Electrochemical characterization of non-chromate surface treatments on AZ80 magnesium

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ARTICLE DATA

Article history:
Received 2 August 2007
Received in revised form 13 September 2007
Accepted 29 December 2007

Keywords:
AZ80 magnesium alloy
Non-chromate
Anodizing
Tafel polarization
AC impedance

ABSTRACT

Surface treatments were applied to AZ80 magnesium alloy (8%Al–92%Mg) within non-chromate environments to develop its anti-corrosion characteristics. The non-chromate process involved chemical conversion using a phosphate and hydrofluoric acid (HF) coating, followed by anodizing. The chemical conversion generated good adhesion between the substrates and the anodic film. The anodizing process formed a 30 μm-thick film on the surface of the AZ80. Electrochemical properties were obtained using Pourbaix diagram, polarization, and EIS (Electrochemical impedance spectroscopy) analyses to characterize the effects on the treated AZ80. Tafel polarization and models of equivalent circuits revealed that the corrosion rate of anodized AZ80 was reduced from 14.44 to 0.28 mpy with passive-film resistance increasing from 428 to 54,200 Ω.

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1. Introduction

The use of AZ80 magnesium alloy for structural applications is growing rapidly [1–3]. Recently, AZ80 has been used in the 3C industries (Computer, Communication, and Consumption electronics production) because of its high strength-to-weight ratios (density: 1.738 g/cm³), anti-electromagnetic field properties and high thermal conductivity (122 W/m K). Nevertheless, due to its chemical reactivity (standard electrode potential: −2.363 V, SHE) and inferior corrosion resistance, the alloy has had limited practical applications [4]. Chromate films are most commonly used for surface treatment of AZ80 alloy, but emerging legislation prohibits the use of chromates in many countries. Alternate surface treatments are urgently needed [5–7]. The following types of protective coatings on AZ80 have been patented [8,9]: (1) oils and waxes for temporary protection, (2) chemical conversion for temporary protection or as a paint base, (3) anodized coatings to improved paint base or wear resistance, (4) paints and powder coatings to protect against corrosion or to preserve appearance, (5) metallic plating for appearance, surface conductivity, and protection against corrosion. Among those patents, chemical conversion limits a stand-alone interior, while anodizing results in a porous coating that needs to be sealed. Anodizing using non-chromates has potential to be the primary surface treatment for AZ80. The most common patented anodizing electrolytes are alkali hydroxide and fluoride [5,6,9]. Anodizing generates an anti-corrosive oxide film on the surfaces after chemical conversion providing a strongly adhesive film. However, very few articles and patents to date have focused on the electrochemical properties of chemical and anodic methods when applied to AZ80 simultaneously.

In this study, electrochemical properties were observed from a Pourbaix diagram, polarization, and impedance analyses [10–15] to characterize the effects of non-chromate surface treatments on AZ80.
2. Experimental Methods

2.1. Chemical Conversion and Anodization

Non-chromate processes, involving chemical conversion using a phosphate and HF coating followed by anodizing, were used for coating specimens as shown in Fig. 1. Specimens of magnesium alloy (AZ80) plates of size 50 mm² x 5 mm were cut and abraded using 1500-grit SiC papers and then pickled in 8% vol. H₂SO₄ solution at 25 °C for 25 s. The solution used for the chemical conversion was 95% vol. H₃PO₄ with 5% vol. HF. The AZ80 was converted at 160 °C for 5 s. The porous surfaces of the converted specimens were then sealed in a 3% vol. HF solution at 25 °C for 45 s and anodized in a 10-cm diameter stainless steel cylinder. The specimens were placed in the cylinder (which functioned as a cathode) and 200 V was applied for 40 min. The specimens were then anodized within a stirred electrolyte with a composition of KOH: 25 g/l, K₂SiO₃: 50 ml/l, KF: 10 g/l with a pH 7.5 at 8 °C. The anodized film, which had a composition of magnesium hydroxide (Mg(OH)₂) was sealed by immersion in 100 °C H₂O(l) for 5 min to obtain a porous structure.

2.2. Electrochemical Measurements

The electrochemical properties of the specimens were determined using a classical three-electrode arrangement [16]. Fig. 2 shows the configuration, which consists of a 3-cm diameter glass cylinder fixed to the surface of a working electrode by an O-ring covering an area of 7.1 cm², a platinum sheet (2 cm x 2 cm) counter electrode, and a saturated calomel reference electrode (SCE). The electrolyte was 0.9% NaCl solution. The polarization

Fig. 1 – Flowchart of experimental process.

