Formation of Anodic Films on Mg–Al Alloys in NaOH solutions at Constant Potentials

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The formation behavior and corrosion characteristics of anodic oxide films on pure magnesium and on Mg–Al alloys were investigated, focusing on the effects of anodization potential, aluminum content, temperature, and NaOH concentration. Pure magnesium and Mg–Al alloys were anodized for 600 s at 3, 10, 40, and 80 V in NaOH solutions. It was found that the anodic film formed at 3 V had the best corrosion resistance, regardless of temperature, NaOH concentration, or aluminum content. An especially high current density was observed at applied potentials of 3–7 V on anodization in alkaline NaOH solutions. XRD analysis detected Mg(OH)₂ and MgO peaks in the films on the anodized specimens. The relative intensity of the Mg(OH)₂ XRD peaks decreased with increasing applied potential, while those of MgO increased. Mg(OH)₂ was generated by an active dissolution reaction with high current density at the specimen surface. Generation of Mg(OH)₂ increased with increasing temperature, while that of MgO increased with NaOH concentration. Moreover, the current density after anodization for 600 s at a constant potential decreased with increasing aluminum content in Mg–Al alloys.

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1. Introduction

Magnesium is easy to recycle because any impurities such as Fe, Ni, *etc.* are easily removed. Of the common commercial metals, magnesium has the lowest density and excellent specific strength. Recently, there has been great interest in using magnesium in automobile parts, mobile personal computers, cellular phones, sports, the leisure industry, *etc.* However, to prevent corrosion magnesium must be surface treated, since it is very active electrochemically. There are many ways to treat the surface of magnesium and its alloys, such as anodization, painting, electroplating, *etc.* One of the most efficient surface treatments is chromate-conversion coating, but this process causes many environmental problems. We therefore studied Mg anodization in alkaline solutions as a non-chromate surface treatment.

Magnesium and Mg–Al alloys are often surface-treated by anodization in alkaline solutions containing additives such as fluoride and chromium ions to enhance corrosion resistance.¹⁾ Few authors have examined the growth behavior of anodic oxide films on magnesium and Mg–Al alloys.^{2–6)} The anodic behavior of magnesium in NaOH solutions at a wide range of potentials was first described in the studies of Emley,²⁾ Huber,³⁾ and Evangelides.⁷⁾ Khaselev *et al.* reported that the aluminum content of Mg–Al alloys and aluminate ions in electrolyte affected the chemical composition of anodic films at applied potentials below the breakdown potential of the film, and that the anodic films formed at a constant applied potential consisted of magnesium, aluminum, and oxygen.⁵⁾

In this study, Mg–Al alloys were anodized in alkaline solutions. The effects of the aluminum content of the alloys, the applied potential, solution temperature, and NaOH concentration on the characteristics of the film were

investigated. The surface morphologies of the anodic oxide films were observed using SEM. The anodic films were estimated from the relative intensity ratios of the XRD patterns for films anodized at each applied potential. The anodic polarization curves of the anodized films were measured in Na₂SO₄ solutions containing chloride ions, and their corrosion resistivity was estimated from their corrosion potentials.

2. Experimental

The specimens were 99.9 mass% purity magnesium and Mg–Al alloys with an aluminum content ranging from 1.5 to 15 mass%. The electrodes were mounted using epoxy resin, with an exposed area of 25 mm², 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 a Ag/AgCl sat. KCl reference electrode. Anodization of Mg–Al alloys with 0, 1.5, 3, 9, and 15 mass% aluminum content was performed as a function of temperature between 273 and 323 K, NaOH concentration varying from 0.5 to 3 kmol/m³, and applied potential at 3, 10, 40, and 80 V below the minimum sparking potential. The solution was stirred during anodization.

The anodic polarization curves for the anodized specimens were measured using a potentiostat with a scan rate of 1 mV/s in a 0.017 kmol/m³ NaCl and 0.1 kmol/m³ Na₂SO₄ solution at 298 K to characterize their corrosion properties. The films formed during anodization in NaOH solutions were analyzed using scanning electron microscopy and X-ray diffraction analysis.

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Fig. 1 Current density-potential curves for pure Mg and Mg–Al alloys at a scan rate of 60 mV/s in 1.0 kmol/m³ NaOH solution at 298 K.

