



Effect of potassium fluoride on structure and corrosion resistance of plasma electrolytic oxidation films formed on AZ31 magnesium alloy

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ABSTRACT

Plasma electrolytic oxidation films on AZ31 magnesium alloy were prepared in silicate–KOH–glycol (base electrolyte) electrolyte with the addition of different KF concentration. The effect of KF on the characteristic of discharge in electrolytes was studied. The compositions, structures and morphologies of the oxide films formed in different KF concentration were determined by energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Corrosion behavior of the oxide films was evaluated in 3.5 wt.% NaCl solution using potentiodynamic polarization tests, electrochemical impedance spectroscopy and potentiodynamic scanning tests. The films were mainly composed of Mg, Al, O, C, Si as well as a trace of Na and K. Major phases were MgSiO_3 and forsterite Mg_2SiO_4 . The appearance of KF in the base electrolyte resulted in the decrease of the equilibrium current density and the appearance of MgF_2 in the films. Corrosion resistance depends on the amount of MgF_2 composition in the films. The films formed in the electrolyte containing 8.0 g/L KF exhibit the highest uniform corrosion resistance and the lowest pitting-corrosion tendency in NaCl solution.

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1. Introduction

Magnesium has a unique combination of high strength/weight ratio, high dimensional stability, good electromagnetic shielding and damping characteristics [1], which makes it one of the most promising metals for light weight industry application. But it is still not widely accepted because of its poor corrosion resistance [2].

Corrosion resistance can be improved by using high purity magnesium, containing limited amounts of iron, nickel and copper [3]. Furthermore, corrosion resistance can be improved significantly by alloying the magnesium with different elements, such as aluminium and manganese [4]. Chromate conversion coatings are typical technology for magnesium coating. This surface treatment is based on hexavalent chromium, which is highly toxic. Its pre-treatment process is also complex which include vapor oil removal, alkali washing, acid washing and so on [5]. Thus, it is necessary to develop chrome-free and simple process surface treatments before using magnesium alloys for structural applications. There are some alternatives to hexavalent chromium for protecting magnesium and its alloys. One of these alternatives is plasma electrolytic oxidation (PEO) [6], which developed from conventional anodic oxidation, has proved to be promising due to some significant properties of the PEO films, such as good adhesion, high hardness and high corrosion

resistance [7]. It has been found that the electrolyte compositions play a crucial role in the PEO process and it is imperative to properly select the electrolyte compositions so that the rapid metal passivation can be promoted and the sparking voltage can be easily reached. Guo and An [8] showed that the addition of compounds containing F^- ion into the electrolyte solution helped to increase the electrolyte conductivity and characterized by complex behavior during PEO process. Liang et al. [9] reported on the effect of the F^- containing compounds added in the electrolyte on the mechanical and tribological behavior of the PEO coatings. However, little has been reported on the effect of F^- concentration in the electrolyte solution on the corrosion resistance performance of PEO films formed with constant voltage.

In this study, PEO surface treatment of magnesium alloy AZ31 was applied. Na_2SiO_3 , KOH and glycol were used as base electrolyte. Effect of different KF concentration on PEO films' structures, composition and morphologies formed on AZ31 magnesium alloy was evaluated. The effect on corrosion resistances of the oxide films was also evaluated.

2. Experimental details

2.1. Preparation of the PEO films

Prior to the oxidation process, AZ31 magnesium alloy sheets with a size of 10 mm × 10 mm × 5 mm (mass fraction: Al 3.1074%, Mn 0.4219%, Zn 0.9075%, balance magnesium) were polished with waterproof abrasive paper up to 2000 grif. Then degreased ultrasonically with acetone and washed with distilled water. DC power supply was employed for the PEO treatment. Magnesium alloy sample and

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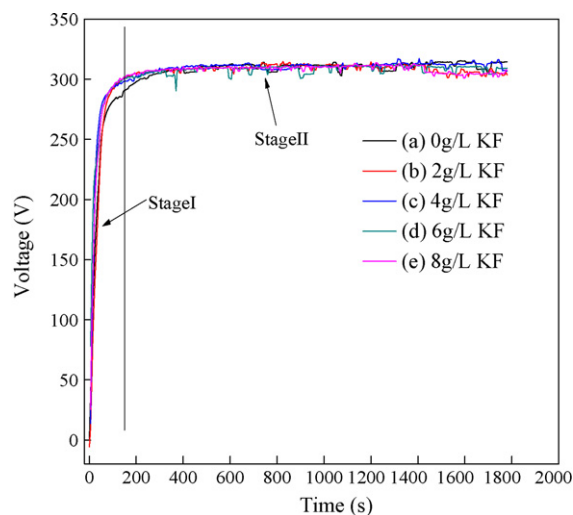


