Sealing Effects of Anodic Oxide Films Formed on Mg-Al Alloys

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Abstract−Mg alloys were anodized in alkaline NaOH solutions with various additives as a non-chromate method. Specimen AZ91 was anodized at a potential that produced a strong surface dissolution reaction and generated a large amount of $Mg(OH)_2$. The effect of sealing after anodizing was investigated, focusing on the effects of sealing time, temperature and solution conditions. The current density decreased with increasing $Al(OH)_3$ concentration in 1 M NaOH solution during anodizing; sparking occurred at potentials above 80 V. The best corrosion resistance with anodizing in 1 M NaOH solution occurred at a potential of 4 V, which caused the strongest active dissolution reaction. The sealing effect improved with increasing time and temperature, and corrosion resistance was proportional to the relative ratio of $Mg(OH)_2$. If the oxygen thickness observed by EDX equaled the film thickness, the film formed at 4 V in 1 M NaOH was 10-15 μm thickness. The optimum corrosion resistance in sealing at various solutions after anodizing was 1M-NaOH solution.

Key words: AZ91, Anodizing, NaOH Solution, Sealing, Corrosion Resistance

INTRODUCTION

Magnesium not only has the lowest density, but it also has an excellent specific strength. However, magnesium and Mg-Al alloys have been often surface-treated by anodizing them in alkaline solutions containing additives, such as fluoride and chromium ions, to enhance their corrosion resistance [The institute of Japan magnesium, 2000]. There are many ways to treat the surface of magnesium and its alloys, such as anodizing, painting, electroplating, etc. Anodic oxide film of magnesium alloys generates multi-porous films of several tens of micrometers thickness. One of the most efficient surface treatments is chromate-conversion coating, but this process causes many environmental problems. Furthermore, it was designated a carcinogenesis substance of class 1 by the pollutant release and transfer register (the PRTR). In Europe, uses of lead, mercury, cadmium and Cr^{+6} for the electric electronic product are prohibited. Therefore, the anodizing of Mg alloys in alkaline NaOH solutions with additives has been investigated as a non-chromate method. Previously, the effects of anodizing potential, anodizing time, and Al content in Mg-Al alloys on anodic oxide films have been studied and the mechanism of anodic oxide film formation during anodizing in 1 M NaOH solution at 298 K has been examined [Mizutani et al., 2001, 2002, 2003; Kim et al., 2003; Hwang et al., 2002]. Anodic films are evaluated by comparing the relative intensity of the XRD patterns of films anodized at each applied potential, and the results are detected in the $Mg(OH)_2$ and MgO peaks. The corrosion resistance of $Mg(OH)_2$ is better than that of MgO. The generation of $Mg(OH)_2$ is affected by temperature and surface dissolution reaction. The current density during anodizing decreases with increasing aluminum ion content in NaOH solutions. Moreover, the corrosion resistance is also improved by the addition of aluminum ions during anodizing. An increase in the anodic current corresponding to the active dissolution reaction has been observed at ca. 3 and 7 V for all specimens. The highest $Mg(OH)_2$ peaks are detected at 3 V, which resulted in an active dissolution reaction and produced the best corrosion resistance, regardless of temperature, NaOH concentration, aluminum contents.

In this study, a specimen AZ91 (Al 8.43%, Mn 0.24%, Zn 0.82%, Si 0.04%, Cu 0.02%, Ni 0.01%, Fe 0.003%, Mg Balance) was anodized at potentials that caused a strong surface dissolution reaction and generated large amounts of $Mg(OH)_2$. The effect of sealing after anodizing on AZ91 was examined, focusing on the effects of sealing time, temperature and solution conditions.

EXPERIMENTAL SECTION

AZ91 electrodes were mounted by using epoxy resin, with an exposed area of $100\,mm^2$, and polished with 0.05-μm alumina powder. The electrode surfaces were carefully degreased with water and acetone. The electrochemical system consisted of a Pt coil as a counter electrode and an Ag/AgCl sat. KCl reference electrode. The solution was stirred during anodizing. Mg-Al alloys were anodized in 1 M NaOH containing various $Al(OH)_3$ concentrations. The effects of the various sealing solutions, temperature, and time in distilled water after anodizing at 4 V or 5 V in 1 M NaOH with or without $Al(OH)_3$ were investigated. The surface morphology of the anodized and sealed films was observed by using SEM and EDX. The anodized and sealed films were evaluated from the relative intensities of the XRD patterns. The anodic polarization curves of the anodized and sealed films were measured in Na_2SO_4 solutions containing chloride ions at 298 K at a scan rate of 2 mV/s, and the corrosion resistance was estimated from the corrosion potential.

