

Environmental friendly plasma electrolytic oxidation of AM60 magnesium alloy and its corrosion resistance

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Abstract: Plasma electrolytic oxidation of Mg-based AM60 alloys was investigated using 50 Hz AC anodizing technique in an alkaline borate solution, which contained a new kind of organic. The anodic film is relatively smooth with some micro pores and cracks, while the anodic film consists of MgO, MgAl₂O₄ and MgSiO₃. The electrochemical behavior of anodic film was studied by electrochemical impedance spectroscopy and potentiodynamic polarization. Polarization results indicate the PEO treatment can decrease corrosion current by 3–4 magnitude compared with blank AM60 alloy. The anodic film presents a good level of corrosion protection for AM60 magnesium alloy, over 272 h of the salt spray test based on ASTM B117. The effect of micro-structure and composition on corrosion protection efficiency was also investigated.

Key words: AM60; plasma electrolytic oxidation; AC technique; corrosion resistance

1 Introduction

Magnesium and its alloys can be used in many applications with protective coatings, which are necessary to improve corrosion and/or wear resistance in aggressive environment[1–2]. The two most successful anodization treatment processes for magnesium alloys are HAE[3] and DOW17[4], existing intensive sparking on the anode to form ceramic-like films, which do not meet the current environment protection regulations. Recently, a few new environmentally friendly anodizing electrolytes have been developed[5–6] on pure magnesium or AZ series magnesium alloy. Among those newly developed anodizing electrolytes, some additives and their concentrations played important roles in affecting the properties of the anodic films[6]. TAKAYA[7] employed secondary ion mass spectroscopy (SIMS) surface analysis to research the atomic concentration profile for anodic film, which mainly

consisted of MgO. Anodic films were shown to be very porous and to have a partially vitrified structure with entrapment of spherical gas bubbles in the sintered material[6], such as MgAl₂O₄, due to the incorporation of some electrolyte into the film. Plasma anodizing differs from the so-called “classical anodizing” in that it involves the application of very high voltages, higher than the dielectric breakdown voltage with intensive sparking. As a result, plasma creates locally yielding sparking on the metal surface. Numerous studies have been published on plasma anodizing of different metals[8–9], but this plasma anodizing technology applied to AM60 magnesium alloy to increase its corrosion resistance is few.

In the present study, the effects of treating time, applied AC voltage, additives Na₂SiO₃ concentration in alkaline borate basic solution on the plasma anodic film on AM60 Mg alloy were investigated. The morphology and composition of the anodic film obtained were then analyzed on the basis of observations made using

scanning electron microscopy(SEM), electron dispersion X-ray spectroscopy(EDX) and X-ray diffractometry (XRD).

2 Experimental

2.1 Materials and specimen preparation

The composition of AM60 magnesium alloy is listed in Table 1. The working electrode consisted of a plat, 2.0 cm×2.0 cm×0.5 cm, cut from the ingot. Both two faces and four sides were mechanically polished using abrasive emery paper, then polished using abrasive paper by hand. Copper wire was used as an electrical contact and to suspend the disc in solution. Before the AC potential was applied, the AM60 electrodes were degreased ultrasonically in acetone for 10 min and then dried by warm air.

Table 1 Composition of AM60 alloy (mass fraction, %)

Al	Zn	Mn	Cu	Fe	Sn	
5.83	0.009	0.32	<0.002	<0.005	<0.002	
Pb	Ni	Be	Cr	Zr	Sr	Mg
<0.002	<0.001	<0.001	<0.001	<0.002	<0.001	Bal.

The morphologies of the as-obtained film and corresponding cross-section were observed using SIRION scanning electron micro-scope(SEM) manufactured by FEI. The composition of the film was examined by EDX components assembled on the SIRION SEM. Cross sectional examination of films was achieved by sectioning of specimens by ultramicrotomy and imaging the cut surface by SEM, using the procedures described in Ref.[10]. The structures of plasma electrolytic oxidation(PEO) films were determined by X-ray diffractometry(XRD) using a Philips X' PERTAPD instrument, with radiation from a copper anode.

2.2 PEO process

The basic anodic electrolyte used for AM60 alloy was composed of 50 g/L NaOH, 10 g/L Na₂B₄O₇, 20 g/L H₃BO₃ and 10 g/L C₆H₅Na₃O₇ (trisodium citrate dihydrate), with 2 g/L organic additive. Anodization of AM60 plates was performed in 300 mL glass cell, with a removable top containing four holes for two electrodes, stirring and gas evolution. The two electrodes stood in stain steel container by clincher, and their distance was controlled in 2 cm. The system was cooled by circular tap water using a squirmy pump.

