Effects of PEG6000 on microstructure and corrosion resistance of plasma electrolytic oxidation coatings on magnesium alloy under different voltages

L. Y. An, C. G. Chang, L. C. Meng, J. H. Peng, J. Yuan, Z. Wang, D. S. Kang

College of Physics and Electronic Information Engineering, Qinghai Minzu University, Qinghai Xining 810007, China
Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lake, Chinese Academy of Sciences
Key Laboratory of Salt Lake Resources Chemistry of Qinghai Province Qinghai Xining 810008, China

Plasma electrolytic oxidation (PEO) coatings were prepared on AZ91D magnesium alloy in aqueous silicate electrolytes without and with polyethylene glycol 6000 (PEG6000). Effects of PEG6000 concentration on microstructures and corrosion resistance of coatings under two voltages were studied. The static contact angles of the coatings were investigated by the contact angle meter, and their anti-corrosion properties were evaluated using the potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). The results show that, after adding PEG6000 into the electrolyte, the thicknesses of the coatings decrease somewhat, and the chemical and phase compositions of the coatings almost remain unchanged, but the content of the deposited phase slightly increases. Meanwhile, the surface roughness of the coatings decreases and their compactness adds by augmenting the adsorptive uniformity of anion ions on anode/electrolyte interface. Therefore, the contact angle of the coating increases and its corrosion resistance is significantly strengthened. As the concentration of PEG6000 grows, the anti-corrosion performance of the coating firstly improves and then deteriorates. When PEG6000 is 5 g/L at low voltage but is 10 g/L under high voltage, the corrosion resistance of the coating is the best.

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1. Introduction

Magnesium and its alloys are extensively utilized as the structural material in engineering industry such as 3C products, automobile along with aerospace fields because of their light weight as well as excellent specific strength and specific stiffness. However, their further usage is severely restricted since they are subjected to corrosion due to the higher chemical activity. For this reason, the surface of magnesium alloys must be treated through the suitable surface modified techniques before being employed.

* Corresponding author: ccg168@126.com
Plasma electrolytic oxidation (PEO), developed recently on the basis of traditional anodization, is a novel surface modification technology for some metals, e.g. Mg, Al, Zn and Ti. Its working principle is to apply a high voltage of several hundred volts to the metal immersed into the electrolyte, making plasma spark discharge occur on the surface of the metal. As a result, a layer of oxide ceramic coating with high hardness, good electrical insulation and superior anti-corrosion performance is generated on the metal surface under a series of complex chemical reactions and the function of high temperature sintering. However, the coatings exhibit a porous structure resulting from the continuous breakdown discharge during PEO treatment, limiting greatly the improvement of the corrosion resistance of the coatings [1-5].

Usually, post-treatments are adopted to enhance the anti-corrosion ability of the PEO coating by sealing the micropores of coating. For example, B. Mingo et al. [6] have studied that the effects of three different post-treatments, based on immersion sealing processes in aqueous solutions of cerium/stannate salts as well as alcoholic solution of ODP respectively, on magnesium alloy PEO coatings, and have found that all post-treatments increase the corrosion resistance of the coatings. Luca Pezzato et al. [7] have reported that sealing treatment carried out in boiling water augments the anti-corrosion performance of PEO coated AZ80 magnesium alloy and avoid the crevice corrosion of the sample. Moreover, the authors have also treated AZ91 magnesium alloy PEO coating in the solutions containing Nd sulfate salt (NaNd(SO$_4$)$_2$), and have suggested that the sealing treatment promotes the resistance to corrosion of the coating by the blocking effect of the micropores and the formation of the protective Nd$_2$O$_3$ [8].

Moreover, electrical parameters including voltage, current density, frequency and duty ratio also significantly affect corrosion resistance of the coatings through influencing the coating thickness, compactness and phase composition and so on. Among these electrical parameters, the influence of the voltage is the greatest. Rising voltage leads to the enlargement of pore size of micropores, but anti-corrosion property of the coating is improved due to increased coating thickness [5].