Fig. 1. Variation of voltages with time added with different KF concentration in base electrolyte.

the stainless steel were used as the anode and the cathode, respectively. The base electrolyte was composed of 4.0 g/L KOH, 20.0 g/L Na_2SiO_3 and 10 mL/L glycol. Concentration of KF varied from 0 to 8.0 g/L. The solution was kept at 294 ± 298 K during the oxidation by circulating cooling water and stirring the electrolyte. Applied voltage was 300 V and the duration of experiments was 30 min. The voltage and the current were measured by data acquisition systems at 5 Hz.

2.2. Characterization of the PEO films

The phase composition of the magnesium films was studied by X-ray diffraction (XRD, D/MAX-3A), using a Cu-K α radiation as the excitation source at a grazing angle 2° . The surface morphology and microstructure of the PEO films were observed with a LEO 1530 VP scanning electron microscope (SEM). The chemical composition in

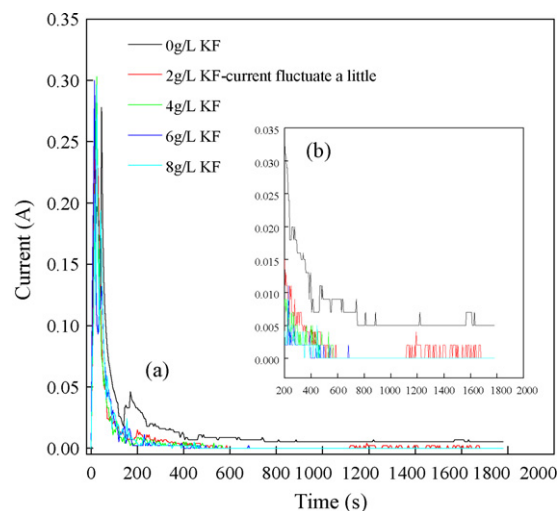


Fig. 2. Variation of currents with time added with different KF concentration in base electrolyte: (a) 0–1800 s and (b) 200–1800 s.

the films was investigated with energy dispersive X-ray spectroscopy (EDS) affiliated with SEM.

2.3. Corrosion testing

Corrosion resistance of the oxide films was assessed by potentiodynamic polarization tests using Autolab system in 3.5 wt.% NaCl solution, temperature of the solution was kept at 294 ± 298 K. Samples were sealed with epoxy resin and immersed into the solution with 0.5 cm^2 exposed area. A saturated calomel electrode (SCE) and a platinum plate were used as a reference and counter electrode, respectively. After 30 min of initial delay, scan was conducted with a constant rate of 1 mV/s from -1.9 V to reach -1.3 V potential versus the reference electrode. The impedance spectroscopy (EIS) was obtained at open circuit potential (OCP) in the