2.3 Electrochemical setup

Potentiodynamic polarization was carried out using CHI660A Potentiostat (CH Instruments Inc., US) at (25±1) °C. A three-electrode cell with pretreated ceramic-like film as working electrode, saturated calomel

electrode as reference electrode and platinum sheet as counter electrode was employed in the test. The ratio of volume of neutral 3.0%(mass fraction) NaCl solutions (pH 7.03) to sample area was 50 mL/cm². When the open circuit potential(OCP) became steady (about 30 min), potential scanning range was conducted at a rate of 1 mV/s from -0.25 V to 1.25 V (vs OCP). Electrochemical impedance spectroscopy(EIS)[11-12] was measured using impedance measurement unit (VMP2, Applied Research Institute) from 100 kHz to 0.01 Hz at six frequency points per decade with voltage amplitude of 10 mV. All EIS tests were carried out at the OCP in neutral 3.0% NaCl solution to determine the corrosion resistance. Before EIS test, the working electrodes were immersed in NaCl solution at least 30 min until the OCP became steady.

2.4 Salt spray test

The aerated salt spray tests were carried out according to the ASTM B117 standard salt spray testing. The round edges and one surface of the disk specimens were sealed with epoxy resin so as to leave only one surface exposed to the salt mist. The specimens were left in the chamber and examined every 12 h. Before examination, they were gently cleaned with running water and then pure alcohol to remove salt deposits from the surfaces, followed by warm air drying and optical examination.

3 Results and discussion

3.1 PEO process kinetics and preparation of film

Under the experimental condition, constant AC potential, such as 100, 110, 120 and 130 V, were applied on the bath containing base electrolyte with 10 g/L silicate. Fig.1 shows the typical current density transient for PEO of AM60 Mg alloy at AC 120 V in first 3 min. The corresponding current decreases sharply in first 20 s due to ivory-white film formation on the AM60 surface. Because the dielectric breakdown value of AM60 magnesium alloy is about 65 V[9], fragmentary sparking with blue light appears on the surface of the metal at this applied voltage accompanied by bubble evolution. Some sparking scans over the whole surface and leaves trace of a white oxide film. After 60 s, the current keeps relatively stable, and no marked sparking is found. At the end of PEO treatment, 10 min, a relatively thin impact film is obtained.

Different applied AC voltage of PEO on AM60 magnesium shows similar corresponding current density transient behavior. With the applied AC voltage increasing, the intensity of sparking increases with strongly gas bubble evolution. At the same time, the time of the corresponding current reaching the minimum

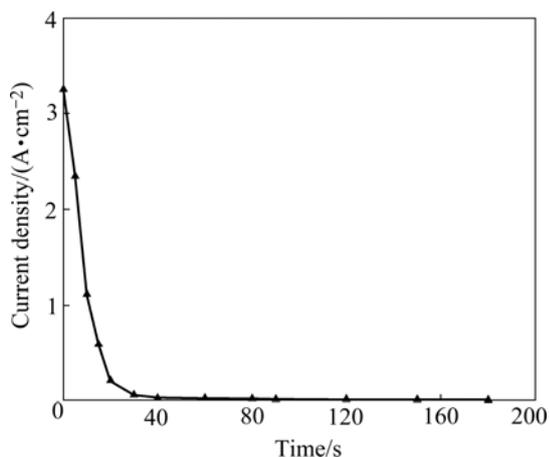


Fig.1 Typical current density transient for PEO of AM60 Mg alloy at AC 120 V in first 3 min

current plateau is shortened to 10–30 s. A continuous impact film is seen on the surface of AM60 magnesium, and the thickness of film increases with applied AC signal except for 130 V. When the applied voltage increases to 130 V, the electrolyte becomes boiling in 25 s, with strong sparking and gas evolution. A coarse surface film is obtained. The effect of silicate additive on PEO of AM60 mainly concentrates on the intensity of sparking, which means that the intensity of sparking decreases without the silicate, while the temperature is also low.

Based on the electrochemical test result (shown in next part), 120 V AC signal is the best choice to improve corrosion resistance of AM60 magnesium alloy. Anodi-

zation time is important technology parameter, so we delay the treatment time to 30 min at 120 V AC voltage. After 3 min, the intensity of sparking decreases significantly. At 10 min, no marked sparking is observed by naked eyes, and the current density decreases to 0.18 A/cm². At the end of PEO treatment, no spark discharge and gas evolution are found. A smooth impact surface film on the AM60 magnesium is found. Due to constant AC voltage, PEO process of AM60 in basic borate electrolyte is distinguished into two stages, plasma anodizing and followed arcing regime, which is different from the results of VERDIER and BOINET[9] using constant current mode.