RESULTS AND DISCUSSION

Anodic polarization curves were measured for AZ91 in 1 M NaOH containing various $Al(OH)_3$ concentrations at 298 K. Fig. 1
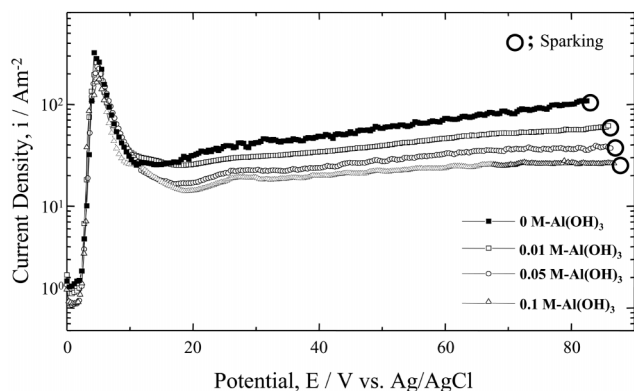
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Fig. 1. The current density/potential profiles at a scan rate of 60 mV/s in 1 M NaOH containing various Al(OH)$_3$ concentrations at 298 K.

shows the current density/potential profiles at a scan rate of 60 mV/s in 1 M NaOH containing various Al(OH)$_3$ concentrations at 298 K. Anodic current equivalent to the active dissolution reaction was increased at the potentials between ca. 3 and 10 V for all specimens. The anodic current decreased at potentials over 10 V and a passive state was achieved for all specimens. The current density in the passive state decreased with increasing Al(OH)$_3$ concentration, while the sparking potential increased with increasing Al(OH)$_3$ concentration. The sparking potentials of 1 M NaOH containing 0, 0.01, 0.05, and 0.1 M Al(OH)$_3$ were 82.44, 85.86, 86.33, and 86.87 V, respectively. Intense sparking was also accompanied by breakdown of the surface film [Khaselev et al., 1998]. The potential at which the maximum current density occurred was 4 V in 1 M NaOH, while it was 5 V in 1 M NaOH containing various Al(OH)$_3$ concentrations. The passivation effect of aluminum ions added to solutions exceeds that of adding aluminum to Mg-Al alloys; when AlO$_2^-$ ions are added to alkaline solutions, the current density effectively decreases with increasing AlO$_2^-$ content [Ono et al., 2000, 2002].

Fig. 2 compares the anodic polarization curves after anodizing for 10 min, at various constant potentials, in 1 M NaOH at 298 K. The corrosio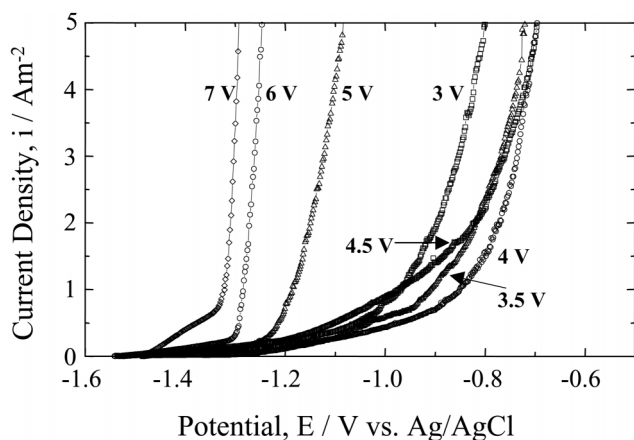n potential was defined as the potential at which the current density reached 1 A/m^2, since the anodic oxide film was not destroyed at a current density of 1 A/m^2, and the corrosion potentials under the various conditions were compared as an indicator of corrosion resistance. The corrosion potentials on anodizing at 3, 3.5, 4, 4.5, 5, 6 and 7 V were −967, −908, −850, −973, −1,183, −1,283 and −1,321 mV, respectively. The best corrosion resistance was seen at a potential of 4 V, at which the strongest active dissolution reaction occurred. According to investigation on formation of anodic films on Mg-Al alloys in NaOH solutions at constant potentials, it was found that the anodic film formed at 3 V had the best corrosion resistance when pure magnesium and Mg-Al alloys were anodized for 600 s at 3, 10, 40 and 80 V. An especially high current density was observed at applied potentials of 3-7 V. In addition, XRD analysis detected Mg, Mg(OH)$_2$ and MgO peaks in the films on the anodized specimens. Mg(OH)$_2$ was generated by an active dissolution reaction with high current density at the specimen surface [Kim et al., 2003].

