting corrosion resistance with ECAP can be ascribed to a decrease in the size of the precipitates in anodic oxide films.

4 Conclusions

The effect of equal-channel angular pressing on the pitting corrosion resistance of anodized Al-Cu alloy was investigated by electrochemical techniques in a solution containing 0.2 mol/L AlCl_3 and also by surface analysis.

1) The time required before initiating pitting corrosion of anodized Al-Cu alloy was longer with ECAP than without, indicating the improvement in the pitting corrosion resistance by application of ECAP.

2) Second phase precipitates were present in Al-Cu alloy matrix and the size of these precipitates was greatly decreased by application of ECAP. The precipitates composed of Si and Al-Cu-Si-Fe-Mn were not oxidized during anodization, and the anodic oxide film was absent at the boundary between the normal oxide films and these impurity precipitates. The pitting corrosion of anodized Al-Cu alloy occurred preferentially around these precipitates, and the improvement of pitting corrosion resistance of anodized Al-Cu alloy by ECAP appears to be attributed to a decrease in the size of precipitates which act as origins of pitting corrosion.

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