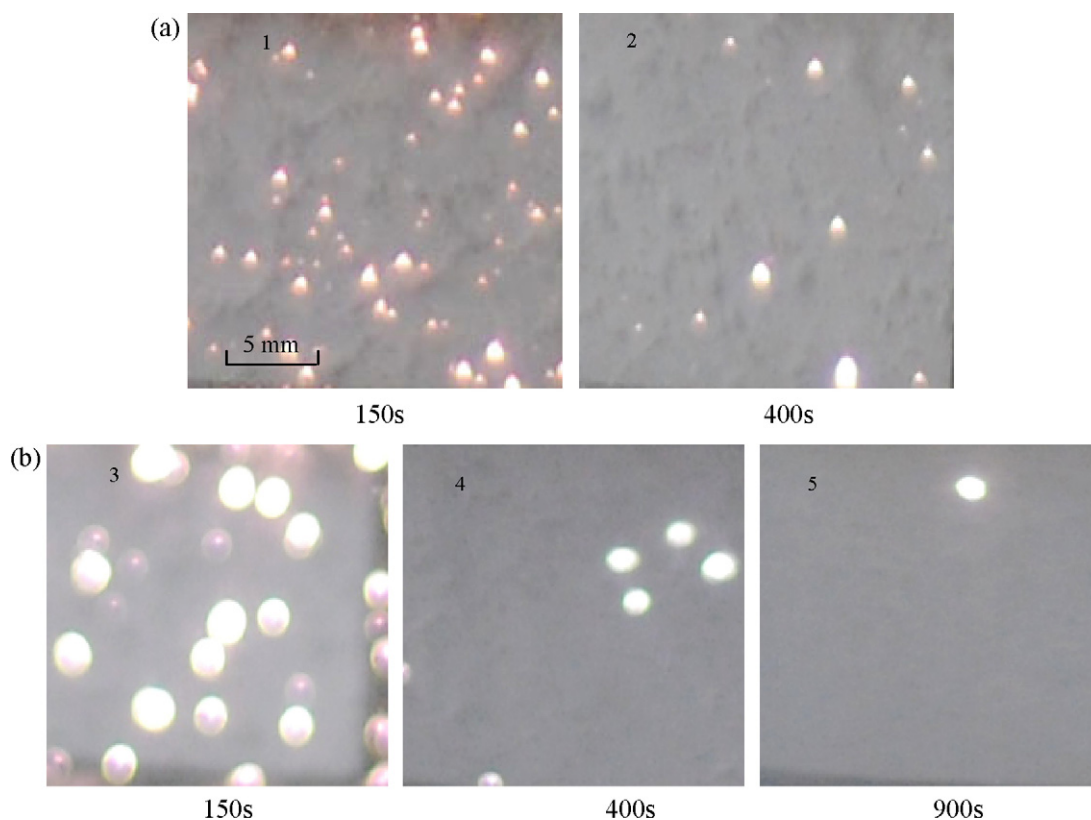


Fig. 3. Discharge characteristics of the samples in base electrolyte and in base electrolyte added with KF: (a) in base electrolyte and (b) in base electrolyte with 8 g/L KF.

