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ORIGINAL PAPER

Effects of severe plastic deformation on the corrosion behavior of aluminum alloys

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Abstract Effects of severe plastic deformation on the corrosion behaviors of Al alloys containing precipitates have been investigated. Al and its alloys were severely deformed by equal-channel angular pressing (ECAP) processes and the corrosion behaviors of the Al alloys were evaluated by means of potentiodynamic polarization in a neutral buffer solution containing 0.002 M chloride ion. Introduction of huge plastic deformation to both of Al-5.4 wt% Ni and Al-5 wt% Cu alloys increased pitting potential. In contrast, ECAP treatment of 4N pure Al resulted in a decrease in open circuit potential, slight increase of passive current and shift of pitting potential to the negative direction. The influence of the change in microstructures caused by severe plastic deformation was investigated.

Keywords Al-Ni alloy · Al-Cu alloy · ECAP · Severe plastic deformation · Corrosion

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Introduction

Severe plastic deformation (SPD) methods such as high-pressure torsion (HPT) and equal-channel angular pressing (ECAP) have been utilized to obtain ultrafine-grained (UFG) materials and the extraordinary mechanical and physical properties of the UFG materials superior than that of conventional coarse-grained materials have been studied with scientific interest [1–4]. ECAP method has greater utilities than HPT because of its potential for scale industrial applications [5]. ECAP gives a huge plastic strain to a material by pressing it through a special die without giving concomitant change in the cross-section dimensions of the pressed sample [6]. The application of ECAP technique to process Al, Cu, Mg, Ti and their alloys, etc. and the properties of ECAPed materials such as exceptional strength and ductility, superplasticity, and magnetic properties, *etc.* have been reported [7–13]. However, the investigation of corrosion behavior of ECAPed materials have seldom been reported although the corrosion property of the newly developed materials is of fundamental interest as well as its practical importance for applications. In this study, effect of microstructural change caused by severe plastic deformation introduced by ECAP process on the corrosion behavior of Al-5.4 wt% Ni and Al-5 wt% Cu alloys have been investigated.

Experimental

Specimen preparation by means of ECAP

The principle of ECAP procedure is schematically illustrated in Fig. 1. The die used for the process has two channels equal in cross-section intersecting at an angle of 90 °. The angle, Ψ, which defines the arc of curvature at the outside

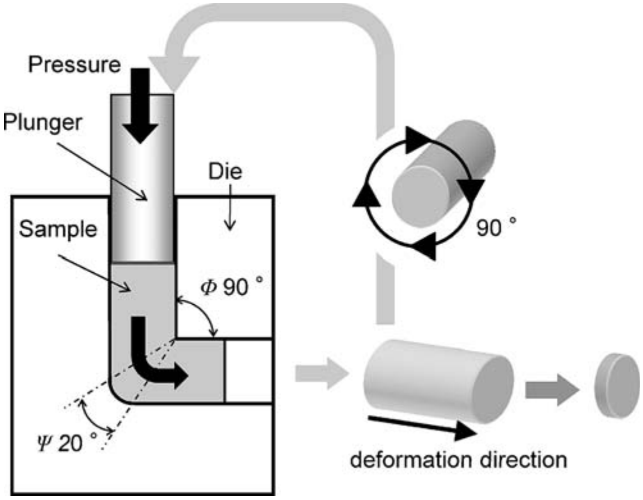

Fig. 1 Schematic drawing of ECAP process through a die

of the elbow is 20°. It was reported that an equivalent strain of about 1.0 was introduced into the processed specimen for each passage through the die [14].

ECAP method can be divided into four distinct processing routes called A, B_A, B_C and C [9]. In route A, the specimen is not rotated between respective pressing through a die; in route B the specimens is rotated to 90° between respective pressing; in route C the sample is rotated to 180° between each pressing. The route B is undertaken either by rotating the sample to 90° in alternate direction between individual pressing, termed route B_A, or by rotating the sample to 90° in the same direction, termed route B_C [16]. Since more homogeneous structure can be obtained through route B_C, route B_C was taken to introduce strain into samples in this study.

An Al-5.4 wt% Ni alloy rod was prepared by casting at 850°C from 99.993 wt% pure Al and an Al-20 wt% Ni ingot, and an Al-5 wt% Cu alloy rod was prepared from the 99.993% pure Al and an industrial ingot of Al-40 wt% Cu. The chemical compositions of the alloys are shown in Table 1. For ECAP processing, rod specimens with a diameter of 10 mm and a length of 60 mm were machined. The ECAP was performed at room temperature with a pressing rate of 0.33 m s^{-1} using MoS_2 as a lubricant. The alloys were subjected to pressing repetitively up to 6 passes.