The researches [9-12] have also shown that the dense coating often possesses a higher anti-corrosion ability, while the composition and concentration of the electrolyte are one of the essential factors affecting the compactness of the PEO coatings. Thereby, most researchers have improved corrosion resistance of the coating by adjusting the composition and concentration of electrolyte, especially doping additives into the base electrolyte, like the solid particles [13-15], soluble salts [16-18] and organic additives [19-28].

The incorporation of solid particles can prepare functional and anti-corrosion coatings owing to the deposition of high quality phases as well as micropores-sealing effect. For instance, adding graphite [13] or PTFE [14] has imparted the coatings the anti-friction or hydrophobic properties, and doping SiO$_2$ and ZrO$_2$ has grown the resistance to corrosion the coating [15]. But the deposition of the second phase is usually nonuniform and even can also cause cracks, which limit the improved extent of coating properties.

As for soluble salts, such as K$_2$TiF$_6$ [16], K$_2$ZrF$_6$ [17] and Na$_2$SiO$_3$ [18], they can increase the conductivity of the electrolyte and reduce the arc voltage, and hence they can improve the thickness and microstructure of the coating. Meanwhile, they also participate in the film-forming reaction by adsorbing on the surface of the matrix or entering into the discharge channels, which will introduce the corresponding phases into the coating. Also, they can form discharge points of impurity particles on the surface of the original oxide layer. If the discharge points of impurity
particles formed by them are homogeneous, it will be helpful for preparing a uniform, dense and anti-corrosion coating. In view of above these points, soluble salts can be able to fortify anti-corrosion capacity of the coating to some extent.

Regarding organic additives, they also achieve close attention from most scholars [19]. Researchers have added potassium stearate, L-Ornithine acetate and EDTA into the electrolyte of plasma electrolyte oxidation, improving corrosion resistance of the coatings ascribed to the combined action among surfactant, arc suppression and inhibition[20-22]. Literatures [23,24] have found that the addition of glyciner into the electrolyte can suppress the large-arc discharge, reduce the pore size, increase the coating’s compactness. As a consequence, the corrosion resistance of the coatings is enhanced. Literature [25] has also confirmed that introducing glyciner improves the corrosion resistance of the PEO coatings because of the relatively thicker and denser inner barrier layer. Similar result has also been obtained by doping various alcohols including ethanol, ethylene glycol, and glycerol into the Na₃PO₄-based electrolyte, which reduces surface roughness of the PEO coatings and increases the thickness and corrosion resistance of the coatings [26]. Feng Zhu et al. [27] have studied the effect of ethylene glycol oligomers on the anti-corrosion performance of the coating too, and have revealed that the addition of PEG minishes the corrosion current density of the coating and boosts the coating’s impedance. Furthermore, in the author’s previous paper, it is found that polyethylene glycol 6000 (PEG6000) can disperse nanoparticles by specific adsorption and further perfect the anti-corrosion property of the coating [28].

In order to further study the impacts of polyethylene glycol 6000 (PEG6000) on the microstructure together with the resistance to corrosion of the coating under the circumstance of different voltages, the PEO coatings were synthesized in the aqueous silicate electrolyte having different concentrations of PEG6000 at high and low voltages in this paper. The affections of PEG6000 on the microstructure and corrosion resistance of the coating were investigated under two voltages, respectively. Moreover, the mechanism of the influences of PEG6000 and voltage on coating was also researched.

2. Experiments

2.1. Preparation

The nominal chemical constituent of 30 × 20 × 12 mm³ of AZ91D magnesium alloy, exploited as the matrix material, is as following: 8.3 wt.% ~ 9.7 wt.% Al, 0.35 wt.% ~ 1.0 wt.% Zn, 0.17 wt.% ~ 0.27 wt.% Mn, 0.1 wt.% Si, 0.03 wt.% Cu, 0.002 wt.% Ni, 0.005 wt.% Fe, and Mg balance. Firstly, AZ91D magnesium alloy was pretreated, including grinding by 300, 600 and 1000 grit of silicon carbide abrasive papers, washed by applying deionized water, and dried in the condition of room temperature. Secondly, AZ91D magnesium alloy was treated for 15 min by a bipolar pulsed power supply [28] under the constant voltage mode of 350 V and 430 V respectively. The sample worked as the anode, at the same time a stainless steel played a role of the cathode. Frequency is set to 2000 Hz and duty ratio is 20 %. The base electrolyte is an aqueous silicate system, which is made up of 15 g/L Na₂SiO₃, 13 g/L KF and 2 g/L NaOH. 5 g/L, 10 g/L and 15 g/L of PEG60000 were separately added into the base electrolyte. During the PEO process, the water cooling system accompanied with stirring was used to maintain the temperature of the electrolyte at approximately 20 °C.
2.2. Characterization