Therefore, sealing was examined in specimens anodized at 4 V in 1 M NaOH for 10 min.

The effect of temperature during sealing for 30 min in distilled water after anodizing at 4 V for 10 min in 1 M NaOH solution at 298 K is shown in Fig. 3. The corrosion potentials after sealing for 30 min in distilled water at temperatures of 353, 363, and 373 K were −822, −780, and −720 mV, respectively. Increasing the sealing temperature in distilled water increased the corrosion potential. The circles and arrow symbols in SEM photographs mean micropores and microcracks. The surface of non-sealed specimens was
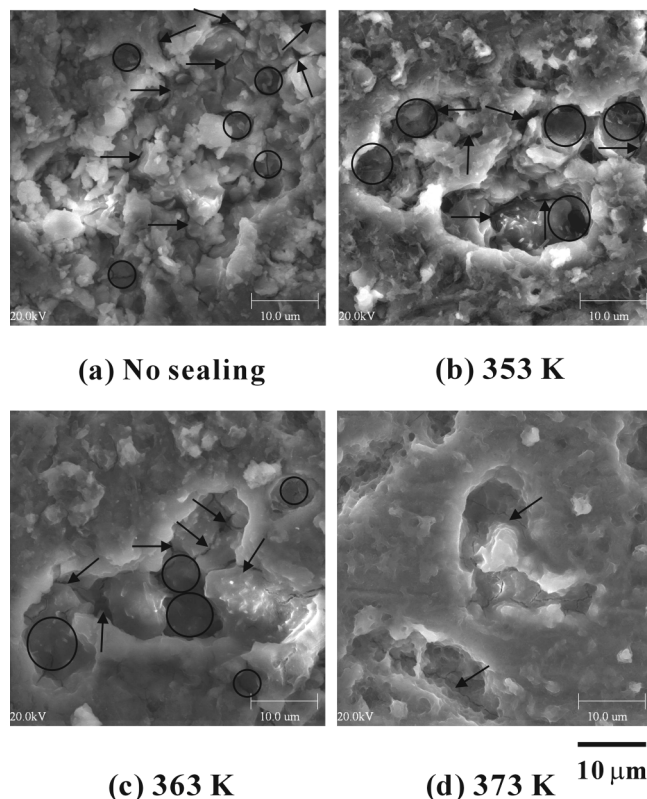

Fig. 2. Comparison of the anodic polarization curves after anodizing for 10 min at various constant potentials in 1 M NaOH at 298 K.

(a) No sealing   (b) 353 K

(c) 363 K   (d) 373 K   10 μm

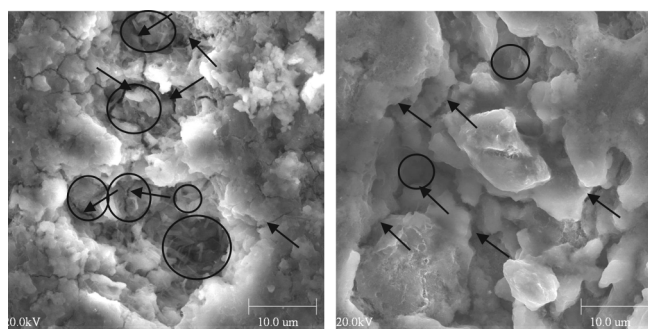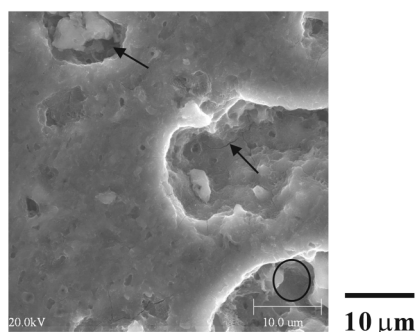**Fig. 3. Effect of temperature during sealing for 30 min in distilled water after anodizing at 4 V for 10 min in 1 M NaOH at 298 K.**