3. Results and Discussion

3.1 Polarization behavior

The anodic behavior of specimens during the anodization process is very important. The active dissolution reaction, passivity, film formation potential, and film destruction depend on anodic polarization behavior. Anodic polarization curves were measured for pure magnesium and magnesium alloys containing various amounts of aluminum. Figure 1 shows the current density-potential profiles at a scan rate of 60 mV/s in 1 kmol/m³ NaOH solution at 298 K for pure magnesium, Mg–3 mass% Al, and Mg–9 mass% Al. Anodic current increases corresponding to the active dissolution reaction ($\text{Mg} = \text{Mg}^{2+} + 2\text{e}^-$) were observed for potentials between ca. 3 and 7 V for all specimens. The current density at 7 V was 100 A/m² for pure magnesium, 35 A/m² for 3 mass% aluminum, and 0.2 A/m² for 9 mass% aluminum. 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.⁶⁾ Moreover, sparking was observed at 81.6, 81.9, and 84.6 V, for pure magnesium and the alloys with 3 and 9 mass% aluminum, respectively. When sparking was observed 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 anodization of magnesium.²⁾ Intense sparking at above 80 V was also accompanied by breakdown of the surface film.

The corrosion resistance of AZ31 alloy is reported to be better than that of Mg–Al alloys containing 3 mass% aluminum, because AZ31 contains a little zinc.⁸⁾ 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.^{9–11)} Khaselev and Yahalom reported on the anodic behavior of binary Mg–Al alloys in KOH solutions over a wide range of applied potentials, with emphasis on the effect of aluminum content on the passivation phenomena and spark potential.⁶⁾ 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

AlO_2^- ions are added to alkaline solutions, the current density effectively decreases with increasing AlO_2^- content.^{12,13)}

3.2 Effect of aluminum content

The Al content of Mg–Al alloys is a very important factor in corrosion resistance. Therefore, the effect of aluminum content on anodization was examined using Mg–Al alloys. Figure 2 compares the current density after anodization for 600 s at each applied potential as a function of aluminum content. Current densities at 10, 40, and 80 V were similar, regardless of the aluminum content. Current densities were lower with increasing aluminum content from 0 to 5 mass%, and constant over the range 5 to 15 mass%. The current density at 3 V gradually diminished with increasing aluminum content.

Figure 3 shows SEM photographs of Mg–Al alloys after anodization for 600 s at 3 V. The dissolution reaction in pure magnesium is initiated by the formation of discrete pits. The number of pits gradually increases, and they eventually join to cover large areas. The process continues until the magnesium surface is completely activated.⁶⁾ Pure magnesium contains no intermetallic compound ($\text{Mg}_{17}\text{Al}_{12}$); the intermetallic compound content increases with increasing aluminum content. It has been confirmed from the SEM photographs that the intermetallic compound ($\text{Mg}_{17}\text{Al}_{12}$) remains as a frame. The anodized surfaces contained the frames, as shown in the photographs of 1.5 and 3.0 mass% aluminum in particular. Large amounts of intermetallic compound were formed at above 7 mass% aluminum. The pores in the magnesium phase are larger and deeper at 3 V than at other applied potentials.⁸⁾

To estimate the effect of applied potential, the surface morphology of 3 mass% aluminum after anodization for 600 s at various potentials in 1 kmol/m³ NaOH at 298 K is shown in Fig. 4. A dissolution reaction occurred at 3 V, at

Fig. 2 Effect of the aluminum content of Mg–Al alloys on the current density after anodization for 600 s at each applied potential in 1.0 kmol/m³ NaOH solution at 298 K.

Fig. 3 SEM photographs of Al–Mg alloys after anodization for 600 s at 3 V in 1.0 kmol/m³ NaOH solution at 298 K.

which pores with several tens of micrometers in size were observed. The dissolution reaction occurred at the surface only in the magnesium phase.

By contrast, many small surface pores were observed at 10 V. These pores are thought to have been located at sites where the dissolution reaction took place at 3 V, and the reaction did not occur on the surface occupied by the intermetallic compound. Moreover, at 40 and 80 V, it was seen that little dissolution took place in the magnesium phase, since there were no pores on the surface. It has been reported that until film breakdown occurs, a thin, compact oxide layer is formed with increasing potential.^{6,14)}

Figure 5 shows the XRD results for 3 mass% aluminum alloy anodized for 600 s in 1 kmol/m³ NaOH solution at 298 K. The highest peaks of Mg, Mg(OH)₂, and MgO was observed at around 36.8, 38.0, and 43.0 degrees, respectively. Mg(OH)₂ was detected at 3 V, while MgO appeared only at 80 V.

The relative intensity ratios (i/i_0) at each applied potential and for various aluminum contents are compared in Fig. 6. The relative intensity ratio is defined as the ratio of the

highest XRD peak for Mg(OH)₂ or MgO (i) to that of Mg (i_0). The relative intensity ratios of Mg(OH)₂ and MgO are not affected by aluminum contents in Mg–Al alloys. The relative intensity ratios of Mg(OH)₂ decreased with increasing applied potential, while those of MgO increased, regardless of the aluminum content of the Mg–Al alloy.

3.3 Effects of temperature and NaOH concentration

It is assumed that the temperature of the solution during anodization affects the film properties, because higher temperatures are more likely to induce an activation reaction.