The coating thicknesses were got through portable digital eddy-current thickness tester (TT260) on the 16 sample surfaces which close to and far away from the cathode respectively. The measurements were performed at least 10 times at arbitrary locations on each sample surface.

The phase composition of the PEO treated AZ91D magnesium alloy was characterized with X-ray diffractometer (XRD) (X’ Pert Pro), whose radiation source is Cu Kα. It was carried out in a range of 20 ° to 80 ° (in 2θ) with a scan step length of 0.0167 °.

The chemical composition of PEO coatings was identified by using the X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo fisher scientific, America). The monochromatized Al Kα radiation with photo energy of 1486.6 eV was used as the excitation source, meanwhile, the binding energy of C 1s of 284.6 eV was adopted to correct all energy values. The obtained data were analyzed by using Xpspeak 4.1 software.

Scanning electron microscope (JSM-5610LV) was adopted to study the surface and cross-sectional morphologies of the resultant coatings. Meantime, applying Image J software to analyze the obtained SEM surface images gave the distribution of the micropore together with the surface porosity of the coatings.

The static contact angle was acquired by using the JC2000C1 static contact angle measurement gauge equipped with auto-captures camera at 10 different positions on the surface of the coating at ambient temperature, and the photos of static water droplet were also taken.

The corrosion resistance of the coatings was evaluated via the potentiodynamic polarization curves using the CHI660D electrochemical workstation with a conventional three-electrode cell. Among them, the PEO-treated samples were used as the working electrode, and the saturated calomel electrode (SCE) was utilized as a reference electrode, meanwhile, the platinum electrode was adopted as a counter electrode. The potentiodynamic polarization test was conducted after the samples possessing an 1 cm² of uncovered area were dipped in 3.5 % NaCl (mass fraction) corrosive liquid for 30 min. The scanning rate is 0.01 V/s and the scan starts from -1.5 to -1.2 V. For accuracy, the potentiodynamic polarization test was implemented no less than 8 times on unlike locations on the surface of the diverse samples. In order to further study the effect of PEG6000 on the deterioration process of PEO coating, the electrochemical impedance spectroscopy (EIS) was investigated by using CS2350 electrochemical workstation which possesses the same parameters with CHI660D electrochemical workstation. The initial potential is the open circuit potential. The frequency is from $10^{-2}$ to $10^{5}$ Hz, and the AC signal amplitude is 20 mV. Moreover, the electrochemical impedance data were fitted by using the ZSimpWin3.2 software.

It should be pointed out that the thickness, the static contact angle and the corrosion current density of the coatings were all the mean values, obtained by eliminating the outlier from the initial observed values according to Grubbs test [29]. Meantime, their standard errors were calculated.
3. Results

3.1. Voltage- and current-time responses for PEO treatment

Fig. 1 shows the transients of voltage and current with time during the PEO process in the electrolytes containing different concentrations of PEG6000. It can be found that the evolution of voltage and current with time in diverse electrolytes exhibits similar tendencies and the variation of the current can be roughly divided into three stages. In the first stage, namely during the first 120 s, the voltage is rapidly loaded to the predetermined values of 350 V (Fig. 1(a)) and 430 V (Fig. 1(b)). At this time, the substrate suffers from the dissolution accompanied by the formation of a thin anodized coating, and so the current also quickly increases ascribed to the smaller thickness and lower resistance. When the voltage separately increases to 350 V and 430 V at 120 s, the corresponding current also reaches the maximum value. In the second stage, as the PEO treatment going on, the voltage maintains constant, and the current decreases gradually owing to the higher resistance caused by the increasement of the coating thickness. Subsequently, the current nearly keeps at a stabilized value because of the coating’s relatively slow growth and the given quantity of applied electricity. In addition, after PEG6000 being added into the electrolyte, peak currents under two voltages all decrease, indicating that the addition of PEG6000 can decrease the intensity of the breakdown discharge to some extent. Among them, the peak current is the lowest in the case of 5 g/L PEG6000 at low voltage and under the condition of 10 g/L PEG6000 at high voltage, suggesting that the optimum added content of PEG6000 is different under two voltages.