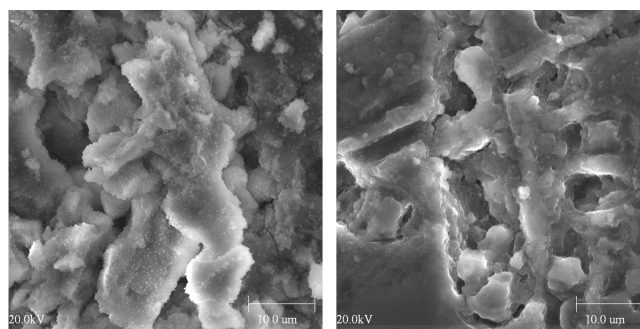**(a) 100 s**   **(b) 20 min**

(c) 60 min

Fig. 4. Effect of immersion time during sealing in distilled water after anodizing at 4 V for 10 min in 1 M NaOH at 298 K.

(a) 1M-NaOH   **(b) 0.1M-Al(OH)$_3$**

(c) 1M-NaOH+0.1M-Al(OH)$_3$

Fig. 5. Effect of sealing solution with sealing for 30 min after anodizing at 4 V for 10 min in 1 M NaOH at 298 K.

rough, containing large micropores and microcracks. The number of micropores and microcracks decreased with increasing water temperature. The reason suggests that the bonding strength of OH⁻ ion with increasing sealing temperature of distilled water is increased. The surface micropores and microcracks disappeared with volume expansion by sealing in distilled water at 373 K, which improved the corrosion resistance. It has been reported that the impedance of anodic oxide films was increased with increasing sealing temperature regardless of the sealing solution used (*i.e.*, distilled, pure, or tap water) in studies of the sealing of anodic oxide films of aluminum [Kawase et al., 1971].

Fig. 4 shows the effect of immersion time during sealing in distilled water after anodizing at 4 V for 10 min in 1 M NaOH at 298 K. The corrosion potential at sealing times of 100 s, 10, 20 and 30 min, and 60 min in distilled water was −822, −777, −725, −720 and −602 mV, respectively. The corrosion potential increased with sealing time. At a sealing time of 100 s, the surface was rough and coarse and many microcracks were seen inside micropores. At 20 min, the surface was smoother than 100 s. Few microcracks were detected at a sealing time of 60 min. It is suggested that the bonding of OH⁻ ion with sealing time is stabilized. The volume of Mg(OH)$_2$ formed in the film is larger than that of Mg. Therefore, the micropores and microcracks in the film were sealed by expansion of Mg(OH)$_2$. According to Koda et al. [1982], the outermost part of the hydrous oxide becomes very resistant to acid dissolution after prolonged hot water treatment. Prolonged sealing results in a dense, isolating boehmite film, which is further resistant to corrosion. It has been reported that the microcracks in anodic oxide films disappear with volume ex-
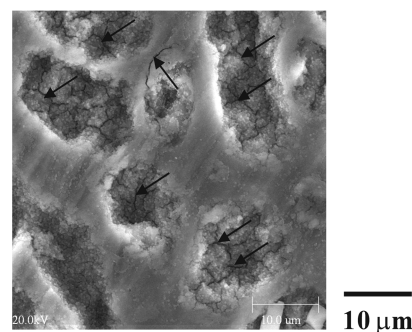
pansion sealing treatment [Hasumi et al., 1980], and that the impedance of anodic oxide films increases with increasing sealing time [Kawase, 1971]. The longer the sealing time, at least up to 30 min to 60 min, the more the fibrous region extends laterally, resulting in more compact cell walls, effectively increasing the diameter of the filled pores [Wood and O'Sullivan, 1969].

