Pitting Corrosion Resistance of Anodized Aluminum Alloy Processed by Severe Plastic Deformation*¹

In-Joon Son^{1,*2}, Hiroaki Nakano², Satoshi Oue², Shigeo Kobayashi³,
Hisaaki Fukushima² and Zenji Horita²

¹Department of Materials Process Engineering, Kyushu University, Fukuoka 819-0395, Japan

²Department of Materials Science & Engineering, Kyushu University, Fukuoka 819-0395, Japan

³Department of Applied Chemistry and Biochemistry, Kyushu Sangyo University, Fukuoka 813-8503, Japan

The effect of equal-channel angular pressing (ECAP) on the pitting corrosion resistance of anodized Al and Al-Mg alloy was investigated by electrochemical techniques in a solution containing 0.2 mol/L of AlCl_3 and by surface analysis. The time required for initiating pitting corrosion of anodized Al was longer with ECAP than without, indicating improvement in the pitting corrosion resistance by application of ECAP. However, in anodized Al-Mg alloy, the pitting corrosion occurred earlier with ECAP than without, showing that the corrosion resistance was worse with ECAP than without. SEM and EPMA observation revealed that pitting corrosion of anodized Al occurred around the impurity precipitates and that the size of the impurity precipitates decreased as a result of the ECAP. The improvement in pitting corrosion resistance of anodized Al by ECAP appears to be attributable to a decrease in the size of impurity precipitates. On the other hand, in anodized Al-Mg alloy, cracks occurred in the anodic oxide films during initial corrosion and the cracks were larger with ECAP than without. It is assumed that the pitting corrosion was promoted by the cracks due to the higher internal stress resulting from ECAP. [doi:10.2320/matertrans.48.21]

(Received August 25, 2006; Accepted November 2, 2006; Published December 25, 2006)

Keywords: aluminum, aluminum-magnesium alloy, equal-channel angular pressing, anodizing, 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)} On the other hand, reducing the grain size of metallic materials to the submicrometer range or even the nanometer range using equal-channel angular pressing (ECAP) is increasingly being studied with the aim of improving aluminum's mechanical properties such as strength and ductility.^{3–8)} The authors have previously reported that the corrosion resistance of Al and Al-Mg alloy can be improved by ECAP.⁹⁾ The observed improvement in pitting corrosion resistance after ECAP 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.^{10–12)} However, the effect of ECAP on the pitting corrosion resistance of anodized Al and Al alloys has so far been very little reported. In this study, Al and Al-Mg alloy processed by ECAP were anodized and the pitting corrosion resistance was investigated using electrochemical techniques. The mechanism of change in the pitting corrosion resistance of anodized Al and Al-Mg alloy with ECAP was also clarified by surface analysis.

Table 1 Chemical compositions of Al and Al-Mg alloy used. (mass%)

Substrate	Al	Cu	Si	Fe	Mn	Zn	Mg	Cr
AA1100	>99	0.15	0.09	0.60	0.005	0.006	0.002	<0.001
AA5052	rest	0.05	0.11	0.24	0.01	0.01	2.5	0.17

2. Experimental

AA1100 (mass%, >99.0% Al, 0.15% Cu, 0.09% Si, 0.60% Fe, 0.005% Mn, 0.006% Zn, 0.002% Mg, <0.001% Cr) and AA5052 (0.05% Cu, 0.11% Si, 0.24% Fe, 0.01% Mn, 2.5% Mg, 0.01% Zn, 0.17% Cr, <0.15% other elements, rest Al) shown in Table 1 were respectively used as specimens of Al and Al-Mg alloy. Figure 1 shows a schematic diagram of the ECAP process. ECAP was conducted for 8 passes (Al) or 4 passes (Al-Mg) at room temperature using a die with a channel angle of 90° , which creates an equivalent strain of ~ 1 during one passage through the die. The sample was rotated by 90° about the longitudinal axis in the same sense between consecutive passes, the generally designated processing route Bc.⁶⁾ The pressings were performed at a rate of $\sim 19 \text{ mm s}^{-1}$ using MoS_2 as a lubricant. The initial grain sizes of Al and Al-Mg alloy prior to ECAP were 30–50 μm . The average grain sizes of Al and Al-Mg alloy after the ECAP process were confirmed by TEM observation to be respectively 0.5–1.0 μm and 0.2–0.5 μm .¹³⁾

Prior to anodizing, Al and Al-Mg alloys were carefully polished down with No. 1500 emery paper and immersed in 0.75 mol/L NaOH solution at 20°C for 30 s, after which they were neutralized in 0.48 mol/L of HNO_3 solution for 30 s and electropolished in a 20°C solution containing methanol and perchloric acid ($\text{MeOH} : \text{HClO}_4 = 4 : 1$) at 10 V for 5 min. Anodizing was conducted in a solution containing 1.53 mol/

*¹This Paper was Originally Published in Japanese in J. Japan Inst. Metals
70 (2006) 534–540.