![Fig. 1. Voltage and current versus time curves during PEO treatments in silicate electrolyte with different concentrations of PEG6000 under constant (a) 350 V and (b) 430 V.](image-url)
3.2. Coating thickness

Fig. 2 presents the influences of PEG6000 content on the thickness of PEO coatings acquired on AZ91D magnesium alloys under two various voltages. The thickness of the coating prepared under high voltage is obviously higher compared with that achieved in the case of low voltage, and the former is nearly twice of the latter one. Increasing PEG6000 concentration, the coating thickness firstly augments and then decreases at the high voltage, while it gradually decreases under low voltage. But the varied extents of the coating thickness under the two different applied voltages are both very small.

![Graph showing thickness evolution of PEO coatings as a function of PEG6000 concentration under two voltages.](image)

*Fig. 2. Thickness evolution of PEO coatings as a function of PEG6000 concentration under two voltages.*

3.3. Chemical composition

XPS spectra of PEO coatings formed in silicate electrolytes with and without PEG6000 are presented in Fig. 3. It can be seen from Fig. 3 (a₁) and (a₂) that two coatings both contain Mg, O, Al, Si and C. The high-resolution spectra of Mg 2p, O 1s and C 1s are illustrated in Fig. 3 (b₁−d₁) and (b₂−d₂), respectively. The Mg 2p peak can be divided into two peaks of 50.3 and 51.5 eV, which separately correspond to MgO and Mg₂SiO₄ [30,31]. The O 1s peak around 530.89 eV can be assigned as MgO, and the one at 531.9 eV associates with Mg₂SiO₄ [30,31]. The C1s spectra of the two coatings are mainly composed of three characteristic signal peaks of binding energy 284.6, 286.5, 287.8 eV. These indicate that the addition of PEG6000 has no obvious influence on the chemical composition of the coatings.
Fig. 3. XPS spectra of PEO coatings obtained in electrolyte $(a_1\sim d_1)$ without PEG6000 and $(a_2 \sim d_2)$ with PEG6000: $(a_1, a_2)$ survey scanning spectra; and high-resolution spectra of $(b_1, b_2)$ Mg 2p, $(c_1, c_2)$ O 1s, and $(d_1, d_2)$ C 1s.
3.4. Phase composition

Fig. 4 displays the XRD patterns of the synthesized coatings in silicate-based electrolytes having or not addition of PEG6000 on AZ91D magnesium alloys under two different applied voltages. The obtained coatings include MgO, MgF₂, Mg₂SiO₄ and MgAl₂O₄ phases. Mg diffraction peaks can also be identified since the X-ray arrives at the substrate through the coatings. Furthermore, voltage and PEG6000 have no noticeable effect on the phase composition of the acquired coating, but with the addition of PEG6000, the diffraction peak intensities of MgO and Mg₂SiO₄ increase slightly, indicating that their contents augment somewhat.

![XRD patterns of PEO coatings](image)

**Fig. 4.** XRD patterns of PEO coatings got in silicate electrolyte having (a₁, b₁) 0 g/L and (a₂, b₂) 10 g/L of PEG6000 at low voltage (a₁, a₂) and high voltage (b₁, b₂).

3.5. Surface morphology and the distribution of corresponding micropores

Fig. 5 illustrates the surface morphology and the corresponding micropore distribution of the PEO coatings prepared in the electrolytes with different PEG6000 concentration under different applied voltages. The quantitative statistics results of large-size micropores (pore size > 3 µm) and the surface porosity are also presented in Fig. 6. As can be observed from Fig. 5, the surface of PEO coatings exhibits the porous structure, which is the inherent property of the PEO coatings and is determined by the PEO mechanism. On the surface of the PEO coating prepared under the high voltage, the generated fusant is easier to flow because of the higher input energy. Therefore, the traces of the sintering are more obvious. At the same time, the surface of the coating becomes rougher, and the molten particles and the diameter of micropores are larger. Moreover, the coating surface possesses much more large-size micropores (Fig. 6(a)).

