Effect of Continuous Rotation Evolutional Control on the Pitting Corrosion Resistance of Anodized Aluminum-Magnesium Alloy

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The effect of continuous rotation evolutional control (CREO) on the pitting corrosion resistance of anodized Al-Mg alloy was investigated by electrochemical techniques in a solution containing 0.2 mol/L of AlCl₃ and by surface analysis. The potentials for pitting corrosion of anodized Al-Mg alloy was evidently shifted to the less noble direction by CREO and the time required before initiating pitting corrosion was shorter with CREO, indicating that the corrosion resistance with CREO was worse than without. The precipitates of Fe-Al intermetallic compounds remained in anodic oxide films of the alloys with CREO was higher than without. It is assumed that the pitting corrosion is promoted by these cracks as a result of the higher internal stress resulting from the CREO.

Keywords: aluminum-magnesium alloy, continuous rotation evolutional control, anodization, pitting corrosion

1. Introduction

Although aluminum is inherently a reactive metal, it shows excellent corrosion resistance over a neutral range of pH 4–8 due to its superficial oxide film. However, in solutions containing Cl⁻, pitting corrosion occurs locally where the oxide film is attacked by Cl⁻.¹,² Recently, reducing the grain size of metallic materials to the submicrometer range or even the nanometer range using the equal-channel angular pressing (ECAP) process³–⁸ or continuous rotation evolutional control (CREO)⁹–¹³ is increasingly being studied with the aim of improving mechanical properties such as strength and ductility. ECAP is conducted using a die with a channel angle of 90°, which creates an equivalent strain during one passage through the die. The sample was rotated by 90° about the longitudinal axis in the same sense between consecutive passes. On the contrary, in CREO, torsion strain can be concentrated in a zone of a columnar specimen heated locally using an induction coil. CREO process is practical, because large strains can be applied continuously to the entire specimen by moving the columnar specimen in the longitudinal axis direction. Authors previously reported that the pitting corrosion resistance of Al-Mg alloy was improved by CREO.¹⁴ The observed improvement in pitting corrosion resistance after CREO appeared to be attributable to both a decrease in the size of impurity precipitates, which act as cathodes during pitting corrosion, and an increase in the rate of formation of Al oxide films.

Al alloys are generally anodized by electrolysis to improve such properties as corrosion resistance and hardness.¹⁵–¹⁷ However, the effect of CREO on the pitting corrosion resistance of anodized Al alloys has so far been very little reported. In this study, Al-Mg alloy processed by CREO were anodized and the pitting corrosion resistance was investigated using electrochemical techniques. The mechanism of change in the pitting corrosion resistance of anodized Al-Mg alloy with CREO was also clarified by surface analysis.

2. Experimental

AA5056 (0.01% Cu, 0.06% Si, 0.14% Fe, 0.06% Mn, 4.94% Mg, 0.01% Zn, 0.06% Cr, <0.15% other elements, rest Al) was used as specimen of Al-Mg alloy. Figure 1 illustrates the principle of the CREO technique. A portion of a rod (15 mm × 2000 mm) was rotated at 66 rpm with respect to the other portion around its longitudinal axis. Torsion strain was introduced in the zone, which separated the two portions rotating in opposite directions. The torsion straining zone was localized by softening the zone more than other portions by local heating (inner 588 K, outer 518 K) and cooling, as shown in Fig. 1. While producing the torsion straining zone, the rod was moved at 5 mm/s along the longitudinal axis, which produced continuous severe plastic strain throughout the rod. To create torsion strain efficiently, the torsion straining zone must be narrow, and the rotation of the rod should be fast relative to the speed of the rod. The torsion strain of the rod was larger at the edge shown by ② in Fig. 1 than at center shown by ①. In this study, the pitting corrosion resistance of anodized Al-Mg alloy was evaluated at the edge of the rod. The initial grain size of the Al–Mg alloy prior to CREO was 30–50 μm. The average grain size of Al–Mg alloy after CREO was confirmed by TEM observation to be 1.0–2.0 μm.⁹