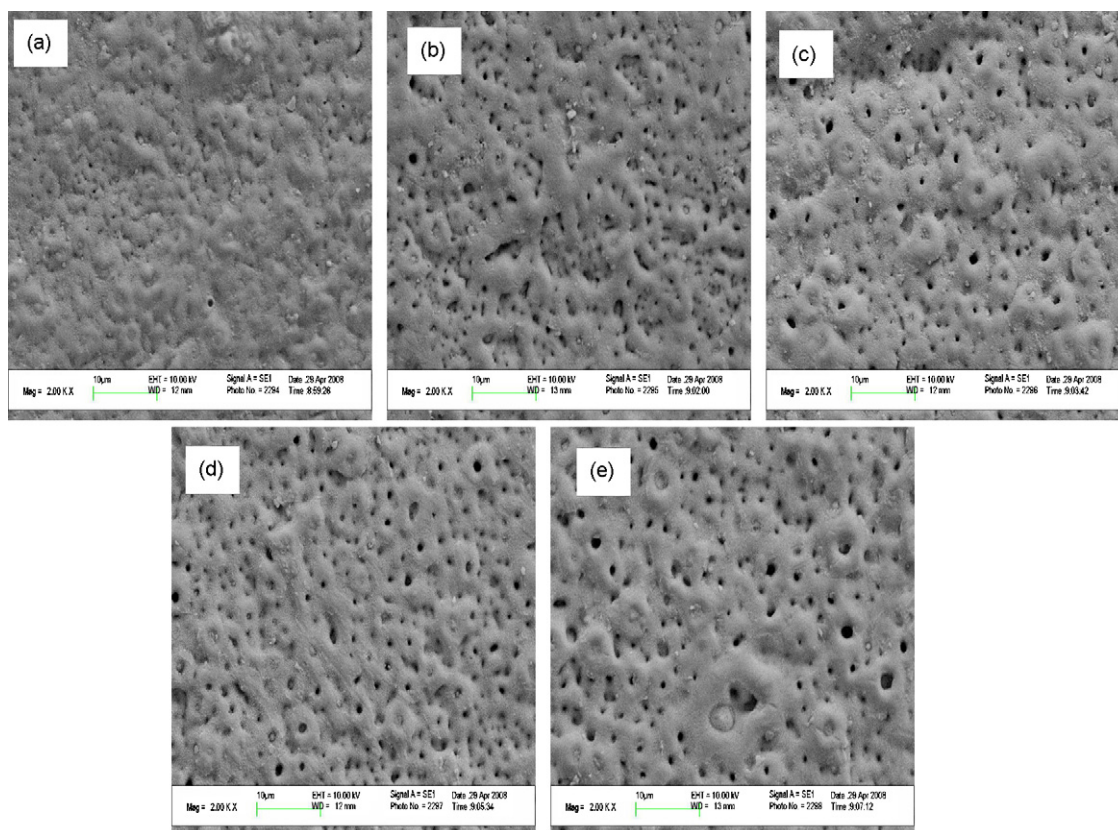


Fig. 4. Surface morphologies of PEO films formed in base electrolyte containing different KF concentration. (a) 0 g/L KF, (b) 2 g/L KF, (c) 4 g/L KF, (d) 6 g/L KF and (e) 8 g/L KF.

same solution using an Autolab system analyzer, the amplitude of the scanning sine waveform was 50 mV and the frequency was logarithmically swept from 10^{-2} to 10^5 Hz. The potentiodynamic scanning curve was scanned from -2.0 to 0 V then back to -2.0 V, scanning rate was 10 mV/s.

3. Results and discussion

3.1. Effect of KF on the discharge characteristics

The voltages in the electrolytes under different KF concentration during the PEO processes are shown in Fig. 1. Fig. 1 shows that KF has no influence on the variations of voltages and two stages can be classified according to the increasing rates of the voltages. Namely, the voltages increase significantly in a short time in stage I and maintain nearly constant in stage II. The voltages increase linearly in stage I for all electrolytes and visible sparking was observed when the applied voltages are higher than their breakdown voltages. In stage II, the voltages and currents maintain nearly constant because of the relative steady discharge and the relative steady growth rate of the films. The relationship between currents and time is shown in Fig. 2. Trends of the current curves are different for different KF concentration. The current decreases to a relatively low value (5–7 mA) without the addition of KF after 750 s and it decreases to nearly 0 mA in the electrolyte with the addition of KF except for the case of 2 g/L KF after 750 s. The discharge sparks in the electrolyte with KF are larger than that without KF during 150–750 s, the sparks move ceaselessly on the surface of the sample during the process as shown in Fig. 3. The low value of the currents may ascribe to the formation of the compact MgF_2 passivation films on the surface of the magnesium alloy, which form an insulated barrier layer. During this period, some small localized discharges still exist, as shown in Fig. 3(b)–5, so it is not an absolute insulated barrier layer.

3.2. Effect of KF on the structure, component and phase composition of PEO films

SEM micrographs of the oxide films on magnesium alloy substrate formed with different KF concentration are shown in Fig. 4. All the PEO films have porous microstructures and some volcano top-like pores. The pores distributed disorderly on the coating surface. The melting products around the volcano pores indicate that the plasma temperature on the magnesium alloy surface during the PEO process is very high. Yerokhin et al. [7] reported that the local temperature is about 2300–3000 K. The introduction of KF into the electrolyte solution leads to a significant change in the surface morphology of the PEO films. The films formed in electrolytes (b)–(e) have much larger pore size than that in electrolyte (a). The films formed in electrolytes (b)–(e) have pore diameters of about 1–2.7 μm , pore diameters are about 0.3–0.7 μm in electrolyte (a). Moreover, the films formed in electrolytes (b)–(e) have relatively rough surface appearance as compared with that formed in electrolyte (a). These differences may owe to the different discharge characteristic of the electrolyte with KF, which is consistent with the results analyzed from Fig. 3 in Section 3.1 that the discharge sparks in the electrolyte with KF are larger than that without KF during 150–750 s.