*²Graduate Student, Kyushu University

Fig. 1 Schematic diagram of ECAP.

L of H_2SO_4 and 0.0185 mol/L of $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ at 20°C under galvanostatic conditions of $100\text{--}400\text{ A/m}^2$ for 40 min, agitated at 100 rpm using a magnetic stirrer.

Specimens 1.0 cm in diameter were prepared for corrosion testing. Their corrosion resistance was investigated over an area 0.6 cm in diameter and the remaining area was sealed with waterproof tape to prevent any corrosion from the edge. After the anodized Al and Al-Mg alloy had been immersed in a solution containing 0.2 mol/L of AlCl_3 at 25°C for 30 min in an air atmosphere, the polarization curves were measured by polarizing the electrode from the less noble to the more noble potential direction using the potential sweep method at 1 mV/s. In addition, the time-dependence of the anodic current density was measured while being maintained at 1.2 V vs. NHE after immersion for 30 min. The electrode potentials were measured using a saturated Ag/AgCl reference electrode (0.199 V vs. NHE, 25°C). 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 and Al-Mg alloy with and without ECAP and the morphology of pitting corrosion were analyzed by FE-SEM, SEM, EPMA and EDX.

3. Results and Discussion

Figure 2 shows the time-dependence of the anode potential of Al and Al-Mg alloy during galvanostatic anodizing at various current densities. Figures 2(b) and (d) are simply a magnification of the anodizing time on the x-axis of Figs. 2(a) and (c), respectively. The anode potentials of Al and Al-Mg alloy rapidly shifted to more anodic values at the initial stage, but later moved gradually to the less noble direction and reached an almost constant level. It is known in the formation of porous-type oxide films that the anode potential shifts to the noble direction due to the formation of

barrier-type oxide films during the first stage, then shifts to the less noble direction due to the formation of porous-type oxide films.¹¹⁾ The time-dependence of the anode potential shown in Fig. 2 indicates the formation of porous-type Al oxide films. There was very little difference in the anode potential of Al and Al-Mg alloy between with ECAP and without. It therefore appears that ECAP has no influence on the formation behavior of oxide films by anodizing.

3.1 Morphology of anodic oxide films

Figure 3 shows the FE-SEM images of anodized Al and Al-Mg alloy without ECAP. Normal area (N) and impurity precipitates (P) were observed in anodized Al and Al-Mg alloy [(b), (e)]. Although anodic oxide films with pores about 10 nm in diameter were formed in normal areas [(a), (d)], no oxide films were formed on the impurity precipitates [(c), (f)]. The anodic oxide film were absent at the boundary between the normal oxide films and the impurity precipitates. Anodized Al and Al-Mg alloys with ECAP showed the same trend as those without ECAP. It was reported by the authors that these precipitates were respectively Fe-Al intermetallic compounds in Al and Si or Fe-Al compounds in Al-Mg alloy.⁹⁾

Figure 4 shows SEM images of Al with anodizing and without. The small precipitates in Fig. 4 are Fe-Al intermetallic compounds. In Al without anodizing [(a), (b)], precipitates were present, irrespective of having undergone ECAP or not; however, the size of the precipitates in Al was greatly decreased due to the increased number of smaller precipitates due to ECAP, as shown by the arrow in Fig. 4(b). It is known that second-phase precipitates can be broken up by the ECAP process,^{7,8,14)} as was also found in this study. In anodized Al, the precipitates remained without being oxidized and their size was smaller with ECAP than without [(c), (d)]: the size of precipitates in Al hardly changed with anodizing.

Figure 5 shows SEM images of Al-Mg alloy with and without anodizing. In non-anodized Al-Mg alloy, the size of the precipitates was decreased by ECAP [(a), (b)]. This trend was also observed in Al. The size of the precipitates in anodized Al-Mg alloy was smaller with ECAP than without [(c), (d)].