It can also be noticed from Figs. 5 and 6 that, after PEG6000 is added to the electrolyte, the size of the micropores, the number of large-size micropores as well as the surface porosity reduces. It is well known that the micropores existed on the coating surface are the entrances for corrosive media to penetrate into the coatings. So that the reduction in pore size, the amount of large-size micropores and the surface porosity will be beneficial to prevent the corrosive media against infiltrating into the coating to corrode the substrate. This indicates that the addition of PEG6000 may improve the corrosion resistance of the coating. Under the low voltage, with the addition of 5 g/L PEG6000, the dimension of the micropores is the minimum, and the quantity of large-size micropores together with the porosity existed on the coating surface is the lowest, yet it is necessary to add 10 g/L of PEG6000 under high voltage to obtain the minimum pore size as well as the lowest porosity. However, continuing to boost PEG6000 concentration results in the
increase of the pore size, the number of large-size micropores as well as the surface porosity, which may deteriorate the coating's corrosion resistance to some extent. In addition, among all the coatings, the number of large-size micropores and surface porosity under 5 g/L PEG6000 and low voltage are the lowest.

Fig. 5 Surface morphologies ($a_1$-$a_4$, $b_1$-$b_4$) and corresponding micro-pore distributions ($a_1'$-$a_4'$, $b_1'$-$b_4'$) of PEO coatings synthesized in silicate electrolyte with ($a_1$, $a_1'$, $b_1$, $b_1'$) 0 g/L ($a_2$, $a_2'$, $b_2$, $b_2'$) 5 g/L, ($a_3$, $a_3'$, $b_3$, $b_3'$) 10 g/L and ($a_4$, $a_4'$, $b_4$, $b_4'$) 15 g/L of PEG6000 at low voltage ($a_1$-$a_4$, $a_1'$-$a_4'$) and high voltage ($b_1$-$b_4$, $b_1'$-$b_4'$).

Fig. 6. Amount of large-size micropores together with surface porosity on synthesized coatings in silicate electrolyte having different concentrations of PEG6000 under two loading voltages.
3.6. Cross-section morphology of the coating

Fig. 7 depicts the cross-section morphology of the PEO coatings as a function of PEG6000 content for two applied voltages. The coating is well bonded to the matrix, and that prepared at high voltage is significantly thicker, which is in agreement with the results obtained by the TT260 digital eddy-current thickness gauge. Furthermore, the coating is roughly comprised of a relatively compact internal layer and an external layer with different-sized of micropores. More micropores and larger pore size were observed for the coating formed under high voltage than that for low voltage. After adding PEG6000 into the electrolyte, the micropores of the coating are reduced, and its compactness is increased. However, the size and number of micropores of the coating firstly decrease and then slightly increase with the PEG6000 concentration under two voltages, resulting in that the compactness of the coating exhibits a similar varied trend. The coating presents the densest microstructure when adding 5 g/L of PEG6000 under low voltage, whereas, in the case of high voltage, 10 g/L of PEG6000 needs to be added.

Fig. 7. Cross-sectional morphologies of acquired coatings from silicate electrolyte having 0 g/L (a1, b1), 5 g/L (a2, b2), 10 g/L (a3, b3) and 15 g/L (a4, b4) of PEG6000 at high voltage (a1~a4) and low voltage (b1~b4).
3.7. Wetting property of coatings

Fig. 8 shows the photographs and static contact angles of the distilled water drop dripped on the surface of the PEO coatings fabricated from silicate electrolyte having different concentrations of PEG6000 at two loading voltages. The contact angle of the coating at low voltage is higher than that obtained at high voltage due to the slightly smooth surface. After adding PEG6000 into the electrolyte, the contact angle of the coatings grows, indicating that the hydrophilicity of the coating reduces yet its hydrophobicity increases, while the improvement of hydrophobic performance of coating is beneficial to prevent corrosive media from spreading on the coating surface, which will be contribution to the enhancement of the coating’s anti-corrosion ability to some extent [14,20]. With the increasing in added content of PEG6000, the contact angle of the coating slightly augments at low voltage. Whereas, in the case of high voltage, it reaches the largest value with the addition of 10 g/L PEG6000, which is 29.948° higher than that of the base electrolyte.