The element contents in oxide films formed in electrolytes (a)–(e) are shown in Fig. 5. The results show that the PEO films are mainly composed of O, Mg, Si as well as a trace of C, Al, Na and K. F was detected in the films formed in electrolytes (b)–(e). Some study [10] indicated that the constituents of PEO films were influenced not only by the electrolyte composition but also by the ions species. It can be concluded that Mg and Al came from the magnesium substrate; Si, C and Na were rooted in the PEO electrolyte containing sodium silicate and glycol. Paulmier et al. [11] reported

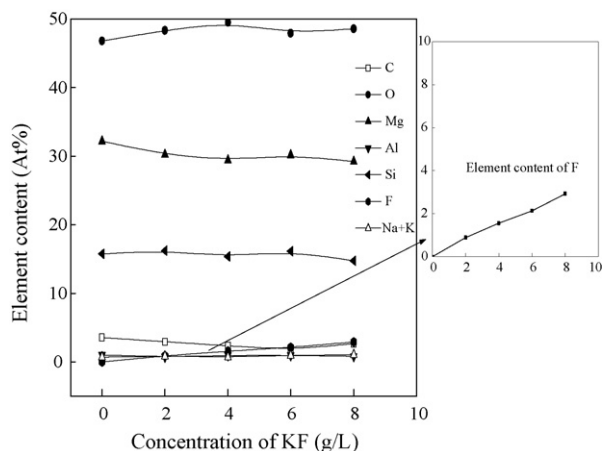


Fig. 5. Qualitative analysis of element contents in the oxide films formed in base electrolyte containing different KF concentration.

that alcohol can produce C^* active species in the high temperature plasma field, the reaction is shown in Eq. (5). The active species C^* may have come from the glycol in the high temperature plasma field during the PEO process. But the derivation of O was complicated because it might be come from the anions such as OH^- and SiO_3^{2-} as shown in Eqs. (2) and (3) or from the oxygen dissolved in PEO electrolyte; F and K came from the potassium fluoride as shown in Eq. (4). The atomic concentration of F in the films increases with an increase in KF concentration in the electrolyte (as shown in Fig. 5).

The XRD patterns of the oxide films formed in electrolytes (b)–(e) are shown in Fig. 6. All the films exhibited $MgSiO_3$, forsterite Mg_2SiO_4 and the diffraction peaks of magnesium substrate as well. The melting point of forsterite Mg_2SiO_4 is about 2183 K, which shows that the temperature of plasma discharge channels is very high. This explains the findings in SEM morphology that some melting products around the volcano pores were observed. A small amount of crystalline MgF_2 is also detected in the films formed in electrolytes (b)–(e), which indicated that F^- ions have participated in the reaction and been incorporated into the oxide films. According to the XRD analysis results of the phases and EDS analysis, the possible reactions during the processes in electrolytes (b)–(e) are listed as follows:

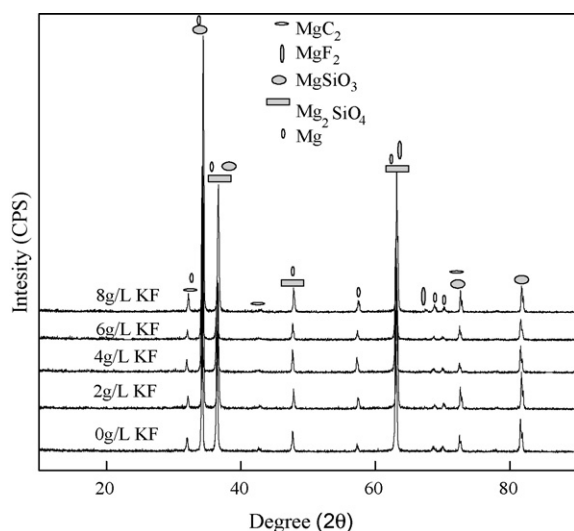
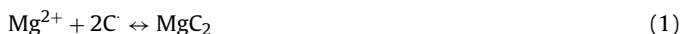


Fig. 6. Phase compositions of the PEO films formed in base electrolyte containing different KF concentration.

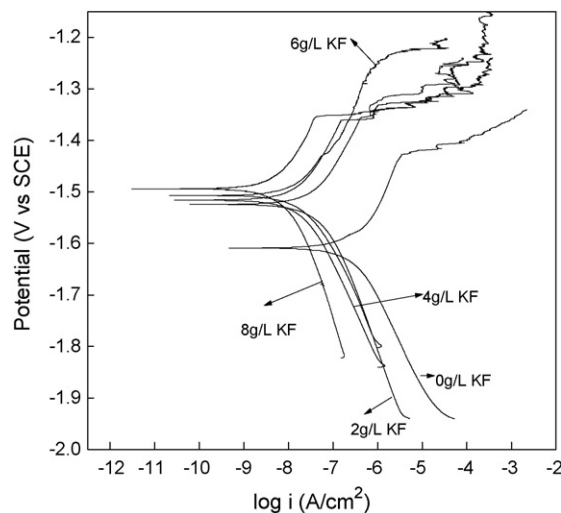


Fig. 7. Potentiodynamic polarization curves of the films formed in base electrolyte containing different KF concentration in 3.5% NaCl solution.



