Pitting Corrosion Resistance of Ultrafine-Grained Aluminum 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 812-8581, Japan

²Department of Materials Science & Engineering, Kyushu University, Fukuoka 812-8581, 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 Al and Al-Mg alloy was investigated by means of polarization curves in solutions containing 300 ppm of Cl^- and by surface analysis. The potentials for pitting corrosion of Al and Al-Mg alloy were clearly shifted in the noble direction by the ECAP process, indicating that this process improves resistance to pitting corrosion. SEM observations revealed that pitting corrosion occurred near impurity precipitates and that the size of the impurity precipitated decreased as a result of the ECAP process. The time-dependence of corrosion potential and the polarization resistance determined using the AC impedance technique suggest that the ECAP process increases the rate of formation of Al oxide films. The improvement in pitting corrosion resistance of Al and Al-Mg alloy by ECAP appears to be attributable to a decrease in the size of impurity precipitates and an increase in the rate of formation of Al oxide films.

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1. Introduction

Although aluminum is inherently an active 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)} Selection of alloying elements, cathodic protection and the organic coating are therefore performed to improve the pitting corrosion resistance of Al alloys. However, these techniques result in poor mechanical properties and increase processing costs. On the other hand, reducing the grain size of metallic materials to the submicrometer range or even the nanometer range using the equal-channel angular pressing (ECAP) process is increasingly being studied with the aim of improving mechanical properties such as strength and ductility.^{3–8)} However, there have been very few studies on the effect of grain size reduction by means of the ECAP process on the resistance to pitting corrosion of Al alloys.^{9,10)} It is also necessary to elucidate the mechanism by which the pitting corrosion resistance of Al alloys is changed by the ECAP process. The conventional rolling process seems to have only a minor effect, since reduction of the impurity precipitate size and the Al grain size are very slight as compared with the ECAP process. Therefore, the effect of the conventional rolling process on pitting corrosion resistance has so far been little reported. In this study, the pitting corrosion resistance of Al and Al-Mg alloy produced by the ECAP process was investigated using electrochemical techniques. In addition, the mechanism of improvement of the pitting corrosion resistance of Al and Al-Mg alloy with ECAP was clarified by surface analysis and electrochemical impedance methods.

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) 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

Fig. 1 Schematic diagram of ECAP.

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^{*2}Graduate Student, Kyushu University

Fig. 2 Effect of ECAP on the polarization curves of Al (a) and Al-Mg alloy (b) in a solution containing $0.1 \text{ mol}\cdot\text{L}^{-1}$ of Na_2SO_4 and 300 ppm Cl^- .

Fig. 3 Time-dependence of the anodic current density of Al (a) and Al-Mg alloy (b) while kept at constant potentials of 0.2 V and 0 V nobler than their pitting corrosion potential.

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 .¹¹⁾

After Al and Al-Mg alloy were carefully polished down with No. 600 emery paper and immersed in a solution containing 0.1 mol/L of Na_2SO_4 and 8.46 mol/L of NaCl (300 ppm Cl^-) at 25°C for an hour in an air atmosphere, the polarization curves were measured by polarizing from the less noble potential to the anodic potential direction using the potential sweep method at 30 mV min^{-1} . The electrode potentials were measured during the potential sweep using a saturated Ag/AgCl reference electrode (0.199 V vs. NHE, 25°C). In the presentation of polarization curves, the potentials were plotted with reference to NHE.

Since the naturally formed Al oxide films are of the barrier type, the time-dependences of anode potential were examined during galvanostatic electrolysis at 1 A/m^2 in a solution containing 0.5 mol/L of H_3BO_3 and 0.05 mol/L of $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$ to form a barrier-type oxide film. The

effect of ECAP on the rate of formation of Al oxide film was assumed to be revealed by these time-dependences of anode potentials.

The AC impedance of the Al and Al-Mg alloy was measured at rest potential in a solution containing 0.1 mol/L of Na_2SO_4 and 8.46 mol/L of NaCl . To obtain Cole-Cole plots, the frequency dependence of the AC impedance and phase difference were measured using a frequency response analyzer at rest potential ($\pm 100 \text{ mV}$ sine wave, 10^{-1} – 10^4 Hz , 10 points/decade).

The morphology of Al and Al-Mg alloy with and without ECAP and the morphology of pitting corrosion were observed by SEM and EPMA.

3. Results and Discussion

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

Figure 2 shows the effect of ECAP on the polarization curve of Al and Al-Mg alloy. The anodic current densities rapidly increased at certain potentials when the anode potentials were shifted from their corrosion potential to the

noble direction. This rapid increase in current density is caused by initiation of pitting corrosion. The pitting corrosion potentials, at which pitting corrosion is initiated, were evidently shifted to the noble direction by ECAP, indicating improvement in the pitting corrosion resistance by application of ECAP. On the other hand, the corrosion potentials of Al and Al-Mg alloy were also slightly shifted to the noble direction by ECAP. The corrosion potential of Al was nobler than that of Al-Mg alloy and the current density needed to initiate pitting corrosion was smaller in Al-Mg alloy than in Al. These results indicate that the pitting corrosion resistance of Al is better than Al-Mg alloy.

