

## Characteristics Comparison of Anodic Films Formed on Mg-Al Alloys by Non-chromate Surface Treatment

Seong-Jong Kim<sup>†</sup> · Seok-Ki Jang\* · Jeong-Il Kim\*

(Manuscript : Received DEC 05, 2003 ; Revised JAN 14, 2004)

**Abstract** : The formation mechanism of anodic oxide films on Mg alloys when anodized in NaOH solution, was investigated by focusing on the effects of anodizing potential, Al content, and anodizing time. Pure Mg and Mg-Al alloys were anodized for 10 min at various potentials in NaOH solutions.  $Mg(OH)_2$  was generated by an active dissolution reaction at the surface, and the product was affected by temperature. The intensity ratio of  $Mg(OH)_2$  in the XRD analysis decreased with increasing applied potential, while that of MgO increased. The anti-corrosion properties of anodized specimens at each constant potential were better than those of non-anodized specimens. The specimen anodized at an applied potential of 3 V had the best anti-corrosion property. And the intensity ratio of  $Mg_{17}Al_{12}/Mg$  increased with aluminum content in Mg-Al alloys. During anodizing, the active dissolution reaction occurred preferentially in  $\beta$  phase( $Mg_{17}Al_{12}$ ) until about 4 mins, and then the current density increased radually until 7 mins. The dissolution reaction progressed in a phase(Mg) which not formed the intermetallic compound, which had a lower Al content. In the anodic polarization test of  $0.017 \text{ mol}\cdot\text{dm}^{-3}$  NaCl and  $0.1 \text{ mol}\cdot\text{dm}^{-3}$   $Na_2SO_4$  at 298 K, the current density of Mg-15 mass% Al alloy anodized for 10 mins increased, since the anodic film that forms on the  $\beta$  phase is a non-compacted film. The anodic film on the  $\beta$  phase for 30 mins was a compact film as compared with that for 10 mins.

**Key words** : Anodizing, Mg and Mg-Al alloy, Anti-corrosion property, NaOH solution, Anodic oxide film

### 1. Introduction

Magnesium is easy to recycle because any impurities such as Fe, Ni, etc. are

easily removed. Magnesium has the lowest density, it also has excellent specific strength. Recently, there has been great interest in using magnesium in automobile parts, mobile personal

---

<sup>†</sup> Corresponding Author(Faculty of Marine Engineering System, Mokpo National Maritime University, Korea). E-mail : kmue43aksj@hanmail.net. Tel : 061)240-7309

\* Mokpo National Maritime University

computers, cellular phones, sports, leisure industry, etc. One of the most efficient surface treatments of Mg-Al alloys is coating in the bath containing chromate. However, chromate causes many problems as environmentally toxic.

Furthermore, it is deemed a Class 1 carcinogenic substance in the Pollutant Release and Transfer Register (PRTR)<sup>(1)</sup>. In Europe, the use of lead, mercury, cadmium, and Cr<sup>+6</sup> in electronic products is prohibited. A waste electrical and electronic equipment (WEEE) collection plan was announced in June 2000. The use of Cr<sup>+6</sup> will be gradually phased out, and prohibited by the year 2007<sup>(2)</sup>. In addition, the environmental load value (ELV) order restricting the use of environmental load substances will be implemented incrementally, beginning in July 2003. The use of Cr<sup>+6</sup> by the automobile industry is prohibited after July 2007<sup>(3)</sup>. It was suggested, therefore, that alternatives to chromate baths for Mg alloys<sup>(4-7)</sup> is needed.

This study characterized anodic oxide films, using parameters such as the anodizing potential, anodizing time, and Al content of Mg-Al alloys in 1.0 mol·dm<sup>-3</sup> NaOH solution at 298 K, and the mechanism of anodic oxide film formation. The anodized film was analyzed using electrochemical techniques, scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), and energy dispersive X-ray spectrometry (EDX).