Table 1 Chemical composition (wt%) of Al–Ni and Al–Cu alloys used in this study

Elemens	Ni	Cu	Si	Fe	O	Others	Al
Al-Ni alloy	5.38	–	0.012	0.019	0.007	–	Bal.
Al-Cu alloy	–	4.95	0.015	0.063	–	0.1	Bal.

Electrochemical measurements and surface observations

ECAPed rods were sliced into specimens with thickness of 1 mm and the specimen surface was finished with SiC paper and buff with alumina polisher.

Potentiodynamic polarization was carried out in a neutral buffer solution consisting of 0.075 M sodium borate ($Na_2B_40_7$) and 0.3 M boric acid (H_3BO_3) with 0.002 M NaCl (pH 8.3) at room temperature at a scan rate of 0.33 mV s^{-1} after open circuit immersion for 20 min. A Pt electrode was used as a counter electrode and a saturated calomel electrode (SCE) as a reference.

Before and after polarization measurements, the surface of all specimens were cleaned using acetone in an ultrasonic cleaner and dried in air.

A JEOL JSM-5400 scanning electron microscope (SEM) was used to observe the sample surfaces before and after polarization tests.

Results and discussion

Potentiodynamic polarization of Al and its alloys

Potentiodynamic polarization tests of 4N pure Al with and without ECAP processing were carried out in a neutral buffer solution with 0.002 M NaCl. In Fig. 2, potentiodynamic polarization curves of Al ECAPed by route B_C with different number of passes are compared. The open circuit potential of Al without ECAP is around −0.15 V (SHE), and the Al sample is spontaneously passive in the solution. At the potential around +0.15 V or higher, the Al sample starts to show spikes corresponding to initiation and repassivation of pitting. Since the chloride concentration in the solution used in this study is relatively low, the rise of pitting current is less significant as that in solution with

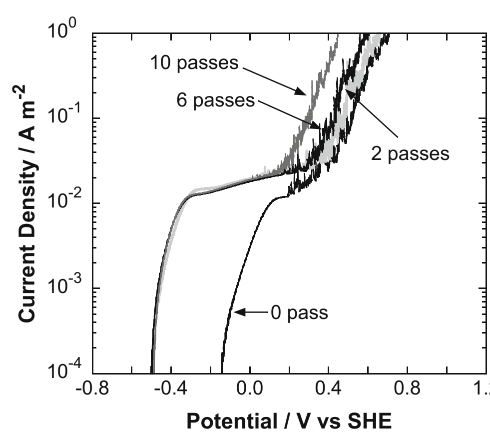

Fig. 2 Potentiodynamic polarization curves of Al with and without ECAP in a borate–boric acid buffer solution with 0.002 M Cl^-. The potential scan rate, dE/dt, is 0.33 mV s^{-1}

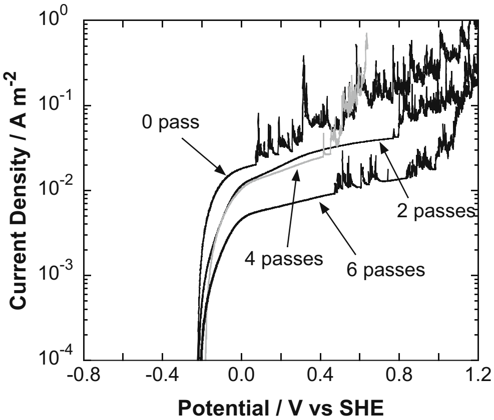

Fig. 3 Potentiodynamic polarization curves of Al-5.4 wt%Ni alloy with and without ECAP in a borate–boric acid buffer solution with 0.002 M Cl^-. The potential scan rate, dE/dt, is 0.33 mV s^{-1}