After investigating the effect of sealing in distilled water, we looked at the effects of additives on the distilled water. Fig. 5 shows the effect of sealing for 30 min after anodizing at 4 V for 10 min in 1 M NaOH at 298 K. After sealing for 30 min in 1 M NaOH, no micropores and microcracks were observed. The film was thick and compact. The corrosion potential after sealing in 1 M NaOH was −353 mV, while the corrosion potential after anodizing for 60 min was approximately −602 mV. Therefore, sealing in 1 M NaOH after anodizing improved the results markedly as compared with sealing in distilled water. By contrast, the anodic oxide film produced in 1 M NaOH containing 0.1 M Al(OH)$_3$ was compact, with small microcracks. Sealing for 30 min in 0.1 M Al(OH)$_3$ observed scratch on specimens, indicating that 0.1 M Al(OH)$_3$ affects film dissolution.

A comparison of the corrosion potential after anodizing in 1 M NaOH containing various Al(OH)$_3$ concentrations for 10 min at 298 K, showed that the best corrosion resistance appeared at a potential of 5 V, regardless of Al(OH)$_3$ concentration. After anodizing at 5 V, the corrosion potentials using 1 M NaOH containing Al(OH)$_3$ concentrations of 0.01, 0.05 and 0.1 M were −738, −694 and −559 mV, respectively.

The results of sealing these anodized specimens are shown in Fig. 6. The sealing solutions examined were 1 M NaOH, 0.1 M Al(OH)$_3$

and 1 M NaOH plus 0.1 M Al(OH)₃; the corrosion potentials were −178, −1,135 and −333 mV, respectively. Sealing for 30 min in 1 M

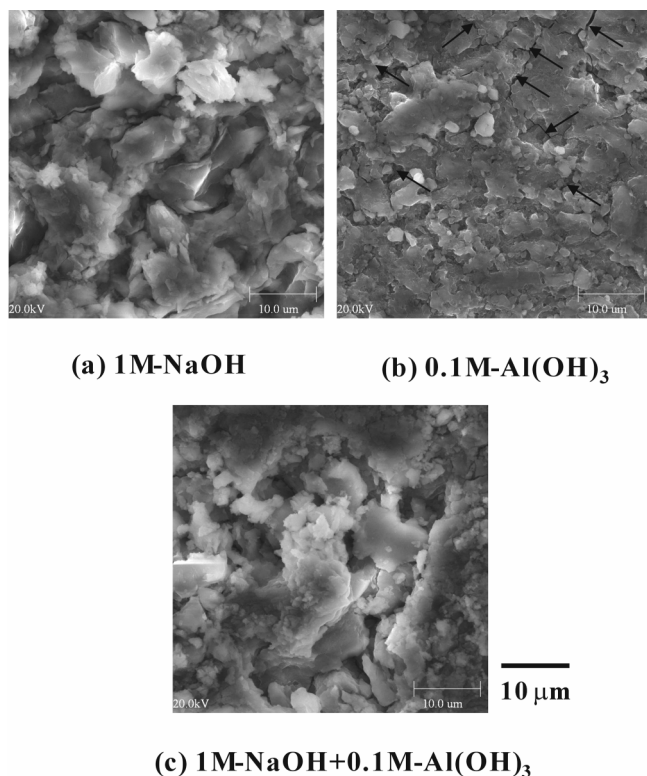**(a) 1M-NaOH**   **(b) 0.1M-Al(OH)₃**

(c) 1M-NaOH+0.1M-Al(OH)₃

Fig. 6. Effect of sealing solution with sealing for 30 min after anodizing at 5 V for 10 min in 1 M NaOH containing 0.1 M Al(OH)₃ at 298 K.

NaOH solution after anodizing at 5 V in 1 M NaOH solution containing 0.1 M Al(OH)₃ resulted in the optimum corrosion resistance, and no microcracks were observed in the sealed specimen. While microcracks were seen in the anodic oxide film produced in 1 M NaOH containing 0.1 M Al(OH)₃, the corrosion potential was −333 mV. Sealing for 30 min in 0.1 M Al(OH)₃ resulted in large microcracks and a corrosion potential of −1,135 mV. Therefore, 0.1 M Al(OH)₃ affects the film dissolution reaction. It is considered that the magnesium hydroxide plays an important part in sealing effects, and then corrosion resistance is improved. The porous anodic oxide films that formed on Al in an oxalic acid solution were hydrated in water at 372.5 K with and without added chromate, phosphate, or nickel acetate [Koda et al., 1985]. The influence of small amounts of different added anions on the sealing effects has been reported [Kawase et al., 1971]. PO_4^{3-} and SiO_3^{2-} have the most detrimental effect on the sealing of anodic oxide films and inhibit the boehmite reaction via strong specific adsorption [Kawase et al., 1971; Murpy, 1967; Altenphol, 1962].