## 2. Experimental section

Mg-Al alloys were prepared by melting

a mixture of pure metals at 1,073 K and allowing the mixture to solidify rapidly. This process was repeated twice to prevent segregation of aluminum. The homogeneous distribution of Al in the alloy was confirmed by ICP-AES (SPS-1500 VR). The purities of the prepared alloy elements were 99.9 mass% for Mg and 99.999 mass% for Al. Alloy electrodes were mounted using epoxy resin, leaving an exposed area of 100 mm<sup>2</sup>, and polished with 0.05- $\mu$ m alumina powder. The specimens were carefully degreased with acetone and water. The constant potential experiment system consisted of a Pt coil as a counter electrode, and an Ag/AgCl sat. KCl reference electrode. The experiments were conducted in 250 ml of 1 mol·dm<sup>-3</sup> NaOH alkaline solution at 298 K. The distance between the working and counter electrodes was approximately 50 mm. The solution was stirred during all of the experiments. The Mg alloys were anodized at constant potentials of 3, 10, 40 and 80 V. The anodic polarization curves of specimens anodized at various potentials were measured in the solution containing 0.017 mol·dm<sup>-3</sup> NaCl and 0.1 mol·dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub> at 298 K at the scan rate of 1 mVs<sup>-1</sup>, in order to characterize the corrosion resistance of anodized films. And the anodized films were also evaluated using SEM, XRD and EDX.

## 3. Results and discussion

First, XRD patterns and relative intensity of Mg<sub>17</sub>Al<sub>12</sub> peak at the surface with Al contents of Mg-Al alloys was

examined. Fig. 1(a) shows typical XRD patterns of Mg-Al alloys containing 1.5, 3, 7 and 9 mass% Al before anodizing. Magnesium and  $Mg_{17}Al_{12}$  were clearly detected in the XRD results.  $Mg_{17}Al_{12}$  is intermetallic compound of 99.9 mass % Mg and 99.999 mass % Al. This intermetallic compound,  $Mg_{17}Al_{12}$ , is  $\beta$  phase. Mg which not the formed intermetallic compound is  $\alpha$  phase. The highest intensity peaks of Mg and  $Mg_{17}Al_{12}$  in XRD correspond to 36.8 and 43.6, respectively. The relative intensity ratio: R of  $Mg_{17}Al_{12}/Mg$  is defined as the ratio at 43.6 to 36.8. Figure 1(b) shows the change in R in the alloys. The intensity ratio of  $Mg_{17}Al_{12}$  increased with increasing Al content in the Mg-Al alloys.

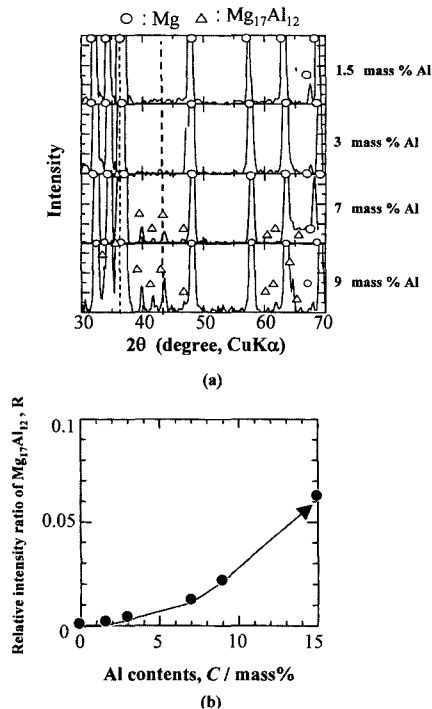


Fig. 1 XRD patterns and relative intensity of  $Mg_{17}Al_{12}$  peak at the surface with Al contents of Mg-Al alloys.

$Mg_{17}Al_{12}$  peaks were barely detected in the Mg-Al alloys containing less than 3 mass% Al. It was not detected the intermetallic compound in 1.5 mass % Al, and 3 mass % Al. However, the intermetallic compound in 7 mass % Al was detected from XRD pattern. Therefore, the results showed Mg-Al alloys containing over 7 mass% Al were composed of  $\alpha$  phase and  $\beta$  phase.