Figure 7 compares the relative intensity ratios of Mg(OH)₂ and MgO in the XRD patterns for anodized specimens of 3 and 9 mass% aluminum alloys. XRD peaks of MgO were barely detected for the specimens anodized at 3 and 10 V. The XRD peaks of Mg(OH)₂ increased with temperature at 3, 10, and 40 V, while the MgO peaks increased very a little with temperature at 40, and 80 V. With increasing applied potential, the relative intensity ratio of Mg(OH)₂ in the film decreased, while that of MgO increased. The tendency was not affected by temperature. This suggests that temperature

Fig. 4 SEM photographs of Mg–3 mass% Al alloy after anodization for 600 s in 1 kmol/m³ NaOH at 298 K.

Fig. 5 XRD results for Mg–3 mass% Al alloy anodized at 3 and 80 V in 1 kmol/m³ NaOH solution at 298 K.

Fig. 6 Comparison of the relative intensity ratios (i/i_0) of the XRD peak heights at each applied potential with various Al contents.

Fig. 7 Comparison of the relative intensity ratios of Mg(OH)₂ and MgO in XRD patterns for anodized specimens of 3 and 9 mass% Al alloys.

affected not only the formation of MgO, but also the formation of Mg(OH)₂, particularly at 3 and 10 V. In addition, at each applied potential the current density after anodization for 600 s increased with increasing temperature.

A constant potential experiment to examine the effect of concentration was conducted at 298 K in NaOH solutions at concentrations of 0.5, 1, and 3.0 kmol/m³. The current density was far greater at 3 V than that at other potentials, for both 3 and 9 mass% aluminum alloys. Overall, the NaOH concentration had little effect on the anodized film compared with the effect of temperature as shown in Fig. 7. It has been reported that the dissolution properties of AZ91 alloy in NaOH do not depend on the NaOH concentration.¹⁵⁾ The XRD analysis of specimens anodized at 80 V at 298 K using several NaOH concentrations showed that the NaOH concentration affected the formation of MgO, but not that of Mg(OH)₂. The relative intensity ratios of MgO increased decreased with increasing applied potential regardless of the NaOH concentration, while those of Mg(OH)₂.

3.4 Corrosion characteristics of the anodized specimens

To characterize the corrosion resistance of the anodized films, we performed an anodic polarization test of the anodized specimens at a scan rate of 1 mV/s in the 0.017 kmol/m³ NaCl and 0.1 kmol/m³ Na₂SO₄ solution at 298 K. Pitting corrosion caused the anodic current density to increase suddenly to above 2 A/m². Therefore, we defined the potential at which the current density reached 1 A/m² as the corrosion potential for the alloy, and compared corrosion potentials between the various alloys as an indicator of corrosion resistance. The corrosion potentials of the various Mg–Al alloys are shown in Fig. 8. All of the anodized specimens had better corrosion resistance than the non-anodized specimens, regardless of the applied potential. The best corrosion resistance, *i.e.*, the highest corrosion potential, was found at an anodization potential of 3 V. The highest corrosion resistance was seen in the Mg–Al alloy containing 9 mass% aluminum anodized at an applied potential of 3 V.

Fig. 8 Comparison of the corrosion potentials of Mg–Al alloys with various Al contents. The corrosion potential was defined as the potential at which the current density reached 1 A/m² because of pitting.

Fig. 9 The effect of temperature during anodization on the corrosion characteristics of Mg–Al alloys with 3 and 9 mass% Al content.

The effect of the temperature during anodization for Mg–Al alloys containing 3 and 9 mass% aluminum on the corrosion characteristics is shown in Fig. 9. The potential increased favorably with temperature. The anodic reaction rate at a temperature of 273 K was too slow for anodic films to form on the surface of the specimens, while the rate at a temperature of 323 K was sufficient. Therefore, the rate at which a film is generated is controlled by temperature. Moreover, anodization at 3 V produced the best corrosion resistance in 3 and 9 mass% aluminum.

4. Conclusions

The effects of temperature, NaOH concentration, and aluminum content on the properties of anodization films formed on Mg–Al alloys were investigated. The anodic films formed at 3 V had the best corrosion resistance, regardless of temperature, NaOH concentration, or aluminum content. Generation of Mg(OH)₂ was affected by temperature and by the surface dissolution reaction. The amount of Mg(OH)₂ increased with increasing temperature, improving corrosion resistance. Generation of MgO increased with increasing NaOH concentration; moreover, corrosion resistance was better at 80 V rather than 10 or 40 V, since generation of MgO increased. Current density after anodization at a constant potential decreased with increasing aluminum content in the Mg–Al alloys. The relative intensity of the XRD peaks of

Mg(OH)₂ decreased with increasing applied potential, while those of MgO increased.

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