Fig. 7 compares EDX analysis of cross sections without and with sealing after anodizing in NaOH solution containing Al(OH)₃ at 4 V. If the thickness of oxygen observed by EDX equaled the film thickness, the anodic oxide film produced after anodizing at 4 V in 1 M NaOH containing Al(OH)₃ solution at 298 K for 10 min was 10-15 μm thickness. A number of microcracks were observed in this cross section, while sealing for 30 min in distilled water and 1 M NaOH solution containing 0.1 M Al(OH)₃ produced almost no microcracks. The corrosion resistance of β phase is more excellent than that of α phase. Therefore, it was thought that the areas with thicker and thinner magnesium layers were the β and α phase, respectively.

Table 1 compares the relative intensity ratios of Mg(OH)₂ and

O   **Mg**

(a) No sealing

(b) Sealing for 30 min in distilled water at 373K
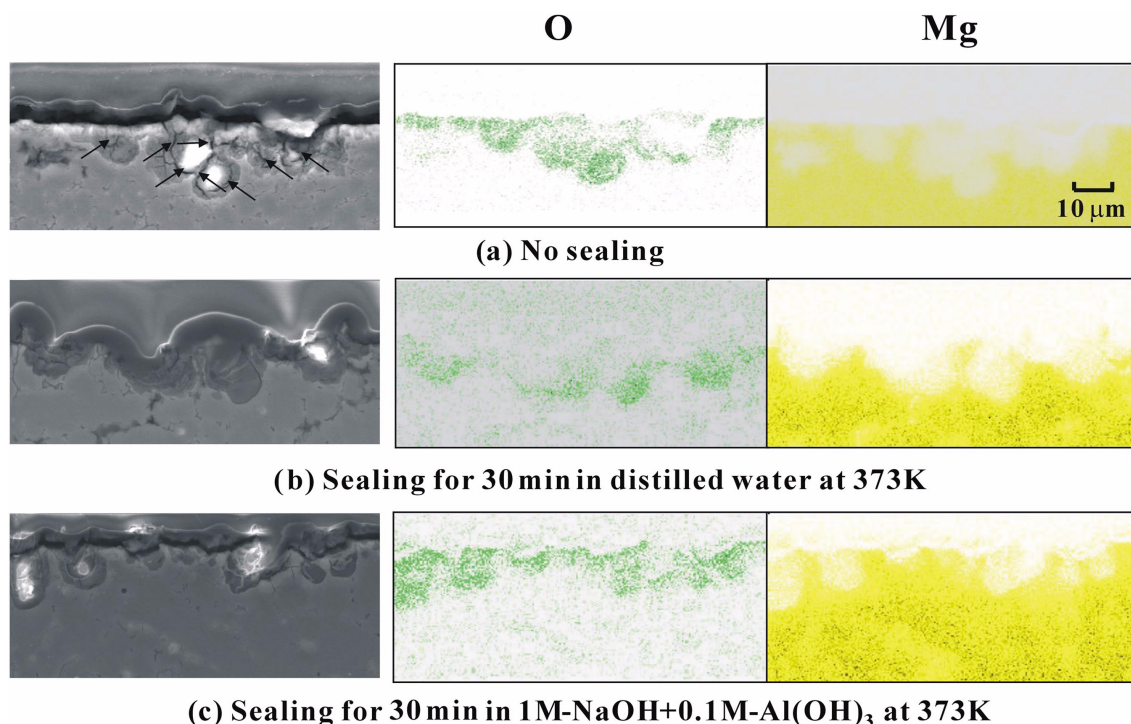
(c) Sealing for 30 min in 1M-NaOH+0.1M-Al(OH)₃ at 373K

Fig. 7. Comparison of the EDX analysis of cross sections without and with sealing after anodizing in NaOH containing Al(OH)₃ solution at 5 V.