On the other hand, anodic polarization trends were carried out in order to evaluate passivation characteristics and effect of Al contents. Anodic polarization curves were measured at the scan rate of 60 mV/s in 1.0 kmol/m<sup>3</sup> NaOH solution at 298 K for pure magnesium, Mg- 3mass% Al alloy and Mg-9mass% Al alloy containing various amounts of aluminum. Anodic current increases corresponding to the active dissolution reaction were observed for potentials between ca 3 and 7 V for all specimens. The anodic current decreased at potentials over 7 V and a passive state was achieved in all specimens. The anodic current decreased at potentials over 7 V and a passive state was achieved in all specimens. The current density in the passive state decreased with increasing aluminum content<sup>(8)</sup>. When sparking was observed at above 80 V on the anode surface, the current density rose suddenly with an increase in the potential. It has been reported that intense sparking and oxygen evolution accompany the anodizing of magnesium<sup>(9)</sup>. It has been suggested that the current density of a Mg-Al alloy with 9 mass % aluminum is lower than that of one with 3 mass%

aluminum, since the addition of aluminum has a beneficial effect on the passivity and corrosion resistance of magnesium<sup>[10, 11]</sup>. It has been reported that the passivation effect of aluminum ions added to solutions is more remarkable than that of aluminum addition to Mg-Al alloys. When  $\text{AlO}_2^-$  ions are added to alkaline solutions, the current density effectively decreases with increasing  $\text{AlO}_2^-$  content<sup>[12, 13]</sup>.

In addition, the XRD analysis for anodized specimens were executed in order to estimate corrosion resistance at various potentials.

Figure 2 shows the potential,  $E_{\text{corr}}$ , corresponding to the current density of  $1 \text{ A} \cdot \text{m}^{-2}$  for Mg-3 mass% Al and Mg-9 mass% Al alloys. Anodized films were destroyed at current densities above  $2 \text{ A} \cdot \text{m}^{-2}$ . Thus, corrosion potentials were compared the potential at a current density of  $1 \text{ A} \cdot \text{m}^{-2}$ . The anti-corrosion property in Mg-9 mass% Al was better than that in Mg-3

mass% Al alloy. The best anti-corrosion property was obtained with anodizing at 3 V, and the next at 80 V. Therefore, anodizing potentials at which active dissolution reaction occurred, i.e. high current density was used in the subsequent experiments.

The XRD analyzed for 3 mass% aluminum alloy anodized for 600 s in  $1 \text{ kmol} \cdot \text{m}^{-3}$  NaOH solution at 298 K at the potential of 3, 10, 40 and 80 V. The highest intensity peaks of Mg,  $\text{Mg}(\text{OH})_2$  and MgO occurred at around 36.8, 38.0 and 43.0 degrees, respectively.  $\text{Mg}(\text{OH})_2$  was detected at 3 V, while MgO appeared only at 80 V. At applied potential of 80 V, the relative intensity ratio of MgO is highest in 3 mass% aluminum alloy, while that of  $\text{Mg}(\text{OH})_2$  is lowest. The relative intensity ratio of the highest XRD peak for  $\text{Mg}(\text{OH})_2$  or MgO ( $i_0$ ) to that of Mg ( $i_0$ ) are not affected to aluminum contents in Mg-Al alloys. The relative intensity ratios of  $\text{Mg}(\text{OH})_2$  decreased