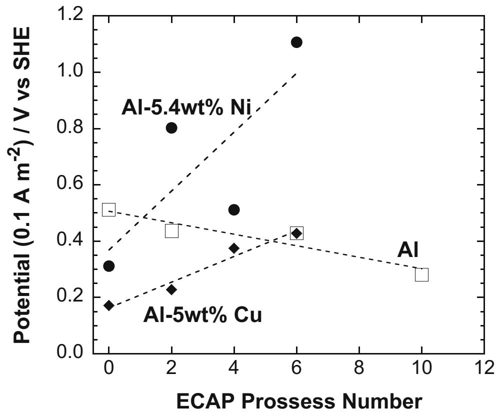

Fig. 5 The potential where the current density reaches to 0.1 A m^{-2} in the potentiodynamic polarization curves of Al, the Al–Ni and Al–Cu alloys with/without ECAP

higher chloride concentration. The pressing of Al with ECAP resulted in a remarkable decrease in the open circuit potential. The potentiodynamic polarization curves for ECAPed Al with different ECAP passes are almost the same to each other and they show slightly higher passive current densities than Al without ECAP. Furthermore, the potential where current spikes start to appear for ECAPed Al showed no obvious change with ECAP passes and the potential is slightly lower than the Al without ECAP. Thus, it is clearly indicated that the corrosion resistance of the pure Al sample is deteriorated by ECAP. It is apparent that huge plastic strain is introduced into the Al sample by ECAP and dislocations and grain boundaries are generated in the α-Al matrix. The introduced dislocations and grain boundaries can improve the mechanical properties such as hardness, tensile strength, etc., but the introduction of them to Al gives rise to a deterioration of the corrosion resistance of Al.

Anodic polarization curves of Al-5.4 wt% Ni alloy with and without ECAP are compared in Fig. 3. In contrast to Al, deformation by ECAP process resulted in an obvious decrease in the passive current density. The observed current spikes can be regarded as initiation and repassivation of pits and the fluctuation of current of Al–Ni alloy is more significant than that of Al. On the other hand, the increase of pitting current with potential of the Al–Ni alloy is slower than that of Al. The fluctuation of current associated with initiation and repassivation of pitting seems to be due to the heterogeneous microstructure of the Al-Ni alloy as it will be discussed later. It is difficult to define pitting potential clearly from the potentiodynamic polarization curves because of the unstable increase in current. Assuming that the lowest potential where the current spike appears is the pitting potential, the pitting potential is shifted remarkably to the positive direction by ECAP. Thus, introducing huge deformation on the Al–Ni alloy can improve its corrosion resistance.

Figure 4 shows potentiodynamic polarization curves of Al-5 wt% Cu alloy with/without ECAP process in the neutral buffer solution with 0.002 M chloride ion. The Al–Cu alloy is spontaneously passive as Al and the Al–Ni alloy and shows pitting at around 0.25 V vs SHE. With increase of the number of ECAP passes, the passive current density

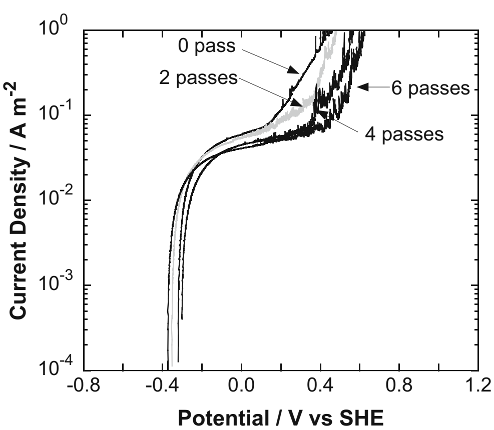

Fig. 4 Potentiodynamic polarization curves of Al-5 wt%Cu alloy with and without ECAP in a borate-boric acid buffer solution with 0.002 M Cl^-. The potential scan rate, dE/dt, is 0.33 mV s^{-1}