Figure 3 shows the time-dependence of the anodic current density of Al and Al-Mg alloy while kept at constant potentials of respectively 0.2 V and 0 V to be nobler than their pitting corrosion potentials. The anodic current densities of Al and Al-Mg alloy increased sharply after certain periods of time due to the initiation of pitting corrosion. The time required before initiating pitting corrosion of Al and Al-Mg alloy was longer with ECAP than without. Further, the anodic current densities of pitting corrosion were smaller with ECAP than without.

3.2 Observation of pitting corrosion area

Figure 4 shows EPMA images of Al produced with ECAP. The back electron image (a) reveals the existence of second-phase precipitates, shown by the arrow in Fig. 4. It was found from the characteristic X-ray images of Al(b), Fe(c) and Si(d) that these precipitates included Fe but no Si. Al without ECAP also showed the same trend as Al with ECAP. It is well known that Fe-Al intermetallic compounds precipitate in Al

Fig. 4 EPMA images of Al with ECAP.

containing trace amounts of Fe.¹²⁾ The precipitates observed in Fig. 4 therefore appear to be Fe-Al intermetallic compounds such as Al_3Fe and Al_6Fe . On the other hand, the precipitates in Al-Mg alloy included Si or Fe, indicating the presence of trace Si and Fe-Al intermetallic compounds.

The surfaces of Al and Al-Mg alloys after immersion in the solution containing 0.6 mol/L of NaCl for 36 hours were analyzed by SEM and EDX. Figure 5 shows the SEM images and EDX spectra. Pits several micrometers in size were

Fig. 5 SEM images and EDX spectra of Al after dipping in 0.6 mol-L⁻¹ of NaCl solution for 36 h.

Fig. 6 SEM images and EDX spectra of Al-Mg alloy after dipping in $0.6 \text{ mol} \cdot \text{L}^{-1}$ of NaCl solution for 36 h.

Fig. 7 Morphology of Al after anodic oxidation for 5 min at 0.2 V nobler than the pitting corrosion potential.

observed around the precipitates, shown with arrows in Fig. 5(a) and (c), irrespective of having undergone the ECAP process or not, indicating the initiation of pitting corrosion. EDX spectra (b) and (d) at areas marked with arrows in Fig. 5(a) and (c) show the presence of Fe, suggesting that

these precipitates are Fe-Al intermetallic compounds. Since Fe-Al intermetallic compounds are nobler than the Al matrix,²⁾ pitting corrosion of Al appears to occur by forming a local-action cell in which an Fe-Al intermetallic compound acts as the cathode.

Fig. 8 Effect of ECAP on the morphology of Al and Al-Mg alloy.

Fig. 9 Time-dependence of corrosion potential of Al (a) and Al-Mg alloy (b) in a solution containing $0.1 \text{ mol} \cdot \text{L}^{-1}$ of Na_2SO_4 and 300 ppm of Cl^- at 25°C .

Pits several micrometers in size were also observed around precipitates in Al-Mg alloy irrespective of having undergone the ECAP process or not, as shown in Fig. 6. It was found from EDX spectra (b) and (d) at areas marked with arrows in Fig. 6(a) and (c) that the precipitate in Al-Mg alloy was trace Si. In Al-Mg alloy, precipitation of Fe-Al intermetallic compounds was also observed, but the pitting corrosion occurred mainly around Si precipitates. The immersion potentials of Si and FeAl_3 in the solution containing 0.9 mol/L of NaCl at 298 K were respectively reported to be -0.26 V and -0.56 V ,¹³⁾ showing that the difference in potential between the precipitate and Al matrix was greater in Si than in FeAl_3 . Local-action cells were therefore more easily to form around Si than around FeAl_3 , resulting in more intensive pitting corrosion around Si.

Figure 7 shows the morphology of Al after anodic reaction for 5 min at 0.2 V nobler than the pitting corrosion potential in a solution containing 0.1 mol/L of Na_2SO_4 and 8.46 mmol/L of NaCl. Crystallographic pits $100\text{--}200 \mu\text{m}$ in size were observed in the both Al produced with and without ECAP, as shown in Fig. 7(a) and (c). As can be seen from the enlarged pitting areas in Fig. 7(b) and (d), since the grain size of Al greatly decreased with ECAP, the crystals in the pitting area were more compact with ECAP than without.

3.3 Mechanism of improvement of pitting corrosion resistance with ECAP

3.3.1 Decrease in size of the second-phase precipitates

Figure 8 shows the morphology of Al and Al-Mg alloy with and without ECAP. The small precipitates in Fig. 8 were

Fig. 10 Time-dependence of the anode potential of Al (a) and Al-Mg alloy (b) at $1 \text{ A} \cdot \text{m}^{-2}$ in a solution containing $0.5 \text{ mol} \cdot \text{L}^{-1}$ of H_3BO_3 and $0.05 \text{ mol} \cdot \text{L}^{-1}$ of $\text{Na}_2\text{B}_4\text{O}_7$.