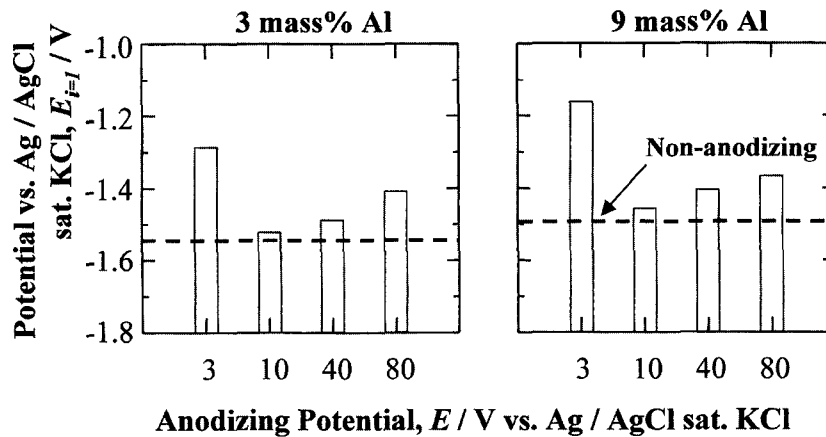


Fig. 2 Comparison of the potential corresponding to the current of  $1 \text{ A} \cdot \text{m}^{-2}$  for Mg-3 mass% Al and Mg-9 mass% Al. Anodic polarization curves in  $0.017 \text{ mol} \cdot \text{dm}^{-3}$  NaCl and  $0.1 \text{ mol} \cdot \text{dm}^{-3}$   $\text{Na}_2\text{SO}_4$  at 298 K after anodized for 10min at each potential in  $1.0 \text{ mol} \cdot \text{dm}^{-3}$  NaOH solution at 298K.

with increasing applied potential, while those of MgO increased, regardless of the aluminum content of Mg-Al alloy. Next, the corrosion behavior of the surface films was examined in Mg-9 mass% Al alloys anodized for 10 min at various potentials. The specimen anodized at the applied potential of 3 V had the best anti-corrosion property because, with an increase in the corrosion current, the potential was largely shifted to noble direction.

The highest current density at current density-potential profiles was 3 V in 1 M-NaOH solution at 298 K for pure magnesium, Mg-3mass% alloy and Mg-9mass% alloy. The reason is that  $\text{Mg}(\text{OH})_2$  was generated by an active dissolution reaction at specimen's surface, resulting in improving corrosion resistance compared with the other potentials. And the current densities with time of alloy specimens anodized for 10 min in  $1.0 \text{ mol} \cdot \text{dm}^{-3}$  NaOH solution at

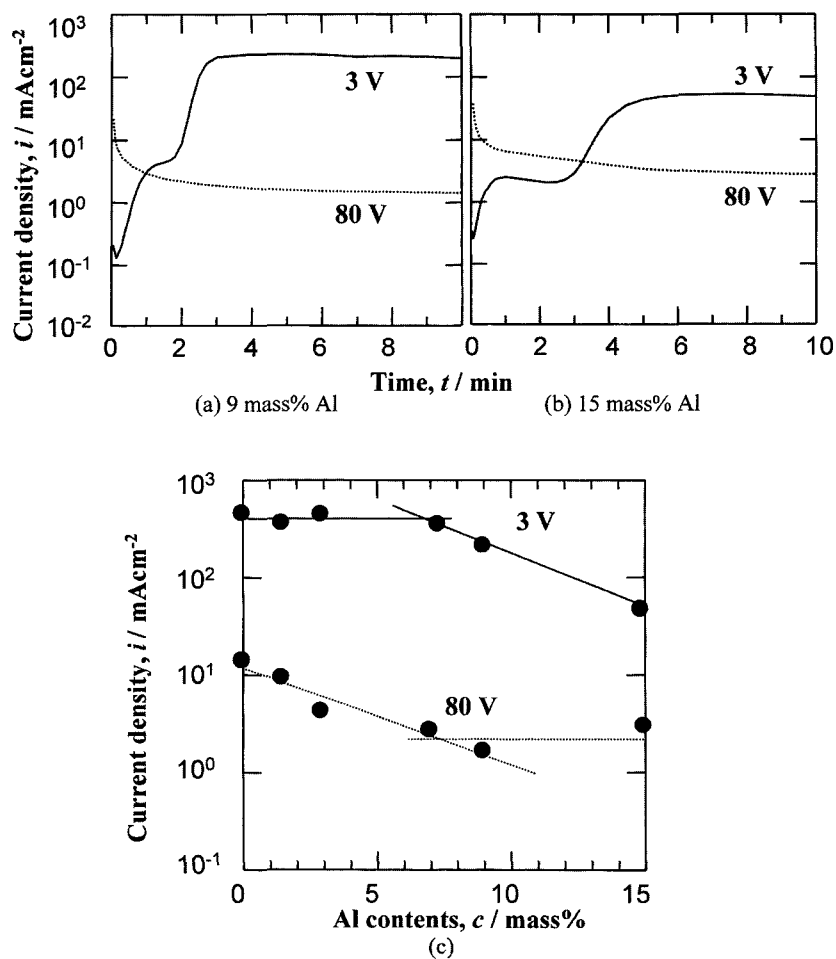
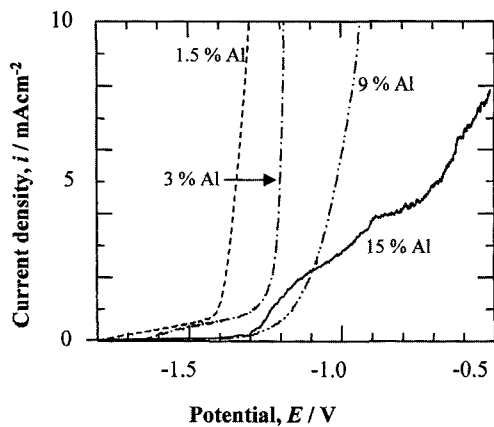