3.2 Morphology and structures of film

Fig.2 shows backscattered electron images of AM60 surface after PEO for 10 min in a bath containing base electrolyte with 10 g/L Na₂SiO₃ under different applied AC voltages. First, we can find that the films are relatively smooth. Secondly, there are some small pores (point *a* in Fig.2) and cracks (point *b*) appearing on the surface. When the applied voltage is over the value of film breakdown, intensive local damage occurs in the anodic film. The pores observed are probably the trace left by the sparks while the cracks are formed during cooling of the anodic film by surrounding relatively cool electrolyte. IKONOPISOV[12] thought this phenomenon was the initial loss of anodic film at the breakdown spot through plasma generation as a result of electron avalanche. Overall, all four surfaces have a fused aspect, probably due to the fact that the film is formed by means

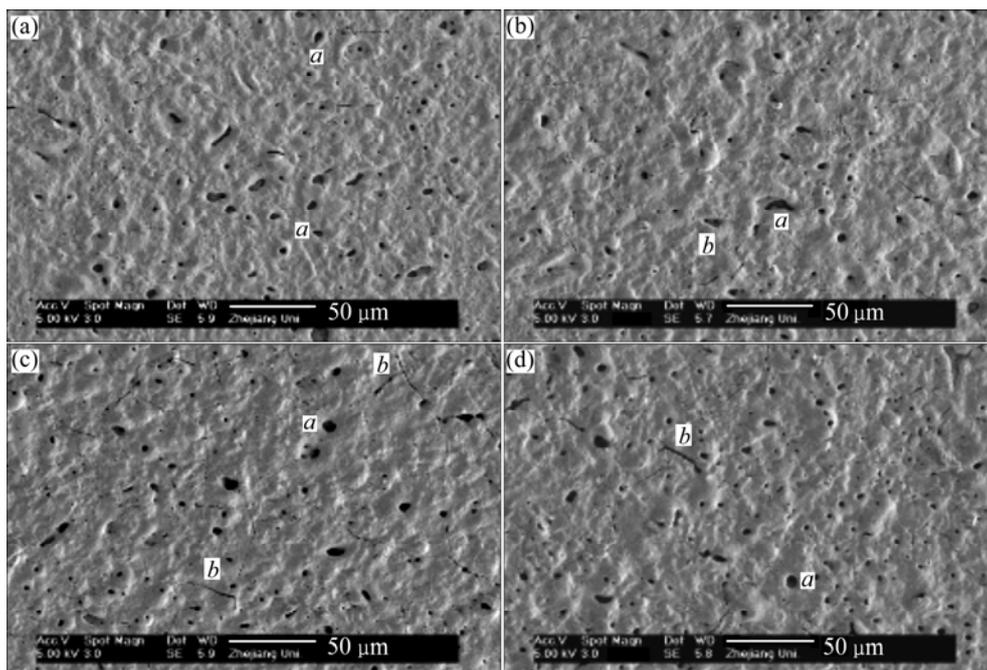


Fig.2 Surface micrographs of AM60 anodic film with different applied AC potentials: (a) 100 V; (b) 110 V; (c) 120 V; (d) 130 V

of plasmas, within which the temperature reaches several thousand degrees[13]. Such high temperature results in the fusion of the film. Secondly, there are no significant cracks at applied 100 V AC voltage, probably due to no exquisite sparking. Thirdly, no marked difference of surface morphology is shown in Fig.2 when the applied voltage increases from 110 to 130 V. This inhomogeneity of the film growth and trapping of gas bubbles in the growing film are responsible for quenching under sparking. The corresponding XRD plots are shown in Fig.3. Firstly, some peaks are related to the AM60 Mg alloy substrate, which mainly consists of primary α solid solution phase due to porous film. Secondly, when the applied AC voltage increases from 120 to 130 V, the relative intensity of Mg increases; while relative intensity of MgO decreases. Thirdly, the film contains three crystallized oxides: magnesium oxide (MgO), a mixed oxide of silicon and magnesium (MgSiO_3) and MgAl_2O_4 spinel, which is different from FUKUDA's work[14]. This difference may be aroused by the kind of Mg alloy and power source model. These oxide materials will benefit to the corrosion resistance of Mg alloy.

With the concentration of Na_2SiO_3 increasing from 5 to 20 g/L, the surface morphology does not show significant difference. There are numerous pores and several cracks on the surface like those shown in Fig.2. When the treating time increases to 30 min, the sparking discharge behavior disappears for 10 min, and no significant film formation appears by naked eyes. The

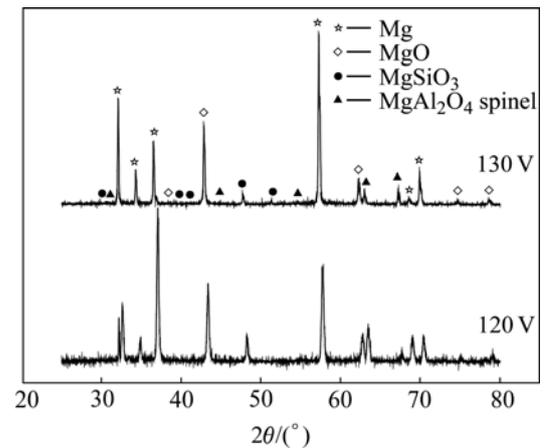


Fig.3 Relative intensities of PEO films formed in bath containing base electrolyte and 10 g/L Na_2SiO_3 with different applied AC voltages

SEM morphology of anodic film formed for different time indicates there are not marked changes on the surface film.