Fig. 2 – Schematic diagram of experimental setup.

Fig. 3 – Porous film on the sample surface after chemical conversion treatment of AZ80.
Curves were measured electrochemically using an EG&G Model 273A Potentiostat/Galvanostat. Electrochemical impedance spectroscopy (EIS) data were obtained using Solartron equipment (a 1286 electrochemical interface and a 1255 frequency response analyzer) [17], which covered a frequency range of $5 \times 10^3$ to $10^6$ Hz with 10 mV rms signal amplitude. The electrochemical data were simulated and written in Microsoft Excel programs.

3. Results and Discussion

3.1. Chemical Conversion

Phosphoric acid is the primary constituent of the solution used for chemical conversion to generate phosphate conversion coatings. The coatings provide lubrication and wear resistance, facilitating cold forming, short-term resistance against mild corrosion, and adhesion in oxide-metal lamination applications [9]. The phosphate coating herein was used to increase the adhesion between AZ80 alloy and its anodic oxide film. The surface morphology of AZ80 appeared porous after conversion, as shown in Fig. 3. The porous layer was sealed immediately using sealing solution at 100 °C. The pores were sealed and their SEM morphologies are shown in Fig. 4. The converted AZ80 had higher nobility than the original specimen, which decreased its corrosion rate from 14.44 (mpy) to 4.86 (mpy) with the open circuit voltage range of $-1.52$ to $-1.48$ V (SCE), as shown in Fig. 5.

Further, Mg$^{2+}$ reacts with H$_2$O to form a thick oxide of Mg (OH)$_2$, which covers the surface of the specimen and evaporates hydrogen from the solution.

$$\text{Mg}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{H}^+$$

$pH = 0.5 \times (16.95 - \log[\text{Mg}^{2+}])$. (2)

When the over-potential is below $-2.7$ V (SHE), a thick layer is also formed; however, this oxide is less protective to AZ80.

$$\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{H}^+ + 2\text{e}^-$$

$\Delta E_2 = -1.862 - 0.059pH$. (3)

At 25 °C, the formation enthalpy of Mg(OH)$_2$ is $-142,580$ cal./g mol, which is less than that of MgO ($-136,136$ cal./g mol). Since Mg(OH)$_2$ is more thermodynamically stable than MgO in the presence of water; the oxide can be easily hydrated according to reaction (4).

$$\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2$$ (4)

The diagram indicates that increasing the applied voltage and reducing the solution pH is essential for AZ80 anodizing.

3.2. Anodization

The pH of the electrolyte and the amount of voltage applied are crucial parameters in controlling AZ80 anodizing. A Pourbaix diagram was constructed for water-immersed AZ80 before anodizing. Fig. 6 describes the relationship between overpotential of AZ80 and its thermodynamical stability based on Nernst’s equations [18]. The Mg$^{2+}$ region is an active region, with its SHE above $-2.7$ V and the pH of the solution has to be less than 11.47 at 25 °C.

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$$

$\Delta E_1 = 0.0295 \times \log[\text{Mg}^{2+}] - 2.363$. (1)

Further, Mg$^{2+}$ reacts with H$_2$O to form a thick oxide of Mg (OH)$_2$, which covers the surface of the specimen and evaporates hydrogen from the solution.

$$\text{Mg}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{H}^+$$

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The diagram indicates that increasing the applied voltage and reducing the solution pH is essential for AZ80 anodizing.
Regarding the composition of the anodizing solution, insufficient alkaline hydroxide increases the decomposition voltage and produces a rough film, such that the anodized voltage does not reach the desired level. In contrast, insufficient fluoride degrades the coating, causing sparks to be generated. Kobayashi [6] found that insufficient silicate will not form a high density oxide on the metal surface; rather, it will precipitate with other constituents of the solution. Fig. 7 shows a good quality dense anodic film covered the AZ80 surface with anodic electrolyte of potassium silicate 50 ml/l, potassium hydroxide 25 g/l and fluoride 10 g/l at pH 7.5. A sealed glassy oxide film composed mainly of forsterite (2MgO·SiO2) formed on the surface of the specimens. The thickness of the anodic film, as shown in Fig. 8, was approximately 30 μm.