Fig. 3 Comparison of the current density after anodizing for 10 min with Al contents in  $1.0 \text{ mol} \cdot \text{dm}^{-3}$  NaOH solution at 298K.

298 K investigated as shown in Fig. 3. As shown this figure, the stagnation of the current density for 9 mass% Al occurred at a current density of about  $2 \text{ mA}\cdot\text{cm}^{-2}$ . The stagnation time increased with the aluminum content, resulting in a decrease in the current density after 10 min. Moreover, at 80 V, the current density after 10 min decreased until 9 mass% Al, but was slightly higher with 15 mass% Al. And also corrosion resistance increased until 9 mass% Al, but that of 15 mass% Al decreased compared with 9 mass% Al.

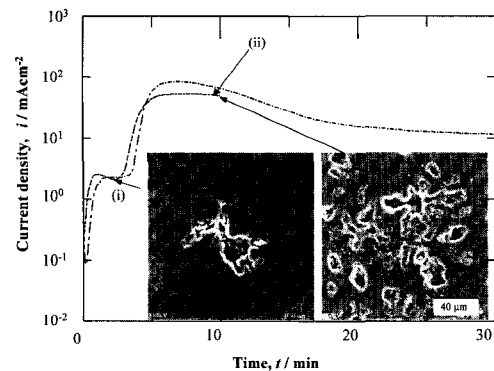


**Fig. 4** Anodic polarization curves in  $0.017 \text{ mol}\cdot\text{dm}^{-3} \text{ NaCl}$  and  $0.1 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}_2\text{SO}_4$  solution at 298K. The specimens were anodized at the applied potential of 3 V with various Al contents in  $1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaOH}$  solution for 10 min at 298K.

Figure 4 shows anodic polarization curves in  $0.017 \text{ mol}\cdot\text{dm}^{-3} \text{ NaCl}$  and  $0.1 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}_2\text{SO}_4$  at 298 K. The specimens were anodized at the applied potential of 3 V with various Al contents in  $1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaOH}$  solution for 10 min at 298 K. The corrosion potential,  $E_{\text{corr}}$ , shifted in the noble direction with increasing

aluminum content, while the polarization curve of Mg-15 mass% Al had a particular shape. The  $E_{\text{corr}}$  of 15 mass% Al was lower than that of 9 mass% Al. The potential of 15 mass% Al for current densities of  $0.15\sim 2.3 \text{ mA}\cdot\text{cm}^{-2}$  was lower than that of 9 mass% Al.