Fig.4 shows some typical cross section of anodic film on AM60 magnesium alloys. The thickness of the film is between 25 and 30 μm after anodizing, which is larger than that shown in Ref.[9]. The thickness of film increases with applied voltage increasing (Figs.4(a), (c) and (d)) and anodizing time (Figs.4(b) and (c)). The thickness of anodic film is heterogeneous, as well as the presence of pores in film, part of them transfixing the

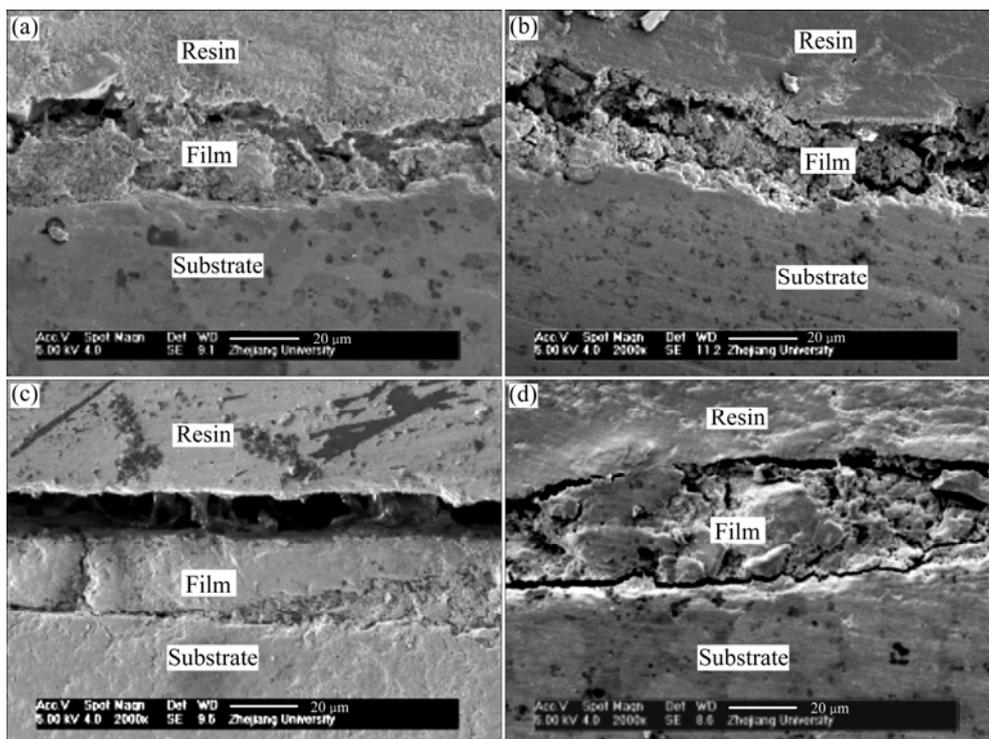


Fig.4 Cross sectional morphologies of anodic film under different experiment conditions in basic electrolyte and 10 g/L Na_2SiO_3 : (a) 110 V, 10 min; (b) 120 V, 3 min; (c) 120 V 10 min; (d) 130 V, 10min

film (Figs.4(b) and (c)) and places where the film is detached from the substrate (Figs.4(b) and (d)). Comparison with other cross sectional morphology, the anodic film formed in alkaline borate solution at 120 V AC voltage for 10 min is the relatively most impact and entire.

Figs.5 and 6 show the X-ray diffraction patterns of AM60 magnesium alloy with different treating time and Na_2SiO_3 concentration respectively. Two types of peaks of XRD are found. One type is related to AM60 magnesium, while the other type is related to oxide formed with electrolyte's element. All XRD patterns of samples indicate there are Mg, MgO, MgSiO_3 and MgAl_2O_4 . The strong Mg peaks are mainly due to the thick anodic film and porous structure, which is only several decades of micron with pores and cracks. With the treating time increasing from 3 min to 30 min, the relative content of MgO increases. Longer anodizing treatment is not always beneficial to film integrality, especially 30 min. The relative intensity of Mg(110) of 30 min is much higher than that treated for 10 min or 3 min, indicating longer anodizing breaks the integrality of

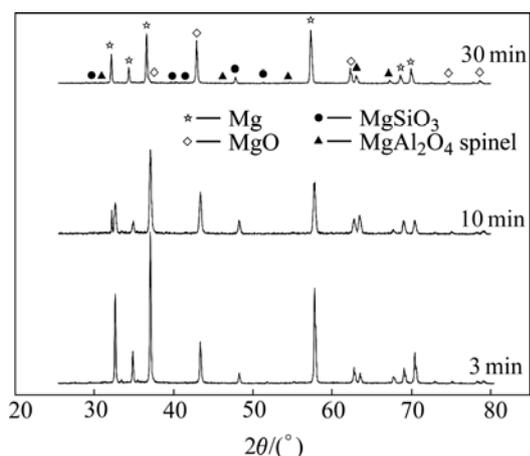


Fig.5 XRD patterns of PEO films formed in bath containing base electrolyte and 10 g/L Na_2SiO_3 for different treating time