3.3. Electrochemical Characteristics

The effects of the converted and anodized AZ80 were electrochemically measured in the 0.9% NaCl solution. The curve of the anodized specimen rose to a higher potential of −0.45 V (SCE), whereas the original and converted AZ80 remained at the low potential of −1.53 V (SCE), as illustrated in Fig. 9. The substrate, along with the converted layer retained numerous pore-generating structures that caused anions (such as Cl− and OH−) to react with AZ80 easily and lower the open circuit potential. In contrast, the dense layer of (Mg(OH)2) on the surface of the anodized AZ80 resulted in an insulated barrier and a higher potential. Fig. 10 shows a plot of the potentiodynamic polarization curves and their Tafel approximation. A shift of the Tafel line toward the upper left of the diagram indicates an increase in the resistance to corrosion and the corrosion current density, and a decrease in corrosion behavior. The anodized specimen

![Fig. 7 – SEM image of AZ80 surface after anodizing and sealing.](image)

![Fig. 8 – SEM examination of cross-section of AZ80 anodic layer (about 30 μm).](image)

![Fig. 9 – Curve comparison of open circuit potential vs. time for AZ80, chemical conversion, and anodizing.](image)

![Fig. 10 – Comparison of Tafel curves of AZ80, chemical conversion, and anodizing.](image)
revealed the highest nobility with a corrosion current density of 0.37 \( \mu A/cm^2 \), which was much lower than that of the original AZ80 (7.62 \( \mu A/cm^2 \)). The respective corrosion rates, 0.28 mpy and 14.44 mpy, are listed, along with other corrosion data, in Table 1.

Polarization resistance can be used to estimate the corrosion resistance at electrochemical equilibrium.

Bode and Nyquist diagrams were obtained using electrochemical impedance spectroscopy (EIS) testing. Fig. 11 shows that the Bode diagram of anodized AZ80 has higher impedance than the original and converted specimens. EIS represents the way in which charges are transferred or impeded between various phases, which may be studied by the status and behavior of interfaces among conducting phases [19]. Fig. 12 presents Nyquist diagrams of semicircles of anodized and original AZ80 that correspond to their double layers and the passive films. The semicircle of original AZ80 is much smaller than that of the anodized film. The reactions across interfaces might thus be explained with reference to the equivalent circuits shown in Fig. 13(a). The resistance of the solution, and the resistance and capacitance of the double layer between the testing solution and the AZ80 substrate, are denoted as \( R_{so} \), \( R_{ct} \), and \( C_{dl} \), respectively. Other components of the resistor and the capacitor are often considered to be associated with the interfaces, resistance of passive film \( R_{pf} \), and capacitance of passive film \( C_{pf} \). A porous or non-condensed oxidation layer should establish an equivalent circuit as shown in Fig. 13(b). The anodic film with dense oxide that coated the AZ80 could be represented using an equivalent circuit as shown in Fig. 13(c).

The Appendix A contains the equations (from a simulation program written in Microsoft Excel) associated with the circuit-models in Fig. 13(a), (b) and (c). Table 1 shows that anodized AZ80 had the highest values of charge transfer resistance \( R_{ct} \) of 402 \( \Omega \) and double layer capacitance \( C_{dl} \) of 1.3 nF, which suggests that the bulk Cl\(^{-}\) and OH\(^{-}\) ions had relative difficulty going through the double layer outside of the anodized film. The excess anions and Mg\(^{2+}\) cations retained inside the double layer resulted in a high value of \( C_{dl} \). The passive capacitance \( C_{pf} \) would be
inversely proportional to its resistance; that is, a lower $C_{pf}$ estimate suggests that fewer ions remain between the interface of the dense oxide film and the substrate. The passive-film resistance ($R_{pf}$) is an important parameter for evaluating the corrosion behavior of specimens. The larger surface areas of porous oxide in the converted and original specimens resulted from more ions remaining on the interface, and consequently, a lower $R_{pf}$. Table 1 shows $R_{pf}$ values of anodized, converted, and original AZ80 of 54,200, 829 and 428 Ω, respectively. Moreover, the lower 0.56 Ω passive capacitance of the anodized specimens explains why the adhesive strength between its active film and substrate would be the strongest.

