Corrosion Protection of AZ91D Magnesium Alloy by Anodization Using Phosphate Electrolyte

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Mechanism of corrosion protection obtained by anodization for die-cast plates of ASTM AZ91D (Mg-9 mass%Al-0.7Zn) magnesium alloy has been studied. Anodization was conducted by conventional Dow17 which utilizes chromium oxide (VI), ammonium fluoride and phosphoric acid, and by environment-friendly Anomag whose electrolyte consists of phosphate and ammonium salt. The anodized surface obtained in Dow17 showed local corrosion in salt spray test (SST) after ~500 ks to form corrosion products consisting of magnesium hydroxides. On the other hand, the surface anodized in Anomag was covered with amorphous film, showed only discoloring in SST and corrosion product was scarcely observed. When the anodized surfaces were trenched with ceramic knife to form locally exposed substrate, corrosion product was formed on the trench in the case of Dow17, but corrosion was well suppressed by formation of new type of protective film in the case of Anomag. Anodic polarization curves indicate that the surface anodized in Dow17 is protected by passive substances through which electrolyte can easily reach the substrate, and that in Anomag show sacrificial function where the anodized layer dissolves quite slowly into the electrolyte prior to the substrate. The excellent corrosion protectivity obtained in Anomag is considered to be based on the formation of a new type of protective film as well as sacrificial function of the original amorphous anodized layer. [doi:10.2320/matertrans.L-MRA2007881]

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1. Introduction

Magnesium alloys are increasingly utilized recently to improve fuel consumption of vehicles by reducing their weight and their rigidity. Suppression of oscillation, shielding of electromagnetic wave and recyclability of the alloys are also advantages in electric and electronic products as well as in automotive applications. However, magnesium is one of the materials which bear stain most easily because of its quite low potential region where metallic magnesium can exist in wet environment¹,² (Fig. 1). As protective coatings for magnesium alloys, conventional anodizations by HAE³,⁴ and Dow17⁵-⁷ treatments have successfully been utilized, but these methods require harmful chemical agents such as chromium oxide (VI) and fluoride which have recently been restricted by RoHS (Restriction of the use of certain Hazardous Substances in electrical and electronic equipment) and current trend for reducing environmental load. Another protection of magnesium alloys by anodization is performed using Anomag⁸-¹¹ whose electrolyte consists of phosphate and ammonium salt. Because of the simple electrolyte of Anomag, its environmental load is quite lighter compared with those of Dow17 and HAE. The main purpose of this research is to clarify the mechanisms of corrosion protection on the above two anodized surfaces by elucidating the difference in modes of protections on those surfaces.

2. Experimental Procedure

A die-cast plate of magnesium alloy (ASTM AZ91D) of 3 mm-thick (as-cast) was used as substrate whose chemical composition is shown in Table 1. After the substrates were degreased and etched in a potassium hydroxide solution and a phosphate solution, respectively, they were anodized either in Dow17⁵-⁷ or in Anomag⁸-¹¹. The electrolysis in Anomag was carried out by using a commercial solution (Anomag CR1 and CR2, Henkel Japan Co., Ltd.) according to its instruction. Part of the anodized specimens underwent salt spray test (SST, JIS Z2371) and electrochemical measure-
ments for assessment of protectivity of the anodized layers. Others were used for electron probe microanalysis (EPMA) and transmission electron microscopy (TEM), and X-ray diffraction patterns were taken under Seemann-Bohlin geometry of $\omega = 1^\circ$ with parallel beam optics. Part of the anodized specimens had their surfaces trenched by ceramic knife, then the corrosion behavior of the exposed areas in the environment of SST was examined by optical and electron microscopies. Hereafter, a specimen anodized in Anomag having the average thickness of the anodized layer, 5 $\mu$m, is designated as ‘Anomag 5 $\mu$m’ for simplicity.

Electrochemical properties of the anodized layers were evaluated by anodic polarization (linear sweep voltammetry, LSV) and by monitoring corrosion current at constant potential (CP). The electrolyte was a solution of 5 mass% sodium chloride whose pH was 6.5, the counter electrode was a plate of titanium coated with platinum, the reference electrode was a standard calomel electrode (SCE) with a saturated solution of potassium chloride, and each working

![Fig. 2 X-ray diffraction patterns taken from the anodized surfaces [(a) Dow17, (b) Anomag 10 $\mu$m].](image)

![Fig. 3 Cross-sectional backscattered electron images and compositions of the anodized layers [(a) Dow17, (b) Anomag 5 $\mu$m, (c) Anomag 10 $\mu$m, (d) Anomag 20 $\mu$m, (e) Compositions of the anodized layers (Anomag)].](image)
The electrode had a square window of $25 \times 25 \text{mm}^2$. The rate of potential sweep was 1 mV/s in the measurement of LSV, and the potential was $-1.4\text{ V vs. SCE}$ in CP.