Table 1. Comparison of relative intensity ratios of Mg(OH)$_2$ and MgO formed under various conditions

Anodizing conditions			Sealing conditions					
1 M-NaOH				Effect of sealing temperature for 30 min				
				353 K		363 K		373 K
Mg(OH)$_2$	MgO			Mg(OH)$_2$	MgO	Mg(OH)$_2$	MgO	Mg(OH)$_2$ / MgO
0.01897	0.00172	Distilled water		0.02705	0.00247	0.02964	0.00323	0.04595 / 1.54368E-04
				Effect of sealing time, at 373 K				
			100 s	10 min	20 min	30 min	60 min	
			Mg(OH)$_2$ MgO	Mg(OH)$_2$ MgO	Mg(OH)$_2$ MgO	Mg(OH)$_2$ MgO	Mg(OH)$_2$ MgO	
			0.01785 0.00698	0.02753 0.00102	0.02964 6.4E-04	0.03765 1.54E-04	0.04608 0.002	
			Sealing Time : 30 min, Temperature : 373 K					
			1 M-NaOH		0.1 M-Al(OH)$_3$		1 M-NaOH+0.1 M-Al(OH)$_3$	
			Mg(OH)$_2$	MgO	Mg(OH)$_2$	MgO	Mg(OH)$_2$	MgO
			0.08277	0.00467	0.01741	0.00371	0.0273	5.48E-04
1 M-NaOH+0.1 M-Al(OH)$_3$			1 M-NaOH		0.1 M-Al(OH)$_3$		1 M-NaOH+0.1 M-Al(OH)$_3$	
Mg(OH)$_2$	MgO		Mg(OH)$_2$	MgO	Mg(OH)$_2$	MgO	Mg(OH)$_2$	MgO
0.06029	0.03216		0.11371	0.0035	0.02023	7.3E-04	0.08321	1.625E-04

MgO formed under various conditions. The anodizing solutions were 1 M NaOH with and without 0.1 M Al(OH)$_3$. First, sealing was conducted in distilled water after anodizing in 1 M NaOH. Under these conditions, the relative intensity ratios of Mg(OH)$_2$ increased with sealing temperature or sealing time, while the relative intensity ratios of MgO did not change. The observations showed that increasing sealing temperature or sealing time improves corrosion resistance. With sealing in 1 M NaOH, 0.1 M Al(OH)$_3$ or 1 M NaOH plus 0.1 M Al(OH)$_3$, the relative intensity ratios of Mg(OH)$_2$ was greatest in 1 M NaOH (0.08277); this was more than double the value in distilled water when sealed for the same time. Moreover, the relative intensity ratios of Mg(OH)$_2$ after anodizing in 1 M NaOH containing 0.1 M Al(OH)$_3$ was much higher than after anodizing in 1 M NaOH, given uniform sealing conditions.

The results imply that corrosion resistance can be improved by considering the following: first, anodizing at the potential causing a surface dissolution reaction, *i.e.*, the potential that produces a high current density; second, using methods to increase the relative intensity ratio of Mg(OH)$_2$, as shown in the XRD analysis; and third, developing methods to reduce the number of micropores and microcracks seen by SEM.

CONCLUSIONS

1. The current density decreased with increasing Al(OH)$_3$ concentration in 1 M NaOH solution during anodizing; sparking occurred at potentials above 80 V.

2. A potential of 4 V, at which the strongest active dissolution reaction occurred, produced the best corrosion resistance when anodizing was done in 1 M NaOH.

3. The sealing effect improved with increasing time and temperature; corrosion resistance increased with the relative intensity ratios of Mg(OH)$_2$.

4. If the thickness of oxygen observed by EDX equals the film thickness, the film formed at 4 V in 1 M NaOH containing 0.1 M Al(OH)$_3$ was 10-15 μm thickness.