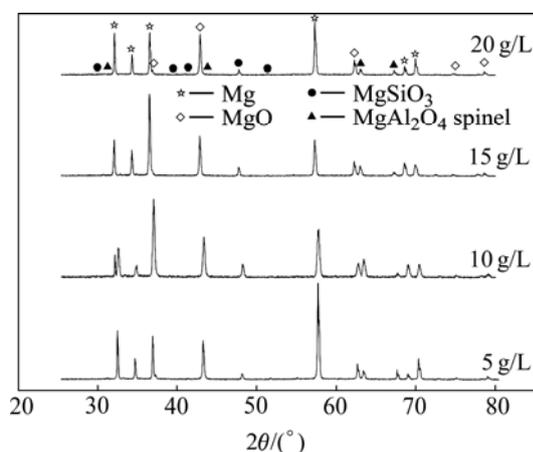


Fig.6 XRD patterns of PEO films formed in bath containing base electrolyte and different Na_2SiO_3 concentrations

film. From Fig.6, the relative intensity of Mg decreases with Na_2SiO_3 concentration increasing from 5 g/L to 15 g/L, while increases at 20 g/L Na_2SiO_3 . The relative intensity of MgO doesn't show marked change except 20 g/L. From Fig.7, it is easy to find that film shows some big crack transfixing the whole film. Compared with 10 g/L Na_2SiO_3 shown in Fig.4, the integrality of the film formed with 20 g/L Na_2SiO_3 becomes worse.

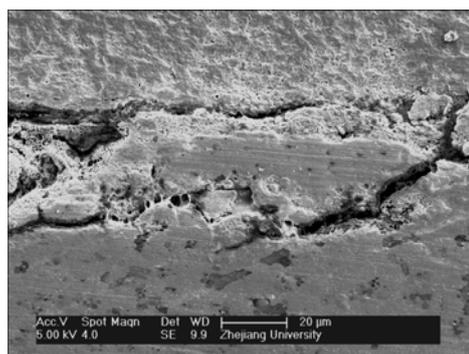


Fig.7 Cross sectional morphology of AM60 anodic film formed with basic electrolyte and 20 g/L Na_2SiO_3 for 10 min at 120 V AC voltage

3.3 Corrosion on film

Fig.8 shows the potentiodynamic polarization curves with different applied AC voltages and naked AM60. With the applied AC voltage increasing from 100 to 120 V, the free current density J_0 decreases from $1.471 \times 10^{-6} \text{ A}\cdot\text{cm}^{-2}$ to $0.731 \times 10^{-6} \text{ A}\cdot\text{cm}^{-2}$, then increases to $1.759 \times 10^{-6} \text{ A}\cdot\text{cm}^{-2}$ at 130 V (as listed in Table 2), which is higher than that of film formed at the lowest voltage. At the low voltage, such as 100 V, the film formation process is restricted while high voltage will promote film breaking, which is consistent with the PEO process and micro morphology discussed above. Although at 130 V the sample presents a longer passivation plateau, higher corrosion potential, lower current in a large potential range, J_0 of this sample is higher and the

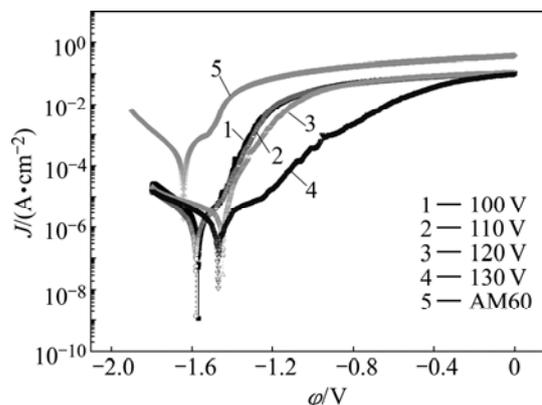


Fig.8 Potentiodynamic polarization curves of anodic film for different applied AC voltages and AM60 magnesium