3.2 Effect of ECAP on the pitting corrosion resistance of anodized Al and Al-Mg alloy

Figure 6 shows the effect of ECAP on the polarization curves of Al and Al-Mg alloy anodized at 400 A/m^2 . In anodized Al, when the anode potentials were shifted from their corrosion potential to the noble direction, no anodic current densities rapidly increased at certain potentials, irrespective of whether they had undergone ECAP or not. This indicates that no pitting corrosion occurred at a potential sweep rate of 1 mV/s even in the region of noble potential. However, the anodic current density of anodized Al was smaller over the range of 0–4 V with ECAP than without, suggesting that ECAP improves pitting corrosion resistance. On the other hand, in anodized Al-Mg alloy, no anodic current densities sharply increased without ECAP, while with ECAP, the current density greatly increased at about 1 V, indicative of pitting corrosion.

Fig. 2 Time-dependence of anode potential of Al (a, b) and Al-Mg alloy (c, d) during anodizing at various current densities in a solution containing $1.53 \text{ mol}\cdot\text{L}^{-1}$ of H_2SO_4 and $0.0185 \text{ mol}\cdot\text{L}^{-1}$ of $\text{Al}_2(\text{SO}_4)_3$ at 293 K.

Fig. 3 FE-SEM images of Al (a, b, c) and Al-Mg alloy (d, e, f) anodized at $400 \text{ A}\cdot\text{m}^{-2}$ for 40 min. (without ECAP)

The time-dependence of the anodic current density of Al and Al-Mg alloy anodized at various current densities is shown in Fig. 7. Samples were held at 1.2 V in the solution containing 0.2 mol/L of AlCl_3 . The anodic current density of anodized Al and Al-Mg alloy increased rapidly after a certain period of time due to the initiation of pitting corrosion. The time required for initiating the pitting corrosion of anodized Al was longer with ECAP than without, regardless of the anodizing current density, showing that ECAP enhanced

pitting corrosion resistance. On the other hand, in anodized Al-Mg alloy, the time to pitting corrosion occurrence was shorter at all anodizing current densities with ECAP than without, indicating that the corrosion resistance was worse with ECAP than without. Particularly with increased anodizing current density, the time to pitting corrosion was greatly shortened by ECAP. The time to pitting corrosion of anodized Al and Al-Mg alloy increased with increased anodizing current density, with the exception of Al-Mg

Fig. 4 Effect of ECAP on the morphology of Al and anodized Al.

Fig. 5 Effect of ECAP on the morphology of Al-Mg alloy and anodized Al-Mg alloy.

anodized at 400 A/m^2 with ECAP. Since the anodizing duration was fixed at 40 min in this study, the thickness of the anodic oxide films increased with increased anodizing current density. The pitting corrosion resistance was therefore mostly improved with increased anodizing current density. Incidentally, small fluctuations in anodic current

density were observed in most of the time-dependence curves of anodic current density. 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.²⁾

Fig. 6 Effect of ECAP on the polarization curves of anodized Al (a) and Al-Mg alloy (b) in a solution containing $0.2 \text{ mol} \cdot \text{L}^{-1}$ of AlCl_3 . (Anodized at $400 \text{ A} \cdot \text{m}^{-2}$)

Fig. 7 Time-dependence of the anodic current density of Al (a) and Al-Mg alloy (b) anodized at 100, 200 and $400 \text{ A} \cdot \text{m}^{-2}$ while kept at constant potential of 1.2 V in $0.2 \text{ mol} \cdot \text{L}^{-1}$ of AlCl_3 solution. $\circ, \bullet$: $100 \text{ A} \cdot \text{m}^{-2}$, $\square, \blacksquare$: $200 \text{ A} \cdot \text{m}^{-2}$, $\triangle, \blacktriangle$: $400 \text{ A} \cdot \text{m}^{-2}$, $\circ, \square, \triangle$: without ECAP, $\bullet, \blacksquare, \blacktriangle$: with ECAP.

The small fluctuations in anodic current density in Fig. 7 suggest the alternate pitting corrosion and repassivation in pitting areas.