3. Experimental Results

3.1 Structure of anodized surface

Figure 2 shows the X-ray diffraction patterns taken from the anodized surfaces. As previously reported, the surface anodized in Dow17 (Fig. 2(a)) shows chromium oxide ($\text{Cr}_2\text{O}_3$), magnesium fluoride ($\text{MgF}_2$) and sodium magnesium fluoride ($\text{NaMgF}_3$) as crystalline substances. On the other hand, that in Anomag 10 µm shows a broad scattering profile (Fig. 2(b)), and the overlying peaks indicates the magnesium matrix of the substrate.

Figure 3 shows the cross-sectional microstructure of the anodized surfaces and concentrations of oxygen, magnesium, aluminum and phosphorus in the anodized layers (Anomag) obtained by EPMA. Most of the pores in the anodized layer formed in Dow17 (Fig. 3(a)) were filled with epoxy resin used for the sample preparation, and many paths were formed linking the surface and the substrate. Figures 3(b)–(d) also show the formation of porous structure in the anodized layers. The atomic ratio of the elements in the anodized layers is roughly $\text{O} : \text{Mg} : \text{Al} : \text{P} = 63 : 20 : 2 : 15$.

![Fig. 4 Transmission electron micrographs of a fragment of anodized layer in Anomag 20 µm (a) Bright-field image, (b) Magnified dark-field image of the dotted rectangular area in (a).]

<table>
<thead>
<tr>
<th>Time [ks]</th>
<th>0</th>
<th>518</th>
<th>2160</th>
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<tr>
<td>Dow 17</td>
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<tr>
<td>Anomag 10 µm</td>
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![Fig. 5 Anodized surfaces after salt spray test (Circles in Dow17-518 ks indicate corrosion products, and light areas enclosed by dotted curve in Anomag 10 µm-2160 ks correspond to reduction in anodized layer).]

![Fig. 6 Corrosion product on the as-cast substrate after salt spray test for 86.4 ks (a) Secondary electron image, (b) X-ray diffraction pattern).]
Figure 4 shows the bright- and dark-field images of the fragment of anodized layer (Anomag 20 μm). Although there was no characteristic microstructure in the fragment at the beginning of the observation, some areas were damaged by a few seconds’ irradiation of electron beam to form bubbles or show swelling. The selected area diffraction pattern taken from the dotted rectangular area in Fig. 4(a) consisted of a strong halo ring, weak Debye rings and diffraction spots. The Debye rings and the diffraction spots matched those of spinel (MgAl₂O₄), and the dark-field image taken using a diffraction spot of spinel including a part of the Debye rings showed particles of 10¹–10² nm in size. Debye rings of magnesium oxide (MgO) were also observed in other fragments, but the rings were diffuser than those of spinel.
3.2 Salt spray test

Figure 5 shows the anodized surfaces after salt spray test (SST) of 0, 518 and 2160 ks. Although corrosion products were observed locally on the surface anodized in Dow17 as indicated by dotted circles, the anodized layer itself was kept as it was before SST even in the areas surrounding the corrosion products. On the other hand, the surface anodized in Anomag (10 μm) was free from visible corrosion products and had only slight discoloration on the entire surface. In the magnified optical images of the discolored surfaces, those areas showed local disappearance of the anodized layers especially inside the broken curves, but no remarkable corrosion product was found on those areas.

Figure 6 shows the corrosion product on the as-cast surface after salt spray test for 86.4 ks. Corrosion products with layered structure (Fig. 6(a)) were found locally on the surface, and they were identified mainly as magnesium hydroxide by X-ray diffraction (Fig. 6(b)).

Figures 7 and 8 show the trenched areas on the anodized surfaces after SST for 1990 ks. Since the trenched area had no anodized layer and the raw magnesium alloy was exposed to the wet environment containing chloride ion, the area became a starting point of corrosion as shown in Fig. 7. On the other hand, Fig. 8(a) shows no remarkable corrosion product (magnesium hydroxide) even in the trenched area, and a cracked film was newly formed on the trenched surface during the test which consists of oxygen, magnesium, aluminum, phosphorus (Fig. 8(b)).