corrosion resistance of salt spray test is low, so the film formed at 120 V AC voltage is the best choice for the following experiment. Fig.9 gives the potentiodynamic polarization curves with different anodizing time and naked AM60. It is clear to find that longer anodizing time doesn't benefit to corrosion resistance from electrochemical test through the simulation results shown in Table 2. Fig.10 shows the potentiodynamic polarization curves with different Na₂SiO₃ concentrations. From Table 2, the anodic film shows the best corrosion resistance when the Na₂SiO₃ concentration is 10 g/L. Much higher or lower Na₂SiO₃ content changes the PEO film formation, morphology and structure of the film, which affects the electrochemical corrosion behavior. From the potentiodynamic polarization figures, two clear results can be obtained. Firstly, the open circuit potential shifts to positive direction after PEO treatment; secondly, both the anodic curve and cathodic curve move to lower current density side. Above results indicate both of anodic and cathodic reactions are restrained by PEO treatment, and the corrosion resistance gives a remarkable increase, while J_0 of naked AM60 magnesium alloy in NaCl solution is only about 10⁻³A/cm. Therefore the PEO treatment of AM60 magnesium alloy can decrease the corrosion current density by three, even four orders of magnitude. From the simulation results (Table 2), polarization resistance R_p is calculated according to Stern-Geary equation[15]:

$$R_p = \frac{\beta_a \times \beta_c}{2.303 \times (\beta_a + \beta_c) \times J_0}$$

where β_a and β_c are the anodic and cathodic Tafel slope.

The similar corrosion behavior of AM60 with different PEO parameters is obtained. In the alkaline borate electrolyte, 120 V AC voltage, 10 g/L Na₂SiO₃, and 10 min are effective parameters to get high corrosion

resistance anodic film of AM60 magnesium alloy.

Fig.11 shows the typical Nyquist and Bode plots of AM60 magnesium alloy anodic film with different concentration of Na₂SiO₃. All EIS plots of anodic film were collected at OCP in 3.0% NaCl solution for 20 min. It is obvious to find that EIS behavior of anodic film with different additives takes on two capacitive time constant

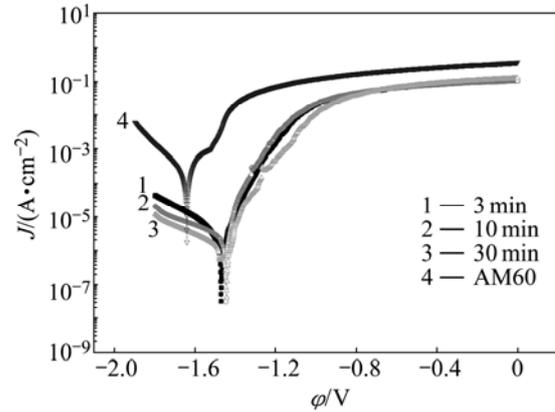


Fig.9 Potentiodynamic polarization curves of anodic film for different anodizing time and AM60 magnesium alloy

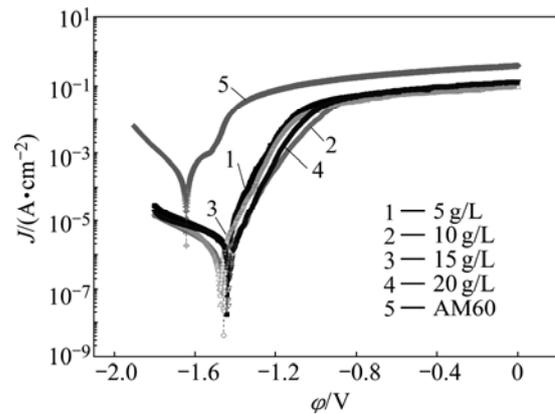


Fig.10 Potentiodynamic polarization curves of anodic film for different Na₂SiO₃ concentrations and AM60 magnesium

Table 2 Simulation of potentiodynamic polarization curves with different treatment parameters

Applied AC voltage/ V	Treatment time/ min	Concentration of Na ₂ SiO ₃ / (g·L ⁻¹)	β_c	β_a	J_0 / (10 ⁻⁶ A·cm ⁻²)	R_p / (10 ⁶ Ω·cm ²)
100	10	10	5.738	10.75	1.471	1.104 32
110	10	10	5.196	9.243	1.249	1.156 35
120	10	10	3.31	12.81	0.731	1.562 43
130	10	10	4.115	4.353	1.759	0.522 18
120	3	10	4.611	12.53	2.154	0.679 47
120	10	10	3.31	12.81	0.731	1.562 43
120	30	10	3.147	8.42	2.470	0.402 70
120	10	5	2.829	12.40	3.469	0.288 33
120	10	10	3.31	12.81	0.731	1.562 43
120	10	15	1.57	13.56	3.113	0.196 27
120	10	20	1.079	10.63	2.607	0.163 15