![Fig. 8. Image and static contact angle of distilled water droplet on surfaces of PEO coatings formed from silicate electrolyte containing different concentrations of PEG6000 under two applied voltages.](image)

3.8. Corrosion resistance of coatings

Fig. 9 demonstrates the potentiodynamic polarization curves of the produced coatings in the electrolyte having various content of PEG6000 at different voltages, and their fitted corrosion potential ($E_{corr}$), corrosion current density ($J_{corr}$) and polarization resistance ($R_p$) are presented in Table 1. As can be observed from Fig. 9 and Table 1, PEO treatment improves significantly the corrosion resistance of AZ91D magnesium alloys. What’s more, the $E_{corr}$ of the coatings shifts to more positive side, their $J_{corr}$ reduces and $R_p$ increases after adding PEG6000 into the electrolyte, indicating that PEG6000 addition facilitates the enhancement of the anti-corrosion ability of the acquired coatings. With the increasing PEG6000 concentration, the $J_{corr}$ of the coating decreases firstly and then increases, and its $R_p$ exhibits an opposite varied tendency. The $J_{corr}$ of the coating is the smallest and its $R_p$ is the largest when adding 5 g/L of PEG6000 at low voltages, but 10 g/L in the case of high voltage. The $J_{corr}$ obtained at 5 g/L PEG6000 at low voltage decreases by 74% compared to that without additive, and its $R_p$ is about 6 times of the base electrolyte. While the $J_{corr}$ attained in the condition of 10 g/L PEG6000 and high voltage is 36% of the absence of PEG6000, simultaneously its $R_p$ is approximately one order of magnitude higher than the latter. Furthermore, under low voltage, the coating exhibits lower $J_{corr}$, higher $R_p$ and more excellent corrosion resistance when the concentration of PEG6000 is lower (0 and 5 g/L).
Fig. 9. Potentiodynamic polarization curves of PEO coatings synthesized in electrolytes having different concentrations of PEG6000 under low voltage (a) and high voltage (b).

Table 1. Fitted results according to potentiodynamic polarization curves shown in Fig. 9.

| Parameter | $E_{corr}$ / V | $J_{corr}$ / (A·cm$^{-2}$) | $R_p$ / (Ω·cm$^2$) |
|-----------|----------------|---------------------------|---------------------|
| Substrate | -1.396         | 3.862×10$^{-5}$           | 9.81×10$^2$         |
| 350 V     | 0 g/L          | -1.401                    | 2.033×10$^{-8}$     | 1.364×10$^6$ |
|           | 5 g/L          | -1.381                    | 5.359×10$^{-9}$     | 7.831×10$^6$ |
|           | 10 g/L         | -1.374                    | 9.781×10$^{-9}$     | 3.221×10$^6$ |
|           | 15 g/L         | -1.370                    | 1.549×10$^{-8}$     | 2.234×10$^6$ |
| 430 V     | 0 g/L          | -1.399                    | 2.356×10$^{-8}$     | 9.712×10$^5$ |
|           | 5 g/L          | -1.359                    | 1.410×10$^{-8}$     | 2.720×10$^6$ |
|           | 10 g/L         | -1.381                    | 8.532×10$^{-9}$     | 4.402×10$^6$ |
|           | 15 g/L         | -1.348                    | 9.920×10$^{-9}$     | 3.908×10$^6$ |