Prior to anodization, Al-Mg alloy was carefully polished down with No. 1500 emery paper and immersed in 0.75 mol L⁻¹ of NaOH solution at 298 K for 30 s, after which it was neutralized in 0.48 mol L⁻¹ of HNO₃ solution for 30 s and electropolished in a solution of 293 K containing...
methanol and perchloric acid (MeOH : HClO₄ = 4 : 1) at 10 V for 5 min. Anodization was conducted in a solution containing 1.53 mol L⁻¹ of H₂SO₄ and 0.0185 mol L⁻¹ of Al₂(SO₄)₃·16H₂O for 10–40 min at 293 K under galvanostatic conditions of 100, 200 and 400 A m⁻², agitated at 100 rpm by using a magnetic stirrer. The thickness of anodic oxide films of Al-Mg alloy was measured using an eddy current type coating thickness meter. Specimens 10 mm in diameter were prepared for corrosion testing. Their corrosion resistance was investigated over an area 6 mm in diameter and the remaining area was sealed with waterproof tape to prevent any corrosion from the edge. After anodized Al-Mg alloy had been immersed in a solution of pH 2.8 containing 0.2 mol L⁻¹ of AlCl₃ at 298 K for 30 min in an air atmosphere, the polarization curves were measured by polarization the electrode from the less noble to the more noble potential direction using the potential sweep method at 1 mV/s. The time-dependence of anodic current density was measured while being maintained at 1.2 V vs. NHE. The electrode potentials were measured using a saturated Ag/AgCl reference electrode (0.199 V vs. NHE, 298 K). In the presentation of anodizing and polarization curves, the potentials were plotted with reference to NHE. Platinum was used as the counter-electrode in all electrochemical techniques. The morphology of anodized Al-Mg alloy with and without CREO and the morphology of pitting corrosion were analyzed by FE-SEM, SEM and EDX.

For internal stress measurement, samples of Al-Mg alloy 10 mm in diameter and 0.325 mm in thickness were prepared by using a glow-discharge cutting machine. The waterproof-type strain gauges were attached to the rear sides of the specimens with an adhesive. The internal stress generated in the oxide film during anodization was estimated by measuring the strain in the Al-Mg alloy samples. The tensile and compressive strains in the Al-Mg alloy showed the presence of residual tensile and compressive stress, respectively, in the anodic oxide film.

3. Results and Discussion

3.1 Effect of CREO on the anodizing behavior

Figure 2 shows the time-dependence of the anode potential of Al-Mg alloy during galvanostatic anodizing at 400 A m⁻². Since the anode potential in Fig. 2 includes the resistance polarization by oxide films, the potential greatly changed according to the resistance of oxide films. Figure 2(b) is simply a magnification of the anodizing time on the x-axis of Fig. 2(a). The anode potential rapidly shifted to the more noble direction at the initial stage. Thereafter, the potential showed the peak value, shifting gradually to the less noble direction and finally reached an almost constant value, irrespective of whether CREO was applied or not. It is known in the formation of porous-type oxide films that the anode potential shifts to the more noble direction due to the formation of barrier-type oxide films during the first stage, then shifts to less noble direction due to the formation of porous-type oxide films. There was very little difference in anode potential of Al-Mg alloy between with CREO and without. However, the thickness of anodic oxide films of Al-Mg alloy was 66.1 and 62.4 μm with and without CREO, respectively, showing the increase in anodic oxide films by CREO. It is well known that the oxidation reaction of metal occurs more quickly at crystalline lattice defects, such as grain boundaries and dislocations, because the lattice defects include segregated impurities. The CREO process markedly increases the number of grain boundaries and the dislocation density in Al-Mg alloy. The oxidation rate of Al-Mg alloy appears to increase as a result of the increase in grain boundary and dislocation density caused by CREO.

3.2 Morphology of anodic oxide films

The surfaces of Al-Mg alloy with CREO after anodization were investigated by SEM and EDX. Figure 3 shows the SEM images and EDX spectra. It was found from the SEM image (a) that many defect areas resulting from precipitates were present on the surface of anodized Al-Mg alloy. Components of oxide films such as Al, O and S were detected in normal area of anodic oxide films, as shown in EDX spectrum (d). EDX spectra (b), (c) in some defect areas of oxide films show the presence of Si (b) and Fe (c) besides Al, O and S, revealing that defect areas are composed of Si (b) and Fe-Al intermetallic compounds. It is supposed that these precipitates remained in anodic oxide films without being oxidized during anodization, resulting in defect areas in oxide films.

Figure 4 shows the FE-SEM images of defect areas in oxide films of anodized Al-Mg alloy without CREO. Fe was detected in defect areas of oxide films, showing the presence...
of Fe-Al intermetallic compounds. Figure 4(b) is simply a magnification of Fig. 4(a). Although anodic oxide films with pores of about 10 nm in diameter were formed in normal areas [N in Fig. 4(b)], the diameter of pores became large at the impurity precipitates marked by arrow in Fig. 4(b). The area with pores of large diameter seems to be oxide films of Fe-Al intermetallic compounds. The voids free from oxide films were observed at the impurity precipitates. The Fe-Al intermetallic compounds were assumed to partially fall off the oxide films during the anodization. The absence of the anodic oxide films at the boundary between the normal oxide films and the precipitates appears to be caused by the difference in oxidation rate between Al matrix and the Fe-Al intermetallic compounds. In the surface morphology, anodized Al-Mg alloy without CREO showed almost the same feature as that without CREO.