The reactions during the processes in electrolyte (a) are reactions (1)–(3).

3.3. Effect of KF on the anti-corrosion property of PEO films

The concentration of KF in the electrolyte influenced the morphology, phase and element composition of the films, and therefore, it is bound to influence the corrosion resistance of the films. The corrosion resistance of the films is evaluated by electrochemical potentiodynamic polarization in 3.5% NaCl solution. Fig. 7 shows the potentiodynamic curves of the films formed in electrolytes (a)–(e). The corrosion potential (E_{CORR}), corrosion current density (i_{CORR}) and corrosion resistance (R_{CORR}) derived from the potentiodynamic curves are shown in Table 1.

Corrosion potential and corrosion current density of the filmed samples are often used to characterize the corrosion protective property of the films. The high corrosion potential and low corrosion current density of the films suggest a low corrosion rate and a high uniform corrosion resistance performance. The results shown in Table 1 demonstrate that the films formed in KF-free base electrolyte has a lower E_{CORR} and higher i_{CORR} , indicating that it has a higher corrosion rate. With the addition of KF in the electrolyte, the corrosion potential increases and the corrosion current density decreases with an increase in KF concentration. The lowest corrosion rates are displayed by the films formed in the electrolyte containing 8.0 g/L KF. If the concentration of KF is higher than 8.0 g/L, the films are hard to be formed because of the point discharge resulted from the high conductivity of the electrolyte.

Table 1
The results of the potentiodynamic corrosion tests in 3.5% NaCl solution.

Concentration of KF (g/L)	E_{CORR} (V)	i_{CORR} ($\times 10^{-6}$ A/cm ²)	R_{CORR} (k Ω)
0	-1.609	6.143	4.064
2	-1.524	0.0701	29.23
4	-1.516	0.0273	60.51
6	-1.513	0.0253	95.8
8	-1.512	0.00983	177.7

Table 2

Typical impedance data of the films formed in electrolytes (a)–(e) in 3.5% NaCl solution.

Concentration of KF (g/L)	R_s (Ω/cm^2)	R_{ct} (Ω/cm^2)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	R_f (Ω/cm^2)	C_f ($\mu\text{F}/\text{cm}^2$)
0	43.1	18.2	0.309	305	0.193
2	124	180.7	0.308	2543	0.0693
4	94.2	277.8	0.135	5180	0.0484
6	114.8	579.0	0.111	6480	0.0400
8	120.0	1290.0	0.121	13190	0.0486

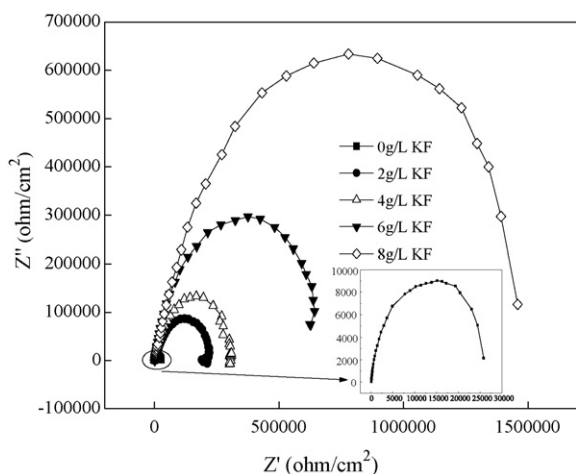
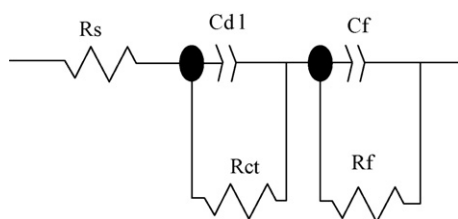
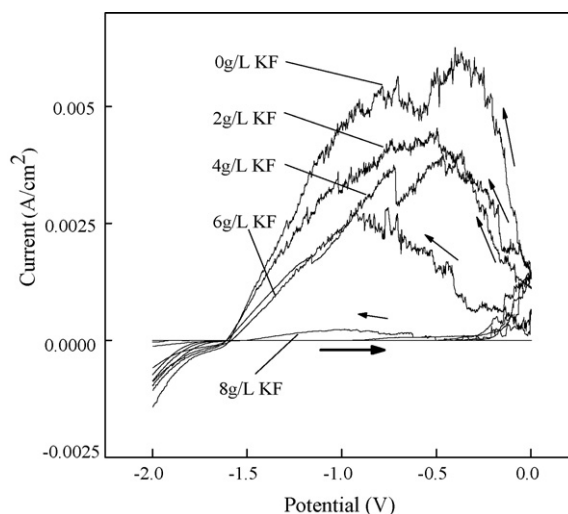
**Fig. 8.** The impedance spectroscopy of the films formed in base electrolyte containing different KF concentration in 3.5% NaCl solution.