Figure 9 shows the anodized surface (Anomag 10 μm) after SST for 346 ks and 1990 ks. The original anodized surface with porous morphology was kept locally after SST for 346 ks (Fig. 9(a)). Intensities of O-Kα and P-Kα characteristic X-rays are comparable on the original porous areas and many parts of the flat ones which lost the original morphology (Fig. 9(b),(d)). This indicates that anodized layer still remains on those areas despite the change in morphology, but most of the anodized layer was lost on the areas where the intensity of Mg-Kα remarkably increases in Fig. 9(c). However, the morphology of the surface drastically changed after SST for 1990 ks, showing cracked areas (dark areas in Fig. 9(e)) and flat areas with less cracks (bright areas in Fig. 9(e)). Intensities of O-Kα and
characteristic X-rays are higher on the small fragments of 10 μm in size which exist in the cracked areas in Fig. 9(e) than on the flat areas which seem to have lost the fragments.

### 3.3 Electrochemical properties of anodized surfaces

Figure 10 shows the electrochemical properties of the anodized surfaces. Anodization in Dow17 (Fig. 10(a) dashed line) can successfully suppress the anodic current or corrosion rate by the order of 2 at $E = 4$ V (vs. SCE) compared with that of the as-cast substrate (Fig. 10(a) solid line). The anodized surfaces obtained in Anomag (Fig. 10(a) dotted and one-point chain lines) have regions with low anodic current at $E < -1.5$ V (vs. SCE) for Anomag 10 μm and at $E < -1.55$ V for Anomag 20 μm before the substrate begins to dissolve into the electrolyte.

When the specimen anodized in Dow17 was held at a potential of $E = 4$ V (Fig. 10(b) dashed line), the anodic current rapidly increased immediately after the beginning of the measurement. However, the anodized surface obtained in Anomag (solid line) showed a plateau where anodic current was around $10^{-1}$ mA/cm$^2$ before the substrate began to show local corrosion and hydrogen gas was correspondingly generated. After these electrochemical measurements, the cross section of the specimen anodized in Dow17 showed corrosion of the substrate above which an anodized layer still remained. On the other hand, corrosion of the substrate was observed only beneath the areas where the anodized layer disappeared in the case of Anomag 20 μm.

### 4. Discussion

#### 4.1 Structure of anodized layer

As Figs. 2, 3 and 4 show, the anodized layers obtained in Anomag mainly consist of amorphous matrix and fine crystallites of spinel and magnesium oxide. Although the anodized layer obtained in Dow17 mainly shows crystalline substances, the layer might contain amorphous magnesium oxide which could not be clearly detected by XRD. Anodizing current at the electrolysis is due to continuing local discharges on the surface covered by insulator or anodized film, where substrate as well as anodized layer melted by spark due to discharge during anodization are considered to be solidified rapidly, forming amorphous-based layer which contain small crystallites of spinel, magnesium oxide and spherical or irregularly shaped pores. Anions in the electrolyte which are attracted at the anodized surface during electrolysis are mainly hydroxide ions and phosphates (PO$_4^{3-}$). Phosphorus detected by EPMA in the anodized layers (Anomag, Fig. 3(e)) is picked up during solidification, and the spherical pores are thought to be filled by oxygen gas which has generated by anodization of oxygen in hydroxide ions ($4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$). This mode of local discharge which is accompanied by rapid solidification and formation of an anodized layer is thought to reach a steady state in a period at a given voltage, which determines the amount or the thickness of the anodized layer.

The formation of the anodized layer in Anomag can qualitatively be understood by solidification of molten magnesium oxide which contains aluminum. Figure 11 shows the binary phase diagram of MgO-Al$_2$O$_3$ system.

![Fig. 11 Binary phase diagram of MgO-Al$_2$O$_3$ system](image-url)

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The difference might be due to the amount of phosphorus in the electrolyte, which modifies the liquidus lines of the system and brings supercooled liquid. During the solidification, magnesium oxide firstly precipitates in the liquid, then the supercooled liquid decomposes into fine crystallites of magnesium oxide and spinel. However, most of the supercooled liquid is considered to solidify in amorphous state because of the large cooling rate in the electrolyte. Since Mg₁₇Al₁₂ phase in the substrate contains large amount of aluminum, aluminum concentration is locally higher than the dotted line in Fig. 11. In that case, spinel firstly precipitates in the liquid, and rather coarse crystallites in Fig. 4(b) are considered to have formed through this process.