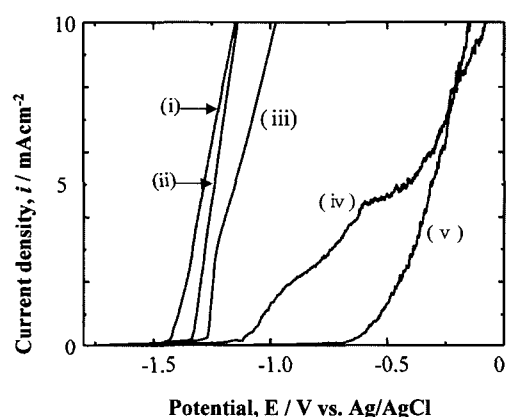
According to kim et al investigation<sup>[5]</sup>, the photographs of the anodized surface show that dissolution of the phase occurred at an applied potential of 3 V regardless of the Al content. The phase in 15 mass% Al took the form of a large hole. Moreover, the two-step current plateau increase was insufficient with anodizing for 10 min. Consequently, Mg-15 mass% Al was anodized for 30 min at 3 V in  $1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaOH}$  at 298 K.



(i) Formation of film on  $\beta$  phase, (ii) Formation of film on  $\alpha$  phase  
**Fig. 5** Effect of anodizing at an applied potential of 3 V in 15 mass % Al in  $1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaOH}$  solution at 298K.

Figure 5 shows the changes in current and surface morphology with time on anodizing at 3 V of 15 mass% Al in  $1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaOH}$  at 298 K. The current density was maximal at an anodizing time of 7 min. Thereafter, the current density gradually diminished and was

about  $10 \text{ mA}\cdot\text{cm}^{-2}$  after 30 min. It seemed that an anodizing film formed via a dissolution reaction on the  $\beta$  phase at  $2 \text{ mA}\cdot\text{cm}^{-2}$  for 1-4 min, as no stagnation of current density with low aluminum content was seen at ca.  $2 \text{ mA}\cdot\text{cm}^{-2}$ , as is seen in pure magnesium. This was ascertained in SEM studies of the surface morphology. It seemed that a film formed on the  $\alpha$  phase at a current density of approximately  $10^2 \text{ mA}\cdot\text{cm}^{-2}$ , because all the specimens were similar.



(i) Non-anodizing, (ii) 3 min, (iii) 5 min, (iv) 10 min, (v) 30 min

**Fig. 6 Anti-corrosion property with anodizing time for 15 mass % Al in  $0.017 \text{ mol}\cdot\text{dm}^{-3}$  NaCl and  $0.1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{Na}_2\text{SO}_4$  solution at 298K. Anodizing was carried out at conditions for non-anodizing, 3, 5, 10, 30 min at 3 V in  $1.0 \text{ mol}\cdot\text{dm}^{-3}$  NaOH solution at 298K.**

Figure 6 shows anti-corrosion property with anodizing time for 15 mass % Al in  $0.017 \text{ mol}\cdot\text{dm}^{-3}$  NaCl and  $0.1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{Na}_2\text{SO}_4$  solution at 298 K. Anodizing was carried out at conditions for non-anodizing, 3, 5, 10, 30 min at 3 V in  $1.0 \text{ mol}\cdot\text{dm}^{-3}$  NaOH solution at 298 K. As compact films did not form on specimens anodized for 10 min, it appears that the

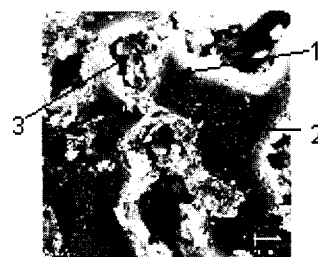
current density increases in the anodic film formed on the  $\alpha$  phase, beginning at around 1.2 V, because the anodic film formed in the phase is a non-compacted film. Subsequently, the current density abruptly increased at a potential of 0.4 V as shown in Fig. 6. When anodized for 30 min, the anodic film on the  $\alpha$  phase was more compact than that at 10 min. Therefore, with anodizing for 30 min, the anodic polarization curve was the same shape as that for specimens anodized at other potentials. In addition, when anodized for more than 30 min, the polarization curves were similar to that for 30 min.