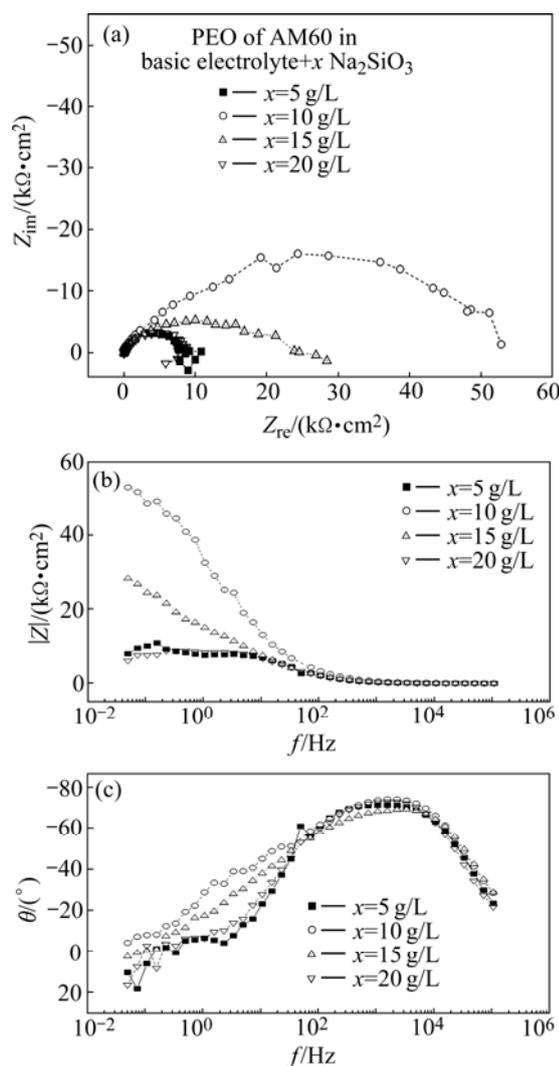


Fig.11 Nyquist and Bode plots for AM60 Mg alloy anodic film formed in basic electrolytes with various concentrations of Na_2SiO_3

at high frequency domain and low frequency domain respectively (Fig.11). According to our previous work [16] and XIA's work[17], the two capacitive arcs of high and low frequency domain represent the information of the outer porous and inner barrier layers of magnesium alloy's anodic film[18–19]. For AM60 magnesium alloy, the two layer structure of anodic film is not remarkable from the cross sectional image shown in Fig.4. In the strong aggressive solution containing Cl^- ions, the film, especially with weakness of film where there are pores and cracks, is attacked. R_{if} (low frequency resistance) is chosen to evaluate the corrosion resistance of anodic film of AM60. From Fig.11, the anodic film formed in basic electrolyte with 10 g/L Na_2SiO_3 at 120 V AC voltage for 10 min shows the best corrosion resistance, while that with 5 g/L and 20 g/L Na_2SiO_3 shows the similar corrosion resistance through EIS results. The more the Na_2SiO_3 is added over 10 g/L, the less the corrosion

resistance appears. The corrosion resistance of AM60 anodic film from EIS is similar from potentiodynamic polarization.

A salt spray testing cabinet (model FYWX/Q-250, made in Jinhua, Wuxi, China) was used to maintain salt spray (fog) test environment. The specimen with anodic film was subjected to a salt spray fog test according to ASTM B117 standard, with 5% NaCl in the spray water at pH 7.0. The exposure zone of the salt spray chamber was maintained at 35 °C, and depositing ratio of salt fog was $0.2 \text{ mL}\cdot\text{cm}^2\cdot\text{h}^{-1}$. The spray nozzle atomized continuously to convert salt solution into uniform small droplets. Four samples without any sealing process were chosen to evaluate corrosion resistance by this salt spray acceleration test, and exposed area of all samples was $2 \text{ cm}\times 2 \text{ cm}$ by epoxy resin. AM60 substrates without PEO treatment have 6–7 relatively large pits on the surface after 16 h, where white corrosion productions are found surrounding the pits. Different applied AC voltage shows strong effect on anti-salt spray time. Samples of 100 V and 130 V show bad corrosion attack in 96 h, and some marked pores appear, while samples of 110 V and 120 V show serious corrosion attack in 248 h, indicating that the intensity of sparking is the most importance factor for increasing corrosion resistance of magnesium alloy. Samples of anodizing 3 min and 30 min in basic electrolyte with Na_2SiO_3 show the similar salt spray result, while 10 min sample shows relatively good corrosion resistance. Different Na_2SiO_3 content samples show similar results, but 10 g/L is still the best choice. According to ASTM B117, anti-salt spray time of these films is about 250–300 h, which is the same level with DOW 17, HAE and Anomag techniques[19]. In our experiments, anodic film with 10 g/L Na_2SiO_3 additives has the best anti-salt spray potential. After being exposed in spray fog for 96 h, only one sample has a little pit observed by naked eye; 192 h later, three samples have pits; 272 h later, four samples all have pits. The whole corrosion area fraction of PEO film is controlled in 8%–12% (four samples) and these corrosion pits are independent, which means that the gas evolution channels become the weakest site of PEO film.

4 Conclusions

1) Convenient AC PEO of AM60 magnesium alloy in an alkaline borate solution with silicate additives is investigated. An ivory-white smooth PEO film of AM60 magnesium alloys with high corrosion resistance is obtained.