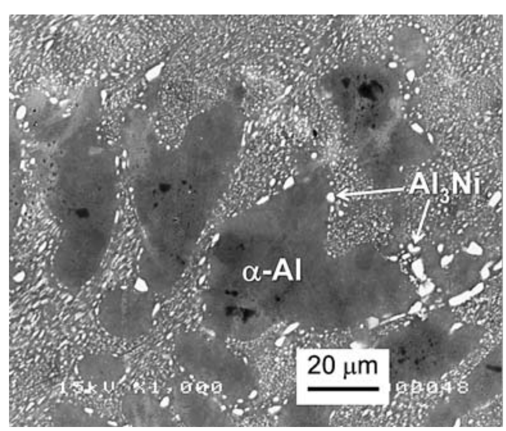

Fig. 6 SEM image of Al-5.4 wt% Ni alloy without ECAP

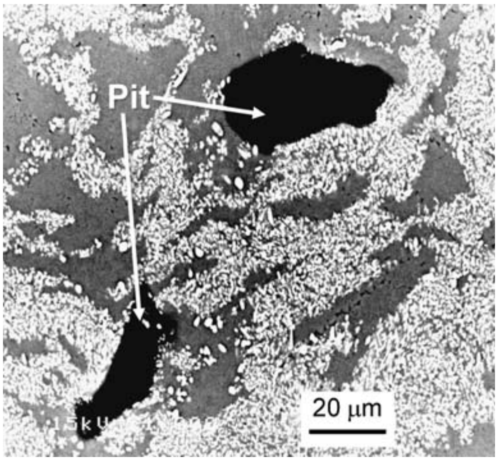

Fig. 7 SEM image of Al-5.4 wt% Ni alloy without ECAP after anodic polarization in a borate–boric acid buffer solution with 0.002 M Cl^-

decreases slightly and the pitting potential increases indicating that the ECAP process improves corrosion resistance of the Al-Cu alloy.

Since it is difficult to define pitting potential because of the unstable current increase, the potential where the current density reaches to 0.1 A m^{-2} was taken from the potentiodynamic polarization curves for Al, Al–Ni and Al–Cu alloys as an parameter to evaluate the corrosion resistance. The potentials obtained are summarized in Fig. 5. The potential at 0.1 A m^{-2} of Al decreases with ECAP process while the potentials of Al–Ni and Al–Cu alloys tend to increase with ECAP process. Consequently, ECAP processing on the Al–Ni and the Al–Cu alloys is beneficial to improve the corrosion resistance of the Al–Ni and Al–Cu alloys.

Surface observation of Al alloys

An SEM image of as-cast Al-5.4 wt% Ni alloy is shown in Fig. 6. The large particle with the size of tens of micrometers is a α-Al phase and the small and white particles are Al_3Ni phase, and the α-Al/Al_3Ni eutectic region is surrounding the α-Al phase [17]. The surface of Al–Ni alloy without ECAP observed after potentiodynamic polarization up to +0.44 V vs SHE is shown in Fig. 7. Some large pits whose sizes are about 40 μm are seen. It was found that the corrosion pits are located preferentially in α-Al crystal regions. This suggests that the large α-Al phase region is less resistant to pitting than α-Al/Al_3Ni eutectic region.

SEM images taken after polarization of the Al–Ni alloy deformed by ECAP is shown in Fig. 8. In the specimen ECAPed 2 passes, the size of the α-Al phase is shrunk by the severe plastic deformation and the area of the α-Al/Al_3Ni eutectic region is increased. Some pits are found in the region of α-Al crystals. Further deformation with six passes of ECAP resulted in a more homogeneous distribution of the α-Al/Al_3Ni eutectic region. Fewer pits are found in the area of a shear band. This shear banding may be associated with a large α-Al crystal region because of lower strength in α-Al crystal region than α-Al/Al_3Ni eutectic region. Chuang et al. reported that the pitting resistance of AA 1050 alloy was improved with increase in ECAP pass number [18]. They found that Si-containing impurities played an important role in pit initiation or pit propagation and the refinement of the impurities resulted in an increase of pitting potential in potentiodynamic polarization test and an increase in polarization resistance measured by means of EIS test after forming pitting. In the case of Al–Ni alloy deformed by ECAP in this study, it is considered that pitting is initiated in the relatively large α-Al crystal region and α-Al/Al_3Ni eutectic region may prevent the initiation and propagation of pitting. According to the huge share strain introduced in to the sample with ECAP process, the α-Al/Al_3Ni eutectic region and α-Al crystal region are mixed together. As a result, the α-Al crystal region shrinks with ECAP passes and more homogeneous microstructure with more uniform distribution of α-Al/Al_3Ni particles is obtained. Despite of the fact that the huge plastic deformation on Al gave rise to decline of its corrosion resistance, the corrosion resistance of the Al–Ni alloy is improved. Therefore, the improvement of corrosion resistance of the Al–Ni alloy can be attributable to this microstructural change by ECAP.