5. The optimum corrosion resistance in sealing at various solutions after anodizing was 1 M-NaOH solution.

REFERENCES

Altenphol, D. G., *Corrosion*, **18**, 43 (1962).
Wood, G. C. and O'Sullivan, J. P., "Electron-optical Examination of Sealed Anodic Alumina Films: Surface and Interior Effects," *J. Electrochem. Soc.*, **116**, 1351 (1969).
Hasumi, A., Itoi, T. and Sato, E., "Anodic Oxidation of Magnesium in Sodium Aluminate Solution," *J. Japan Institute of Light Metals*, **30**, 437 (1980).
Hwang, S. K., Jeong, S. H., Hwang, H. Y., Lee, O. J. and Lee, K. H., "Fabrication of Highly Ordered Pore Array in Anodic Aluminum Oxide," *Korean J. Chem. Eng.*, **19**, 467 (2002).
Murpy, J. F., "Symposium on Anodizing," *Aluminum*, 3 (1967).
Kawase, H., "Studies on Effects of Electrolytic and Sealing Conditions on Anodic Oxide Films on Aluminum - Studies on Sealing of Anodic Oxide Films of Aluminum (1st report)," *J. Japan Institute of Light Metals*, **21**, 12 (1971).
Kawase, H., "Effects of Small Amounts of Anions Contained in Sealing Solution for Anodic Oxide Films," *J. Japan Institute of Light Metals*, **21**, 120(1971).
Khaselev, O. and Yahalon, J., "The Anodic Behavior of Binary Mg-Al Alloys in KOH-Aluminate Solutions," *Corros. Sci.*, **40**, 1149 (1998).
Kim, S. J., Okido, M., Mizutani, Y., Ichino, R., Tanikawa, S. and Hasegawa, S., "Formation of Anodic Films on Mg-Al Alloys in NaOH Solutions at Constant Potentials," *Materials Transactions*, **44**, 1036 (2003).
Kim, S. J., Mizutani, R., Ichino, R., Okido, M. and Tanikawa, S., "The

Electrochemical Properties and Formation Mechanism of Anodic Oxide Films on Mg-Al Alloys," *Bulletin of the Korean Chemical Society*, **24**, 975 (2003).

Kim, S. J., Okido, M., Mizutani, Y. and Ichino, R., "Yazawa International Symposium, Metallurgical and Materials Processing: Principles and Technologies, Aqueous and Electrochemical Processing," *TMS*, **3**, 31 (2003).

Koda, M., Takahashi, H. and Nagatama, M., "Reaction of Porous Anodic Oxide Films on Aluminum with Hot Water I. Effect of Film thickness and Reaction Time on the Degree of Hydration and Acid-Dissolution Characteristics," *J. of the Surface Finishing Society of Japan*, **33**, 242 (1982).

Koda, M., Takahashi, H. and Nagayama, M., "Reaction of Porous Anodic Oxide Films on Aluminum with Hot Water V. Effect of Additives in Hot Water on the Hydration Behavior," *J. of the Surface Finishing Society of Japan*, **36**, 27 (1985).

Mizutani, Y., Kim, S. J., Ichino, R. and Okido, M., "Anodizing of Mg Alloys in Alkaline Solutions," *Surface and Coatings Technology*, **169-170**, 143 (2003).

Mizutani, Y., Kim, S. J., Ichino, Y. and Okido, M., "Anodizing of Mg Alloys in Alkaline Solutions," Frontiers of Surface Engineering 2001 (6th ASFF, AEPSE 2001, 5th APIC, and 4th JKSPTFT) Conference and Exhibition, Nagoya Japan, 178 (2001).

Mizutani, Y., Kim, S. J., Ichino, R., Okido, M., Tanikawa, S. and Hasegawa, S., "Anodizing of Mg-Al Alloys and Film Characterization," Japan Institute of Light Metals, 102nd Annual Meeting Proceeding, 179 (2002).

Ono, S., Kijima, H. and Masuko, N., "Microstructure and Voltage-Current Characteristics of Anodic Films Formed on Magnesium in Fluoride Electrolytes," *J. Japan Institute of Light Metals*, **52**, 115 (2002).

Ono, S., Kijima, H. and Masuko, N., "Effects of Substrate Composition and Aluminum Ion Addition on the Formation Voltage-Current Relation for Anodizing of Aluminum," *J. of the Surface Finishing Society of Japan*, **51**, 1168 (2000).

The Institute of Japan Magnesium, "Handbook of Advanced Magnesium Technology," Kallos Publishing Co., LTD, 311 (2000).