Fig. 3 SEM and EDX spectra of anodized Al-Mg alloy with CREO.

Fig. 4 FE-SEM images of Fe-Al precipitate in Al-Mg alloy without CREO anodized at 400 A·m⁻² for 40 min.
Figure 5 shows SEM images of anodized Al-Mg alloy with and without CREO. The small precipitates in Fig. 5 are Si and Fe-Al intermetallic compounds. The precipitates were present, irrespective of having undergone CREO or not; however, the size of the precipitates in Al-Mg alloy was greatly decreased by CREO. It is known that second-phase precipitates can be broken up by the ECAP (equal-channel angular pressing) process, which produced severe plastic strain, as was also found by CREO in this study. In anodized Al-Mg alloy, small pits were formed in oxide films where the precipitates were present and their size was smaller with CREO than without; the size of precipitates in Al-Mg alloy hardly changed with anodization.

3.3 Effect of CREO on the pitting corrosion resistance of anodized Al-Mg alloy

Figure 6 shows the effect of CREO on the polarization curves of Al-Mg alloy anodized at 400 A/m² for 40 min. When the anode potentials were shifted from their corrosion potential to the noble direction, anodic current densities rapidly increased at 0.5 to 1.0 V, irrespective of whether they had undergone CREO or not. This rapid increase in current density is caused by initiation of pitting corrosion. The anodic current densities gradually increased when the anode potentials were further shifted from their pitting corrosion potential (E_pit) to the more noble direction. This gradual increase in current density was caused by growth of the pits. The corrosion potential of anodized Al-Mg alloy was slightly shifted to the less noble direction by CREO. The anodic current density with CREO was larger over the range of E_pit to 1.5 V than without; suggesting that the pitting corrosion resistance was worse with CREO.

Figure 7 shows the time-dependence of the anodic current densities of Al-Mg alloy anodized at 400 A/m² for 40 min. Samples were held at 1.0 V in the solution containing 0.2 mol/L of AlCl₃. The anodic current density of anodized Al-Mg alloy increased rapidly after a certain period of time due to the initiation of pitting corrosion, irrespective of whether they had undergone CREO or not. The time required for initiating the pitting corrosion with CREO was shorter than without, showing that the corrosion resistance with CREO was worse than without.

It has been reported that the corrosion resistance of Al-Mg alloy without anodization can be improved by CREO. However, the corrosion resistance of Al-Mg alloy with anodization was found to be worse by CREO. Then, the effect of CREO on the corrosion resistance of Al-Mg alloy anodized at various conditions was investigated, because the effect of CREO seemed to depend on the degree of anodization. Figure 8 shows the time-dependence of the anodic current densities at 1.0 V of Al-Mg alloy anodized at 400 A/m² for 10 min. Although the time to pitting corrosion occurrence was shorter with CREO, showing that the corrosion resistance was worse with CREO, the degree of deterioration by CREO was smaller with anodization at 400 A/m² for 10 min than that at 400 A/m² for 40 min shown in Fig. 7. The thickness of oxide films formed with anodiza-
tion at 400 A/m$^2$ for 40 min was about 65 µm, while it was about 20 µm with anodization at 400 A/m$^2$ for 10 min.

Figure 9 shows the time-dependence of the anodic current densities at 1.0 V of Al-Mg alloy with oxide films about 10 µm in thickness anodized at 100 A/m$^2$ for 10 min. With anodization at 100 A/m$^2$ for 10 min, the time to pitting corrosion occurrence was longer with CREO, showing improvement in the pitting corrosion resistance by application of CREO. This trend agreed with the report that the corrosion resistance of Al-Mg alloy without anodization can be improved by CREO. The effect of CREO on the corrosion resistance of Al-Mg alloy depended on the thickness of anodic oxide films; the degree of deterioration by CREO increased with thickness of anodic oxide films. Incidentally, small fluctuations in anodic current density were observed in the time-dependence curves of anodic current density in Figs. 8 and 9. It has been reported from electron microscope observations that multiple pitting corrosion occurs at the initial stage, but only pits that grow readily at the initial stage ultimately develop into macro pits, since most pits are unstable and are immediately repassivated.\textsuperscript{2) The small fluctuations in anodic current density in Figs. 8 and 9 suggest the alternate pitting corrosion and repassivation in pitting areas.