4. Conclusions

The anti-corrosion characteristics of AZ80 magnesium alloy were improved in non-chromate processes involving chemical conversion with anodizing. Anodizing generated a 30 μm thick layer as a result of chemical conversion providing an adhesive film on the substrate. The anodizing film, which had a SEM morphology of a scale pattern exhibited a slow corrosion rate of 0.28 mpy. Anodizing results in a higher resistance and a decrease in capacitance values of passive film. The corresponding Tafel polarization curves and simulated equivalent circuits showed evidence of fewer ions remaining in the film, which explains why the adhesive strength between the active film and substrate would be very strong.

Appendix A. Mathematical calculation of equivalent circuits for Nyquist diagram analysis

(a) Without passive film on the substrate surface

\[
Z = R_{so} + (Z_{C_{di}} R_{ct})
\]

\[
Z = R_{so} + \frac{R_{ct} \times Z_{C_{di}}}{R_{ct} + Z_{C_{di}}} = R_{so} + \frac{1}{\frac{1}{R_{ct} + \frac{1}{Z_{C_{di}}}} + \frac{1}{Z_{C_{di}}}} = R_{so} + \frac{R_{ct}}{\frac{1}{R_{ct} + \frac{1}{Z_{C_{di}}}}} + \frac{1}{\frac{1}{R_{ct} + \frac{1}{Z_{C_{di}}}}}
\]

\[
Z_{ad} = \left[ R_{so} + \frac{R_{ct}}{1 + (\omega R_{ct} C_{di})^2} \right] \frac{Z_{M}}{1 + (\omega R_{ct} C_{di})^2} = \left[ \frac{R_{ct}}{1 + (\omega R_{ct} C_{di})^2} \right] \frac{Z_{M}}{1 + (\omega R_{ct} C_{di})^2}
\]

(b) With a porous or non-dense passive film on the substrate

\[
Z = R_{so} + \left( Z_{C_{di}} R_{ct} \right)
\]

\[
Z = R_{so} + \frac{R_{ct} \times Z_{C_{di}}}{R_{ct} + Z_{C_{di}}} = R_{so} + \frac{1}{\frac{1}{R_{ct} + \frac{1}{Z_{C_{di}}}} + \frac{1}{Z_{C_{di}}}} = R_{so} + \frac{R_{ct}}{\frac{1}{R_{ct} + \frac{1}{Z_{C_{di}}}}} + \frac{1}{\frac{1}{R_{ct} + \frac{1}{Z_{C_{di}}}}}
\]

\[
Z_{ad} = \left[ R_{so} + \frac{R_{ct}}{1 + (\omega R_{ct} C_{di})^2} \right] \frac{Z_{M}}{1 + (\omega R_{ct} C_{di})^2} = \left[ \frac{R_{ct}}{1 + (\omega R_{ct} C_{di})^2} \right] \frac{Z_{M}}{1 + (\omega R_{ct} C_{di})^2}
\]

(c) With a compact passive film on the substrate

\[
Z = R_{so} + (Z_{C_{di}} R_{ct})
\]

\[
Z = R_{so} + \frac{R_{ct} \times Z_{C_{di}}}{R_{ct} + Z_{C_{di}}} = R_{so} + \frac{1}{\frac{1}{R_{ct} + \frac{1}{Z_{C_{di}}}} + \frac{1}{Z_{C_{di}}}} = R_{so} + \frac{R_{ct}}{\frac{1}{R_{ct} + \frac{1}{Z_{C_{di}}}}} + \frac{1}{\frac{1}{R_{ct} + \frac{1}{Z_{C_{di}}}}}
\]

\[
Z_{ad} = \left[ R_{so} + \frac{R_{ct}}{1 + (\omega R_{ct} C_{di})^2} \right] \frac{Z_{M}}{1 + (\omega R_{ct} C_{di})^2} = \left[ \frac{R_{ct}}{1 + (\omega R_{ct} C_{di})^2} \right] \frac{Z_{M}}{1 + (\omega R_{ct} C_{di})^2}
\]

\[
Z_{ad} = R_{so} + \frac{R_{ct}}{1 + (\omega R_{ct} C_{di})^2} \frac{Z_{ad}}{1 + (\omega R_{ct} C_{di})^2} = \left[ \frac{R_{ct}}{1 + (\omega R_{ct} C_{di})^2} \right] \frac{Z_{M}}{1 + (\omega R_{ct} C_{di})^2}
\]
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