Fe-Al intermetallic compounds and Si. The precipitates were present, irrespective of having undergone the ECAP process or not; however, the size of the precipitates in Al and Al-Mg alloy was greatly decreased by ECAP. It is well known that second-phase precipitates can be broken up by the ECAP process,^{7,8)} as was also found in this study. Since the precipitates of impurities act as cathodes for the Al matrix, the precipitates nucleate the pitting corrosion of Al. Pitting corrosion is less likely to occur with a decrease in the size of the precipitate, that is, with a decrease in cathode area. It has been reported from electron microscope observations that multiple pitting corrosion occurred 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⁾ Pits readily grow around large precipitates at the initial stage and continue to grow to become macro pits. The improvement of pitting corrosion resistance with ECAP can thus be partially ascribed to a decrease in the size of the precipitates.

3.3.2 Increment in rate of formation of Al oxide films

Figure 9 shows the time-dependence of the corrosion potential of Al and Al-Mg alloy in a solution containing 0.1 mol/L of Na_2SO_4 and 300 ppm of Cl^- at 25°C . All the corrosion potentials shifted in the noble direction with increased time. This can be ascribed to the Al oxide films that form naturally in the solution. The corrosion potentials of Al and Al-Mg alloy shifted to the noble direction more rapidly with ECAP than without, suggesting that the rate of formation of Al oxide film increased with ECAP. 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.^{1,2)} The ECAP process markedly increases the number of grain boundaries and the dislocation density in Al. The oxidation rate of Al appears to increase as a result of the increase in grain boundary and dislocation density caused by ECAP. It appears that a more rapid shift to the noble direction of the corrosion potential of Al and Al-Mg alloy produced with ECAP is caused by an increase in the rate of formation of Al oxide films. In the discussion described

above, the average magnitude of the oxidation rate of Al over the Al surface is taken into consideration, because it was estimated by the corrosion potential. Since pitting corrosion occurred around the precipitates, it is necessary to investigate the rate of formation of Al oxide films immediately around the precipitates. However, in this study, it was assumed that the oxidation rate of Al around the precipitates was almost identical to the average of that of the entire Al surface.

Since the naturally formed Al oxide films are of the barrier type, the anode potentials were measured during galvanostatic electrolysis in a neutral solution containing a boric salt to form a barrier-type oxide film. Figure 10 shows the time-dependence of anode potentials of Al and Al-Mg alloy at 1 A/m^2 in a solution containing 0.5 mol/L of H_3BO_3 and 0.05 mol/L of $\text{Na}_2\text{B}_4\text{O}_7$. The anode potentials of Al and Al-Mg alloy shifted to the noble direction with increased duration of electrolysis, and the shift was faster with ECAP than without. The shift of the anodic potential corresponds to the rate of formation of Al oxide films. Therefore, it was apparent that the barrier type of Al oxide film was formed more quickly with ECAP than without in a neutral solution. These results fully correspond to the time-dependence of the corrosion potentials in Na_2SO_4 solution containing Cl^- shown in Fig. 9. As discussed above, it can be assumed that the increment in rate of formation of Al oxide films, and therefore the thickness of the Al oxide film, also contributes to the improvement of pitting corrosion resistance of Al and Al-Mg alloy with ECAP.

To evaluate the polarization resistance for the corrosion reaction of Al and Al-Mg alloy, the AC impedance was measured at the corrosion potential in a solution containing 0.1 mol/L of Na_2SO_4 and 300 ppm of Cl^- . Figure 11 shows Cole-Cole plots for Al and Al-Mg alloy measured after immersion in the solution for an hour. The diameters of the Cole-Cole plots of Al and Al-Mg alloy increased with ECAP, indicating that polarization resistance to the corrosion reaction increased with ECAP. The increase in polarization resistance with ECAP can be ascribed to the increase in oxidation rate of Al.

Fig. 11 Effect of ECAP on the Cole-Cole plots of Al (a) and Al-Mg alloy (b).

4. Conclusion

The effect of reducing the grain size by ECAP on the pitting corrosion resistance of Al and Al-Mg alloy was investigated using electrochemical techniques. The potentials for pitting corrosion of Al and Al-Mg alloy were clearly shifted to the noble direction by ECAP, leading to improvement in pitting corrosion resistance. Al and Al-Mg alloy contained such precipitates as Al-Fe intermetallic compounds and trace quantities of Si, around which pitting corrosion occurred. ECAP pulverized these precipitates. It is evident from the time-dependence of corrosion potential and the polarization resistance for corrosion reaction that the rate of formation of Al oxide films increased as a result of the ECAP process. Therefore, it was concluded that the improvement of pitting corrosion resistance of Al and Al-Mg alloy with ECAP was caused by both decreasing the size of precipitates which acted as cathodes during corrosion and increasing the oxidation rate of Al.

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