Al Quantity

1 >> 2

Region 1:  $\beta$  phase, Region 2:  $\alpha$  phase



Al Quantity

2 >> 1 > 3

Region 2:  $\beta$  phase, Region 1, and:  $\alpha$  phase

**Fig. 7 Surface morphologies in without(a) and with (b) anodized for 10 min at 3 V in 15 mass % Al in  $1.0 \text{ mol}\cdot\text{dm}^{-3}$  NaOH solution at 298K.**

However, it was not convinced that the  $\alpha$  and  $\beta$  phases are present in Fig. 5. Therefore, EDX analysis was used to verify the presence of the  $\alpha$  and  $\beta$  phases without (a) and with (b) anodization for 10 min at 3 V for 15 mass% Al in 1 mol-dm<sup>-3</sup> NaOH, as shown in Fig. 7. Without anodizing (a), the EDX analysis confirmed the phases in regions (1) and (2). The Al content in region (1) far exceeds that in region (2). This indicated that region (1) is the  $\beta$  phase and region (2) is the  $\alpha$  phase. With anodizing (b), the Al content in regions (1) to (3) was in the order: region (2) >> region (1) > region (3). Over time, the active dissolution reaction during anodizing occurred preferentially at the  $\beta$  phase until about 4 min. Then, the current density gradually increased until 7 min. The dissolution reaction progressed on  $\alpha$  phase, which had a lower Al content.

#### 4. Conclusion

In the anodic polarization experiment, an active dissolution reaction was observed in the potential region from 3~7 V for all specimens. The anti-corrosion properties of anodized specimens were excellent, as compared with those of non-anodized specimens. When Mg-Al alloys were anodized, a Mg(OH)<sub>2</sub> film was primarily seen at an applied potential of 3 V, while a MgO film appeared at an applied potential of 80 V. The intensity ratio of the  $\beta$  phase increased with aluminum content in the Mg-Al alloys. Over time, the active dissolution reaction during anodizing occurred preferentially

on the  $\beta$  phase until about 4 mins. Then, the current density increased gradually with time until 7 mins. After anodizing for 10 mins, the current density increased when the aluminum content was 15 mass%, since the anodic film that forms on the phase is a non-compact film. The anodic film on the  $\alpha$  phase at 30 mins was compact compared with that at 10 mins.

#### References

- [1] K. Suzuki, *Alutopia*, vol. 5, p. 40, 2000.
- [2] The European Parliament and Council, Draft proposal for a direct on the restriction of the use of certain hazardous substances in electrical and electronic equipment, June, 2000.
- [3] N. Kunieda, *107th Meeting of the Surface Finishing Society of Japan*, p. 296, 2003.
- [4] Kim S. J., Okido M., "The electrochemical properties and mechanism of formation of anodic oxide films on Mg-Al alloys", *Bull. Korea Chem. Soc.*, vol. 24, pp. 975-980, 2003.
- [5] Kim S. J., Okido M., Ichino R., Mizutani Y., Tanikawa S., and Hasegawa H., "Formation of anodic films on Mg-Al alloys in NaOH solutions at constant potentials", *Materials Transactions*, vol. 44, p. 1036, 2003.
- [6] Kim S. J., Zhou T., Ichino R., Okido M., Tanikawa S., "Characterization of chemical conversion film that form on Mg-Al alloys in colloidal silica



- solution". *Metals and materials international*, vol. 9, p. 207, 2003.
- [7] Kim S. J., Hara R., Ichino R., Okido M., Wada N., "Characterization of silica film formed by chemical conversion on zinc coated steels", *Materials Transactions*, vol. 44, pp. 782-786, 2003.
- [8] E. F. Emely, *Principle of magnesium technology*, Pergamon press, London, 1966.
- [9] O.Khaselev and J. Yahalon, *Corros. Sci.*, vol. 40, pp. 1149-1160, 1998.
- [10] O. Lunder, J. E. Lein, T. K. Aune and K. Nisancioglu, *Corrosion*, vol. 45, pp. 741-748, 1989.
- [11] G. L. Makar and J. Kruger, *J. Electrochem. Soc.*, vol. 137, pp. 414-421, 1990.
- [12] S. Ono, H. Kijima and N. Masuko, *J. Jpn. Inst. Light. Met.*, vol. 52, pp. 115-121, 2002.
- [13] S. Ono, H. Kijima and N. Masuko, *J. Surf. Finish. Soc. Jpn*, vol. 51, pp. 1168-1169, 2000.