2) Numerous pores and cracks appear on the anodic film surface, while some pores and cracks even transfix the whole PEO film from cross sectional SEM images. XRD results indicate that the anodic film is mainly

composed of Mg, MgO, MgSiO₃ and MgAl₂O₄.

3) PEO treatment can decrease the corrosion current density by three, even four orders of magnitude by dynamic potential scan experiment. Two characteristically capacitive arcs are found in the high and low frequency domain of EIS respectively. Salt frog experiment also gives a accelerated corrosion test, and the results indicate that the PEO film (naked, unsealing) with 10 g/L Na₂SiO₃ has over 272 h anti-salt spray time based on ASTM B117 standard.

References

- [1] BONILLA F A, BERKANI A, LIU Y, SKELDON P, THOMPSON G E, HABAZAKI H, SHIMIZU K, JOHN C, STEVENS K. Formation of anodic films on magnesium alloys in an alkaline phosphate electrolyte [J]. *J Electrochem Soc*, 2002, 149(1): B4–B13.
- [2] DING J, LIANG J, HU L T, HAO J C, XUE Q J. Effects of sodium tungstate on characteristics of microarc oxidation coatings formed on magnesium alloy in silicate-KOH electrolyte [J]. *Trans Nonferrous Met Soc China*, 2007, 17(2): 244–249.
- [3] EVANGELIDES H A. Method of electrolytically coating magnesium and electrolyte therefor [P]. US 2723952, 1955.
- [4] The Dow Chemical Company. Bath for method of producing a corrosion resistant coating upon light metals [P]. GB 762195, 1956.
- [5] ZHANG Y, YAN C, WANG F, LOU H, CAO C. Study on the environmentally friendly anodizing of AZ91D magnesium alloy [J]. *Surf Coat Tech*, 2002, 161(1): 36–43.
- [6] MIZUTANI Y, KIM S J, ICHNO R, OKIDO M. Anodizing of Mg alloys in alkaline solutions [J]. *Surf Coat Tech*, 2003, 169: 143–146.
- [7] TAKAYA M. Luminescence phenomena on anodized coating surface of magnesium alloys [J]. *Aluminum*, 1989, 65: 1244–1248.
- [8] MONTERO I, FERNANDEZ M, ALBELLA J M. Pore formation during the breakdown process in anodic Ta₂O₅ films [J]. *Electrochim Acta*, 1987, 32(1): 171–174.
- [9] VERDIER S, BOINET M, Maximovitch S, Dalard F. Formation, structure and composition of anodic films on AM60 magnesium alloy obtained by DC plasma anodizing [J]. *Corros Sci*, 2005, 47: 1429–1444.
- [10] ECHEVERRIA E, SKELDON P, THOMPSON G E, HABAZAKI H, SHIMIZU K. Examination of cross sections of thin films by atomic force microscopy [J]. *J Electrochem Soc*, 1999, 146: 3711–3715.
- [11] UDHAYAN R, BHATT D P. On the corrosion behavior of magnesium and its alloys using electrochemical techniques [J]. *J Power Sources*, 1996, 63: 103–107.
- [12] IKONOPISOV S. Theory of electrical breakdown during formation of barrier anodic films [J]. *Electrochim Acta*, 1977, 22: 1077–1082.
- [13] YEROKHIN A L, NIE X, LEYLAND A, MATTHEWS A, DOWEY S J. Plasma electrolysis for surface engineering [J]. *Surf Coat Tech*, 1999, 122: 73–93.
- [14] FUKUDA H, MATSUMOTO Y. Effects of Na₂SiO₃ on anodization of Mg-Al-Zn alloy in 3 M KOH solution [J]. *Corros Sci*, 2004, 46: 2135–2142.
- [15] STERN M, GEARY A L. Electrochemical polarization (I): A theoretical analysis of the shape of polarization curves [J]. *J Electrochem Soc*, 1957, 104: 56–63.
- [16] CAO F H, ZHANG Z, ZHANG J Q, CAO C N. Plasma electrolytic oxidation of AZ91D magnesium alloy with different additives and its corrosion behavior [J]. *Materials and Corrosion*, 2007, 58(9): 696–703.
- [17] XIA S J, YUE R, RATEICK R G, BRISS V I. Electrochemical studies of AC/DC anodized Mg alloy in NaCl solution [J]. *J Electrochem Soc*, 2004, 151(3): B179–B187.
- [18] SUAY J J, GIMENEZ E, RODRIGUEZ T, HABBIB K, SAURA J J. Characterization of anodized and sealed aluminum by EIS [J]. *Corros Sci*, 2003, 45: 611–624.
- [19] BLAWERT C, DIETZEL W, GHALI E, SONG G. Anodizing treatments for magnesium alloys and their effect on corrosion resistance in various environments [J]. *Advanced Engineering Materials*, 2006, 8(6): 511–533.

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