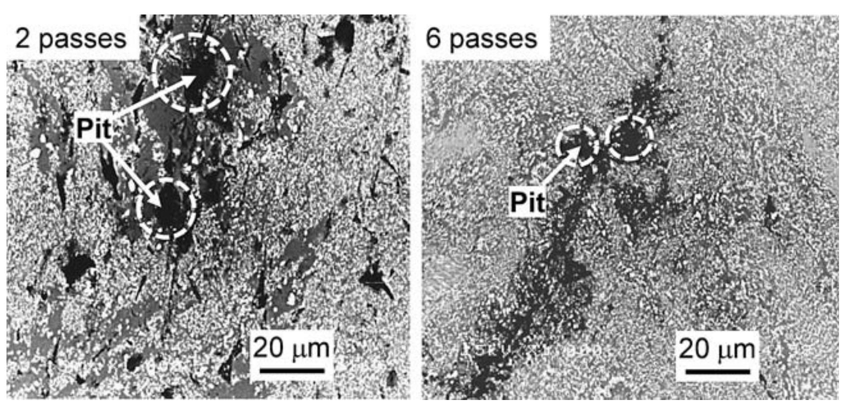

Fig. 8 SEM images of Al-5.4 wt% Ni alloy ECAPed 2 and 6 passes after anodic polarization in a borate–boric acid buffer solution with 0.002 M Cl^-. Typical pits are surrounded by *dotted circles*

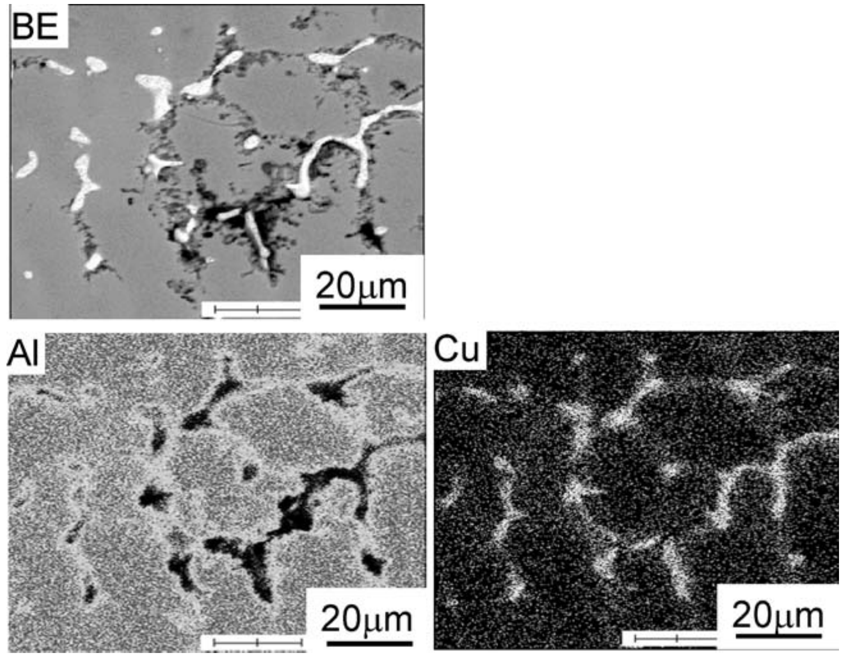

Fig. 9 EDX mapping image of Al-5 wt% Cu alloy without ECAP after anodic polarization in a borate-boric acid buffer solution with 0.002 M Cl^-

As shown before, the potentiodynamic polarization curves of Al-Ni alloy show fluctuation of the current probably due to initiation and repassivation of pitting and the pitting current increase is unstable. The fluctuation of current seems to be due to the pit initiation in α-Al crystal and prevention of grows by α-Al/Al_3Ni eutectic region.

Figure 9 shows EDX mapping image of Al-5 wt% Cu alloy after pit formation by anodic polarization. Pits are observed in the surroundings of θ phase where Cu concentration is lower than that in Al matrix [19]. It is generally agreed that the microstructure of an aged Al-4% Cu alloy has a three-phase system consisting of copper-