By assuming that valences of oxygen, magnesium, aluminum and phosphorus are 2, 2, 3 and 5, respectively, composition of the anodized layers (Anomag) is roughly expressed as \((\text{MgO})_{x_1}(\text{MgAl}_2\text{O}_4)_{x_2}(\text{Al}_2\text{O}_3)_{x_3}(\text{P}_2\text{O}_5)_{x_4}\) from Fig. 3(e). Here, each substance does not necessarily mean crystalline phase which forms meaningful diffraction, but the elements in the amorphous phase are assumed to be close to the substances in terms of short-range order. Additional oxygen \((63 - x + 4(20 - x) + 3(x - 15) + 5 \times 7.5) = 2.5\) is thought to be contained in the anodized layer as water molecules especially in the cases of thicker anodized layers, considering the swellings by electron beam irradiation on the fragments of the anodized layers in TEM observation. Other substances as \(\text{MgPO}_4\), \(\text{Al(OH)}\) and \(\text{AlPO}_4\), detected by X-ray photoelectron spectroscopy in the previous research,\(^{10}\) indicate the composition being more complex. Since those components are the ones detected at the top surface \((\sim 10^2 \text{nm in depth})\), chemical state of each element and its environmental information in the anodized layer should be determined in detail by other methods as nuclear magnetic resonance (NMR) and X-ray absorption fine structure (XAFS) in soft X-ray region.

4.2 Mechanism of corrosion protection

Figures 5, 7, 8 show that the mechanism of corrosion protection is largely different between the case of Dow17 and that of Anomag. Since paths exist in the porous anodized layer (Dow17) which link the substrate and the surface, corrosion begins at the points where the substrate contacts water which infiltrates from the surface within 500 ks after the initiation of SST. From the point that the anodized layer obtained in Dow17 was kept as it had been after the anodization even at the areas which surround the corrosion products (Fig. 5), its mode of corrosion protection is close to that by tin plating on iron, where red rust is brought immediately by defects or damages on the plated surface which expose iron substrate.

On the other hand, morphology of the anodized layers in Anomag changed from porous one (Fig. 3) to cracked one (Fig. 9(e)–(h)) as the time passed in SST. The cracked areas are similar to the newly formed surfaces (Fig. 8) in the trenched area, and their morphology is also similar to that obtained by conversion treatment which utilizes phosphate solution.\(^{18}\) From electrochemical properties (Fig. 10), the anodized surfaces obtained in Anomag show sacrificial function for the substrate, and some chemical agents in the anodized layer are considered to oxidize magnesium to newly form protective films in a wet environment similar to the ones obtained by conversion treatment. That is, corrosion protectivity is maintained even on the areas where the original anodized layer is mechanically lost, as long as the remaining one nearby can provide the components required for the formation of another protective layer observed in Figs. 8 and 9(e)–(h).

Although the anodized layer obtained in Anomag has electrochemically less nobleness than the substrate, Fig. 10 shows its dissolving rate into water or corrosion rate is quite low, and the increase in thickness of the anodized layer corresponds to the enlargement in the range of sacrificial protection, which means elongated duration in practical use. In addition to the sacrificial protection (thermodynamics) and the low dissolving rate (kinetics) of the anodized layer in Anomag, the wet environment containing dissolved components as phosphate, which have originally existed in the anodized layer, is considered to have an appropriate pH and work as a solution for conversion treatment to form another protective layer on the substrate. The amorphous structure of the anodized layer in Anomag might be one of the reasons for those electrochemical phenomena or excellent corrosion protectivity, and detailed analyses of conversion coatings should give additional information on anodization in Anomag. The elements working in the sacrificial function and the changes in oxidation number, as well as the mechanism of the following formation of another protective layer are also to be studied in the future.

5. Conclusion

In this research, die-cast plates of magnesium alloy (ASTM AZ91D) were anodized in environment-friendly anodization (Anomag), which utilizes a solution consisting mainly of phosphate and ammonium salt, and in conventional Dow17 where chromium oxide (VI) and fluoride are used to obtain passive surfaces. Those surfaces were subjected to salt spray test (SST) and electrochemical measurements for estimation of the corrosion protectivities, and the structure was analyzed by X-ray diffraction and electron microscopy. The main results can be summarized as follows.

1. The anodized layer obtained in Anomag shows sacrificial function in SST, while that in Dow17 shows barrier protection by passive film.
2. The protectivity in Anomag is based on electrochemically less nobleness of the original anodized layer, whose structure is mainly amorphous and dissolving rate is quite low, that is, ideal sacrificial function for the substrate in terms of thermodynamics and kinetics.
3. In addition to the ideal sacrificial function, formation of another protective film on the areas where the original anodized layer is lost prevents the substrate from bearing remarkable corrosion product.

REFERENCES