3.3 Surface analysis of pitting areas

3.3.1 Pitting areas of anodized Al

Pitting corrosion of anodized Al without ECAP occurred while being held at 1.2 V in 0.2 mol/L of AlCl_3 solution. Figure 8 shows SEM images and EDX spectra of the pitting area at the initial stage. A pitting area of $20 \mu\text{m}$ in size was observed at the center in Fig. 8(a). Small cracks resulted in the breaking of the anodic oxide films in this pitting area. EDX spectrum (b) in the area of the precipitates shows the presence of Fe, revealing that these precipitates are Fe-Al intermetallic compounds. Since EDX spectrum (c) inside the pitting area also shows the presence of Fe, pitting corrosion of anodized Al appears to occur around the precipitates of Fe-Al intermetallic compounds. Components of oxide films such as Al, O and S were detected in normal areas of anodic oxide films, as shown in EDX spectra (d).

Pitting areas of anodized Al without ECAP were further

observed in detail by EPMA. Figure 9 shows the EPMA images. As can be seen from the characteristic X-ray images, Al (b) and O (c) were not detected in the pitting area shown at the center in Fig. 9(a), indicating that this pitting area was deep. Iron resulting from the presence of Fe-Al intermetallic compounds in the precipitates was distributed all over the films, but the content was slightly higher at the edges of the pitting area (d). These results indicate that pitting corrosion occurs around the Fe-Al intermetallic compound precipitates, noticeably occurring preferentially around large ones. Vacancies in the anodic oxide film were observed at the boundary between oxide films and impurity precipitates, showing no formation of normal anodic oxide films at that boundary (Fig. 3). Therefore, the pitting corrosion of anodized Al appears to occur preferentially around Fe-Al intermetallic compounds. The intermetallic compounds were assumed to fall off the anodic oxide films during the pitting corrosion process, since large voids were formed in the pitting areas. Anodized Al with ECAP showed almost the same trend as the surface morphology of the pitting areas as anodized Al without ECAP.

Fig. 8 SEM image and EDX spectra of anodized Al without ECAP after kept at 1.2 V in 0.2 mol·L⁻¹ of AlCl₃ solution.

Fig. 9 EPMA images of anodized Al without ECAP after kept at 1.2 V in 0.2 mol·L⁻¹ of AlCl₃ solution.

The pitting corrosion resistance of anodized Al was improved by ECAP, as shown in Figs. 6 and 7. Since the size of Fe-Al intermetallic compound precipitates remaining in anodic oxide films was decreased by ECAP [Fig. 4(c), (d)] and 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.

3.3.2 Pitting areas of anodized Al-Mg alloy

Anodized Al-Mg alloy was kept at a constant potential of

Fig. 10 SEM images of anodized Al-Mg alloy after kept at 1.2 V in 0.2 mol·L⁻¹ of AlCl₃ solution.

1.2 V in 0.2 mol/L of AlCl₃ solution to generate pitting corrosion. The morphology of the pitting area is shown in Fig. 10. Pitting corrosion occurred around the precipitates, irrespective of whether ECAP was applied or not, and cracks proceeded in the anodic oxide films through the pitting area. The cracks were larger with ECAP than without. Since no cracks were present in anodic oxide films before the corrosion tests, as shown in Fig. 5(c) and (d), they most likely occur during pitting corrosion. It is clear that the pitting corrosion originates around the precipitates and generates cracks in the anodic oxide films. The pitting corrosion seems to be accelerated by cracks due to the exposure of Al-Mg alloy substrate unprotected by anodic oxide films.

When the anodic oxide films are formed on metal, internal stress is generally produced in the oxide films due to the difference in molecular volume between the metal substrate and the oxide film. It has been reported that the compressive internal stress remained in barrier-type oxide film of Al₂O₃/Al system whose Pilling-Bedworth ratio (molecular volume ratio of oxide film to metal substrate) was 1.28, exceeding 1.0.¹⁵⁾ However, the direction of the internal stress of the porous-type Al₂O₃ in this study depends on the anodizing current density. In the oxide film of Al anodized above 100 A/m², the tensile internal stress remains¹⁶⁾ and causes the cracks in the oxide films through the pitting area. Cracks readily occur in oxide films that experience high levels of internal tensile stress. The ECAP process of severe plastic deformation applies large internal stresses to the Al-Mg alloy.¹⁷⁾ It therefore appears that the higher internal stress of Al-Mg alloy resulting from ECAP is also likely to remain in anodic oxide films, increasing the likelihood of cracks. As can be seen from Figs. 6 and 7, ECAP 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 adverse influence of ECAP on pitting corrosion resistance increased with increased anodizing current density, as shown in Fig. 7. This can be ascribed to the cracks appearing more readily due to the increased thickness of the anodic oxide films. Cracks occur more readily in oxide films of ECAP-treated Al-Mg alloy than with ECAP-treated Al. This seems