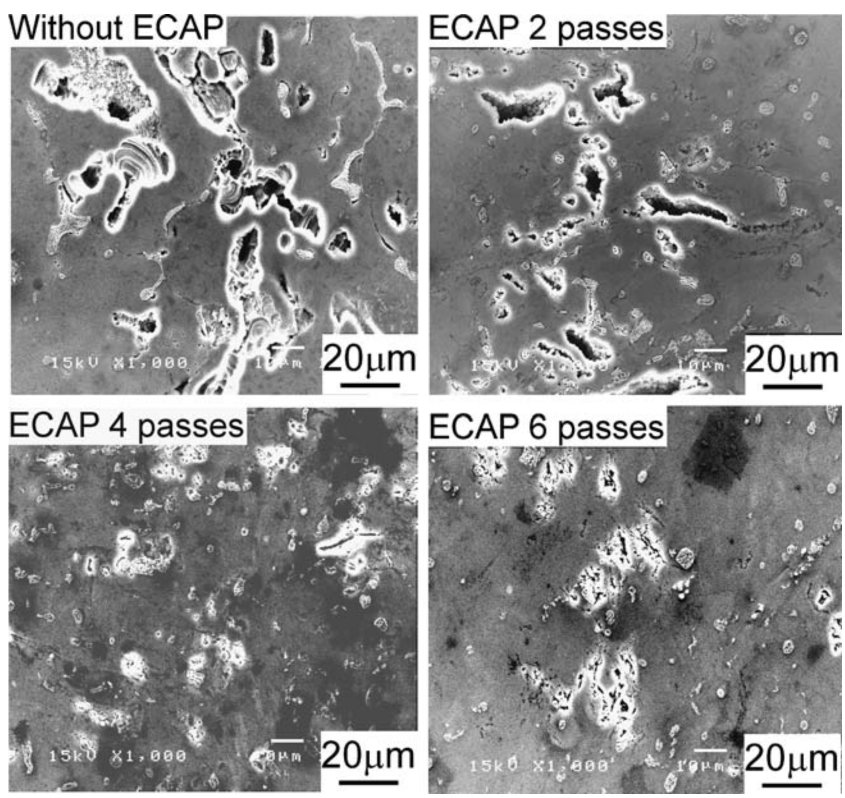

Fig. 10 SEM images of Al-5 wt% Cu alloy ECAPed 0, 2, 4, 6 passes after anodic polarization in a borate–boric acid buffer solution with 0.002 M Cl^-

depleted zone along the grain boundaries (phase I), the grain bodies (phase II) and the intermetallic Al_2Cu (phase III, θ phase) In the generally accepted mechanism of intergranular corrosion of the alloys the phase I acts as the anode whilst the phases II and III act as cathodes [19]. It is considered that the Cu depleted zone is susceptible to pitting. As can be seen in Fig. 9, the surroundings of the θ phase are preferentially attacked.

Figure 10 shows SEM images of the Al-5 wt% Cu alloy deformed by ECAP after pitting. The sample experienced ECAP lost net-shape Al_2Cu particles and the size of Al_2Cu particles is obviously smaller than that in the Al–Cu alloy without ECAP. The size of Al_2Cu particles is reduced with the repetition of ECAP passes. On top of that the total area of Al_2Cu particles is reduced with ECAP passes. Murayama et al. investigated the microstructural changes of an aged Al-1.7 wt% Cu alloy deformed by ECAP and found that supersaturated solid solution was generated by ECAP and equiaxed θ phase grains precipitated at grain boundaries by re-aging treatment [20]. The reduction of total area of θ phase in this study can be attributed to the dissolving Cu atoms to the α-Al matrix. The refining of Al_2Cu particles by huge plastic strain given by ECAP reduces the area of each Al_2Cu particle which act as cathode, and furthermore, the Cu-depleted zone surrounding Al_2Cu particles where pitting preferentially takes place could be diminished by severe plastic deformation. These changes in microstructure seem to be responsible for the improvement of the pitting resistance of Al-Cu alloy by ECAP.

Conclusions

Potentiodynamic polarization measurements were carried out for ECAPed Al-5.4 wt% Ni alloy, Al-5 wt% Cu alloy and Al and the influence of introduction of huge plastic strain on the corrosion behavior was investigated. The huge plastic deformation onto both Al–Ni and Al–Cu alloys improves the corrosion resistance and the pitting potentials of the alloys are increased and the passive current densities are decreased by ECAP passes. The improvement of corrosion resistance of the Al–Ni alloy by ECAP is attributed to the refining α-Al crystals where pit initiation and growth take place preferentially. The introduction of huge plastic deformation is also effective to enhance the corrosion resistance of the Al-Cu alloy by reducing the weak point of Al-Cu alloy that is the Cu-depleted zone surrounding θ phase precipitates.

In contrast, ECAP process on Al gives rise to deterioration of its corrosion resistance presumably because of the introduction of dislocations and grain boundaries by the huge plastic strain. In spite of this inimical influence on the corrosion resistance, ECAP on Al-Ni and Al-Cu alloys can enhance the corrosion resistance of the alloys probably because the beneficial influence of the microstructural change on corrosion resistance is dominant.

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