3.4 Surface analysis of pitting areas

Anodized Al-Mg alloy with CREO was kept at a constant potential of 1.0 V in 0.2 mol/L of AlCl$_3$ solution to generate pitting corrosion. The morphology of pitting area at an initial stage of anodic current density of 2 A/m$^2$ is shown in Fig. 10. Figure 10(b) is a magnification of the different area from Fig. 10(a). Figures 10(a) and (b) show that cracks proceeded in the anodic oxide films at initial stage of corrosion. Since no cracks were present in anodic oxide films before the corrosion tests, as shown in Fig. 3, they most likely occur during pitting corrosion. Impurity precipitates present in Al-Mg alloy remained without being oxidized during anodization as shown in Figs. 3 and 5. The pitting corrosion of Al is reported to originate around these precipitates not oxidized.\textsuperscript{18–21) It is clear that the pitting corrosion originates around the precipitates and generates cracks through the pitting area in the anodic oxide films, as shown in Fig. 10(a). The pitting corrosion seems to be accelerated by cracks due to exposure of Al-Mg alloy substrate unprotected by anodic oxide films. In the morphology of cracks in the anodic oxide films at an initial stage of pitting corrosion, anodized Al-Mg alloy without CREO showed almost the same feature as that with CREO.

Figure 11 shows the morphology of stable pitting corrosion with anodic current density of 50 A/m$^2$ at a constant potential of 1.0 V in 0.2 mol/L of AlCl$_3$. Figures 11(a) to (d) were SEM images of various areas after the pitting corrosion proceeded. The initial cracks expanded and finally connected to form circles with other cracks during pitting corrosion.
Some anodic oxide films with circular cracks were exfoliated (d), resulting in exposure of the Al–Mg alloy substrate. Many pittings were observed at the exposure of the Al–Mg alloy substrate.

Figure 12 shows the time-dependence of the strain of Al–Mg alloy sample during anodization at 400 A/m². The positive and negative strains in the Al-Mg alloy showed the presence of internal tensile and compressive stress, respectively, in the anodic oxide film. Although the internal stress generated in the anodic oxide film on the Al–Mg alloy was a tensile at the initial stage of anodization, the stresses changed to a compressive one after 30 s, and the compressive strain increased with anodization duration, irrespective whether the sample had undergone CREO or not. The internal stress of Al-Mg alloy with CREO was higher than without. The compressive stress further increased when the anodization was stopped.

Compressive residual stress in anodic oxide film remains in oxide film because oxide film can not be extended by constraint of bulk substrate, though oxide film intends to expand due to expansion of volume of oxide film. The tensile stress in oxide film is generated without the constraint of bulk substrate. It is assumed that anodic oxide films are free from constraint by the substrate in the pitting corrosion area around precipitates and, consequently, tensile stress is generated locally in oxide films, resulting in decrease in residual compressive stress in oxide films due to the propagation of cracks. It has been reported from the internal stress of Al-Mg
substrate estimated by using a strain gauge during corrosion test that the compressive stress in oxide films was obviously relieved when the pitting corrosion proceeded in some degree.\textsuperscript{22,23}

The CREO process of severe plastic deformation applies large internal stresses to the Al-Mg alloy.\textsuperscript{9} It therefore appears that the higher internal stress of Al-Mg alloy resulting from CREO is also likely to remain in anodic oxide films, increasing the likelihood of cracks. As can be seen from Figs. 6 and 7, CREO caused poor pitting corrosion resistance in anodized Al-Mg alloy in spite of the decreased size of the precipitates in the anodic oxide films. This can be explained by assuming that the increased number of cracks in the anodic oxide films has a greater influence on the pitting corrosion resistance of anodized Al-Mg alloy than the decreased size of precipitates in the oxide films. The increase in adverse influence of CREO on pitting corrosion resistance with thickness of the anodic oxide films, as shown in Figs. 7–9, can be ascribed to the cracks appearing more readily.

In the induction period for initiating pitting corrosion, the corrosion of Al occurs and generates the cracks around the precipitates. It is assumed that the macro pits are originated when these cracks become large to some degree.

4. Conclusion

The pitting corrosion resistance of anodized Al-Mg alloy processed by CREO was investigated by electrochemical techniques. The potential for pitting corrosion of anodized Al-Mg alloy was shifted to the less noble direction by CREO, and the time to the pitting corrosion with CREO was shorter than without, indicating that application of CREO has a harmful effect on the resistance to pitting corrosion. Fe-Al intermetallic compounds of Al-Mg alloy were present in the oxide films without being oxidized during anodization. Cracks occurred in the anodic oxide films through the pitting. Around the precipitates during initial corrosion, and the pitting corrosion was accelerated by cracks. The strain gauge attached to Al–Mg alloy revealed that the compressive internal stress remained in the anodic oxide films and that the stress with CREO was larger than without. It appears that the higher internal stress of the anodic oxide films resulting from CREO increases the likelihood of cracks. It is assumed that the pitting corrosion is promoted by these cracks in spite of the decreased size of the precipitates in the anodic oxide films.

REFERENCES