to be due to the higher internal stresses in ECAP-treated Al-Mg alloy.¹⁸⁾

4. Conclusion

The pitting corrosion resistance of anodized Al and Al-Mg alloy processed by ECAP was investigated by electrochemical techniques. The time to the pitting corrosion of anodized Al was longer with ECAP than without, indicating that application of ECAP improves resistance to pitting corrosion. However, in anodized Al-Mg alloy, pitting corrosion occurred earlier with ECAP than without, showing that the corrosion resistance was decreased by ECAP. FE-SEM observation revealed that impurity precipitates were present in the oxide films of anodized Al and Al-Mg alloy and the anodic oxide films were absent around the impurity precipitates. It was found from SEM and EPMA observations that pitting corrosion of anodized Al occurred around the impurity precipitates, and that the size of the impurity precipitates decreased as a result of ECAP. The improvement in the resistance to pitting corrosion of anodized Al caused by ECAP appears to be due to decreased size of the impurity precipitates. On the other hand, in anodized Al-Mg alloy, cracks occurred in the anodic oxide films during initial corrosion. The cracks were larger with ECAP than without, suggesting that the pitting corrosion of anodized Al-Mg alloy was promoted by the cracks due to the higher internal stress resulting from ECAP.

REFERENCES

- 1) H. H. Uhlig: *Corrosion and Corrosion Control* (in Japanese, Sangyo Tosho, Tokyo, 1968) pp. 320–332.
- 2) G. Ito: *Corrosion Science and Engineering* (in Japanese, Corona Publishing Co., Tokyo, 1973) pp. 306–315.
- 3) R. Z. Valiev, N. A. Krasilnikov and N. K. Tsenev: *Mater. Sci. Eng. A137* (1991) 35–41.
- 4) R. Z. Valiev, R. K. Islamgaliev and I. V. Alexandrov: *Prog. Mater. Sci.* **45** (2000) 103–109.
- 5) Y. T. Zhu, T. G. Langdon, R. S. Mishra, S. L. Semiatin, M. J. Saran and T. C. Lowe: *Ultrafine Grained Materials II*, (The Minerals, Metals & Materials Society, Warrendale, PA, 2002).
- 6) Z. Horita, M. Furukawa, M. Nemoto and T. G. Langdon: *Mater. Sci. Tach.* **16** (2000) 1239–1245.
- 7) Z. Horita: *J. Jpn. Weld. Soc.* **74** (2005) 88–91.
- 8) Z. Horita: *Materia Japan* **41** (2002) 422–426.

- 9) I. J. Son, H. Nakano, S. Oue, S. Kobayashi, H. Fukushima and Z. Horita: *J. Japan Inst. Metal.* **69** (2005) 892–898.
- 10) T. Asada: *J. Met. Finish. Soc. Jpn.* **21** (1970) 490–497.
- 11) M. Nagayama, H. Takahashi and M. Koda: *J. Met. Finish. Soc. Jpn.* **30** (1979) 438–456.
- 12) N. Baba: *Anodic Oxide Films Produced by Electrolysis* (in Japanese, Maki Syoten, Tokyo, 1996) pp. 14–47.
- 13) Z. Horita, T. Fujinami, M. Nemoto and T. G. Langdon: *Metallurgical and Mater. Trans. A* **31A** (2000) 691–701.
- 14) V. V. Stolyarov, R. Lapovok, I. G. Brodova and P. F. Thomson: *Mater. Sci. Eng.* **A357** (2003) 159–167.
- 15) M. Seo and K. Ueno: *J. Finish. Soc. Jpn.* **51** (2000) 365–370.
- 16) S. M. Moon and S. I. Pyun: *Electrochimica Acta* **43** (1998) 3117–3126.
- 17) H. B. Geng, S. B. Kang and B. K. Min: *Mater. Sci. Eng.* **A373** (2004) 229–238.
- 18) Y. Iwahashi, Z. Horita, M. Nemoto and T. G. Langdon: *Metallurgical and Mater. Trans. A* **29A** (1998) 2503–2510.