

Enhancement of Corrosion Resistance of Amorphous Aluminum Alloys by Alloying Additions

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In recent years, it has been found that alloying additions of corrosion-resistant elements such as Ti, Zr, Nb, Ta, Cr, Mo and W to Al are effective in producing amorphous Al alloys with high corrosion resistance(1). In these alloys, however, the open circuit potentials of Al-Ti and Al-Cr alloys are in active region of Ti and Cr, respectively and passivation does not occur for these alloys. In order to improve the corrosion resistance of the alloys, addition of third elements, such as Ni and Mo to Al-Ti and Al-Cr alloys, respectively, and simultaneous addition of Ti and Cr to Al has been performed(2-5). The effect of Mg addition on the corrosion behavior of Al-Ti alloys in chloride-containing neutral solution is also examined expecting enrichment of Ti in the surface film caused by enhancement of activity of alloy and rapid dissolution of unnecessary alloying constituents for passivation(6).

In this paper, the effect of alloying additions on the improvement of corrosion resistance of amorphous Al alloys is reviewed. Furthermore, in-depth structure of passive films analyzed by means of angle-resolved X-ray photoelectron spectroscopy (XPS) is also discussed.

For the preparation of the amorphous alloys, D.C. magnetron sputtering was used. Potentiodynamic and potentiostatic polarization curves were measured in 1 M HCl for Al-Ti-Ni, Al-Cr-Ti and Al-Cr-Mo alloys and 0.075 M Na₂B₄O₇+0.3 M H₃BO₃+0.5 M NaCl buffer solution for Al-Ti-Mg alloys.

After potentiostatic polarization and open circuit immersion, X-ray photoelectron spectra were measured and the composition of the films were determined.

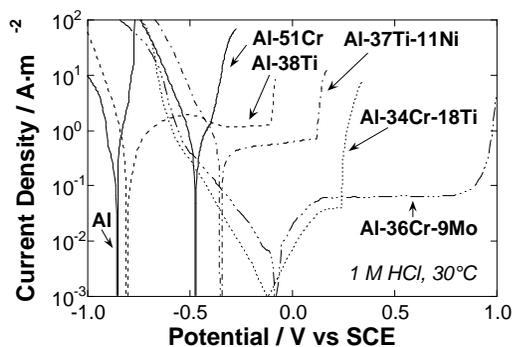


Fig. 1 Potentiodynamic polarization curves of amorphous Al alloys in 1 M HCl.

The comparison of potentiodynamic polarization curves of Al-Ti and Al-Cr binary alloys and the ternary alloys is shown in Fig.1. The Al-Ti alloy shows an active-passive transition and suffers from pitting at -0.2 V(SCE). The addition of Ni increases the cathodic current, and also

decreases the anodic current. Thus, Ni addition leads to spontaneous passivation. The open circuit potential of the Al-Cr binary alloy is in the active region of Cr and the alloy easily suffers from pitting. In contrast, the Al-34Cr-18Ti (at%) alloy is spontaneously passivated and show apparently lower anodic current and higher pitting potential than Al-Ti and Al-Cr alloys. Although Al-Mo alloys show significant increase in anodic current by anodic polarization because of trans-passive dissolution of Mo, the Al-Cr-Mo ternary alloy has wide passive region with low anodic current. Al-36Ti-7Mg alloy shows apparently higher pitting potential than Al-38Ti binary alloy in chloride-containing neutral solution, though an excessive addition of Mg lowers the stability of the passive film(6).

XPS measurements revealed that Ti and Cr were enriched in the passive films formed on the Al-Cr-Mo, Al-Ti-Mg and Al-Ti-Ni alloys. Since Cr and Ti oxyhydroxides are more stable than Al oxyhydroxide in acidic or chloride containing solutions, the enrichment of Cr and Ti in the passive films corresponds to the protective ability of the films. In order to characterize the in-depth distribution of constituents in the passive film, angle-resolved XPS analyses were performed. It was found that Cr and Ti are enriched especially at the outer part of passive films. In the case of Al-Cr-Mo alloy, Cr is slightly deficient at inner part of the passive film. The in-depth profile of cations in the passive films were estimated by using a model expected from the generalized Fick's first law, in which the dissolution rate at the top-most surface of the passive film, and migration and diffusion of cations are determining a concentration gradients(7, 8). Diffusion coefficients of metal cations, $D(\text{Al})$, and $D(\text{Cr})$ in the passive film on the Al-36Cr-9Mo alloy are 4.0×10^{-19} and $6.5 \times 10^{-19} \text{ cm}^2 \text{ s}^{-1}$, respectively. $D(\text{Al})$ and $D(\text{Ti})$ for the Al-Ti-Mg alloy are 3.2×10^{-19} and $2.4 \times 10^{-19} \text{ cm}^2 \text{ s}^{-1}$, and the ratios of mobility, $\mu(\text{Cr})/\mu(\text{Al})$ and $\mu(\text{Ti})/\mu(\text{Al})$ are 1.6 and 0.74, respectively.

The analysis indicates that the migration of Cr cation in the passive film on the Al-36Cr-9Mo alloy is faster than that of Al cation although chromium oxyhydroxide has obviously higher stability than Al oxyhydroxide in 1 M HCl. It can therefore be said that the passive film does not act as a diffusion barrier but the protective ability of the passive film is attributed to the low dissolution rate of the surface layer of the passive film in which the passivating elements are enriched. In other words, the corrosion rate is determined by the stability of the topmost surface of the passive film at the film/solution interface.

References

1. H. Yoshioka et al, *Corrosion Science*, **31**, 349 (1990).
2. E. Akiyama et al, *Materials Science Forum*, **185-188**, 809 (1995).
3. E. Akiyama et al, in *Corrosion, Electrochemistry and Catalysis of Metastable Alloys and Intermetallics*, K. Hashimoto and C. R. Clayton, Eds., p. 26, The Electrochemical Society, Pennington, (1993).
4. E. Akiyama, A. Kawashima, K. Asami and K. Hashimoto, *Corrosion Science*, **38**, 279 (1996).
5. E. Akiyama, A. Kawashima, K. Asami and K. Hashimoto, *Corrosion Science*, **38**, 1281 (1996).
6. E. Akiyama et al, *Corrosion Science*, **34**, 27 (1993).
7. E. Akiyama, A. Kawashima, K. Asami and K. Hashimoto, *Corrosion Science*, **39**, 1351 (1997).
8. E. Akiyama, A. Kawashima, K. Asami and K. Hashimoto, *Corrosion Science*, **38**, 1127 (1996).