Fig. 8 demonstrates the impedance spectroscopy (Nyquist) of PEO films obtained in electrolytes (a)–(e). Usually, the equivalent circuit for the metal with oxide film in aqueous solution can be expressed as that, in Fig. 9, which is composed of two time constants in series with PEO film impedance and film/solution impedance. In this model, R_s is the resistance of the solution, R_{ct} and C_{dl} represent the charge transfer resistance and double layer capacitance, R_f and C_f represent the resistance and capacitance contributed to the PEO films. C_{dl} and C_f are dispersed capacitances, which can be explained as being caused by the irregular character of the surfaces of the oxide films. The impedance parameters derived from the plots are given in Table 2. It can be seen that the impedance of the spectrum is mainly determined by R_{ct} . R_{ct} increases with an increase in KF concentration in the electrolyte, which has the similar tendency with the results of R_{corr} in Table 1. The bigger the charge transfer resistance, the harder the corrosion ions (Cl^-) penetrate through the films, the harder the films could be corroded. So the films have better corrosion resistance with an increase in KF concentration.

The potentiodynamic scanning curves in NaCl solution can be used to assess the pitting-corrosion resistance of the filmed sample, the larger the area of the closed curves has, the easier the pitting-corrosion occurs. If the reverse curve scans back from the top of the forward curve, the pitting-corrosion occurs. It can be seen that all the reverse curves scanned back from the top of the forward

**Fig. 9.** Equivalent circuits for modeling the behavior of PEO films.**Fig. 10.** The potentiodynamic scanning curves of the films formed in base electrolyte containing different KF concentration in 3.5% NaCl solution.

curves in Fig. 10, so the pitting-corrosion occurred on all the samples. But the area of the closed curves decreases with an increase in KF concentration in the electrolyte which indicates that the pitting-corrosion resistance of the films increases with an increase in KF concentration.

Though the films formed in electrolyte (a) have a relatively smaller micropores and intact microstructure, it has the lowest corrosion resistance. The intact microstructure and smaller micropores on the films' surface are not the crucial factors to provide a superior corrosion protection in this study which is different from the results reported by Liang et al. [12]. As for Mg and Mg alloy, it could be fast passivated in the presence of NaF or KF, with the generation of an undissolved MgF_2 film on the surface [7]. This makes it possible to avoid the excessive anodic dissolution of the Mg substrate with a high chemical reactivity in the initial stage of PEO treatment, and also makes it possible to prevent the corrosion ions (Cl^-) penetrating through the PEO films to corrode the Mg substrate. The different MgF_2 composition endows the films formed in electrolytes (b)–(e) a superior corrosion protection than the films formed in electrolyte (a). The films have higher corrosion resistance with an increase in atomic concentration of F. The difference in corrosion resistance depends on the different amount of MgF_2 composition because F in the films could just be present in the MgF_2 composition in this study according to the XRD analysis as shown in Fig. 6.

4. Conclusions

- (1) The addition of KF in the base electrolyte solution contributes to decrease the work current density and change the characteristics of the microdischarge.
- (2) The addition of KF increases the pore diameter of the PEO films. At the same time, it leads to the phase composition transform in the films because of F^- participates in the reaction and is incorporated into the oxide films.

(3) The corrosion resistance depends on the different amount of phase composition of MgF_2 . The films formed in the electrolyte have higher corrosion resistance and a decrease pitting-corrosion tendency with an increase in KF concentration, which have larger amount of phase composition of MgF_2 .

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