Fig. 10 illustrates the experimental and fitted electrochemical impedance spectra (EIS) of PEO coatings obtained in base electrolyte at high voltage. It can be seen from Fig.10 (b) and (c) that, the phase angle is negative value during the immersion from 0.5 to 10 h, and the phase plot exhibits two “peaks and valleys”, at the same time, the corresponding Nyquist plot are composed of two capacitive arcs that separately appear at high and low frequencies, suggesting that the coating possesses two time constants. Hence, the EIS of the coating can be fitted by the equivalent circuit presented in Fig.11 (a), where $R_s$ corresponds to the electrolyte resistance, $R_p$ parallelled to the constant phase element $Q_p$ represents the resistance for the coating’s outer porous layer, and the corrosion resistance concerning the inner compact layer of the coating is characterized by the parallel resistance $R_b$ and constant phase element $Q_b$. When the immersion time is extended to 24 h, the low-frequency phase angle becomes positive value, and the inductive arc also appears at low frequency in the Nyquist diagram. Therefore, the equivalent circuit displayed in Fig.11 (b) can be used to fit the coating's EIS obtained in the immersion from 24 to 72 h. In Fig.11 (b), $R_t$ is the coating resistance, which is in parallel with the constant phase angle element $CPE_t$; $R_{ct}$ is the charge transfer resistance, parallelled with the electric double layer capacitor $C_d$; $R_p$ is the resistance corresponding to pitting corrosion, which is connected with the inductance $L$.

The results fitted according to the equivalent circuit in Fig.11 are listed in Tables 2 and 3. The coating possesses a higher $R_t$ value, indicating that the inner layer of the coating plays a critical role in inhibiting corrosive media from eroding the substrate. With the immersion time extending from 0.5 to 10 h, $R_t$ value of the coating firstly decreases and then increases. This is because the corrosion products generated during the corrosion process are retained in the
micropores of the coating, blocking the micropores of the coating and increasing the difficulty that the corrosive media further enter the coating. This delays the damage of the corrosive media to the substrate, and improves the corrosion resistance of the coating. When the immersion time reaches 24 h, the $R_i$ value of the coating is significantly reduced, and the pitting corrosion appears on the surface of the coating, suggesting that the local area of the coating is damaged somewhat. Furthermore, the $R_i$ value fluctuates during the immersion 24-96 h due to the formation, dissolution and regeneration of corrosion products. But it is worthy to note that the coating still possesses a protective effect on the substrate when immersion is prolonged up to 96 hours.

Fig. 10. Experimental and fitted (a and b) Bode and (c) Nyquist plots of synthesized coatings in electrolytes without PEG6000 at high voltage.

Fig. 11. Equivalent circuits utilized for fitting the EIS of PEO coatings immersed in 3.5 wt.% NaCl corrosive media: (a) before pitting corrosion; (b) after pitting corrosion.
Table 2. Fitted EIS data of PEO coatings immersed in 3.5 wt.% NaCl corrosive media for 0.5 to 10 h.

| Time / h | $R_s$ / (Ω·cm$^2$) | CPE | $R_i$ / (Ω·cm$^2$) | CPE | $R_t$ / (Ω·cm$^2$) | $X^2$ Value |
|----------|---------------------|-----|---------------------|-----|---------------------|------------|
|          |                     |     |                     |     |                     |            |
| 1        | 25.59               | 1.36E-8 | 0.806               | 2.11E+5 | 4.78E-8 | 0.7817 | 8.69E+6 | 1.47E-3 |
| 6        | 34.99               | 1.81E-8 | 0.7983              | 3.25E+5 | 1.45E-7 | 0.7978 | 6.78E+6 | 2.98E-3 |
| 10       | 79.6                | 7.59E-8 | 0.811               | 3.73E+5 | 1.60E-7 | 0.685 | 8.94E+6 | 2.63E-3 |

Table 3. Fitted EIS data of PEO coatings immersed in 3.5 wt.% NaCl corrosive media for 24 to 96 h.

| Time / h | $R_s$ / (Ω·cm$^2$) | CPE | $R_i$ / (Ω·cm$^2$) | CPE | $R_t$ / (Ω·cm$^2$) | $L$ / H | $X^2$ value |
|----------|---------------------|-----|---------------------|-----|---------------------|--------|------------|
|          |                     |     |                     |     |                     |        |            |
| 24       | 23.19               | 1.36E-7 | 0.7654              | 2.03E+5 | 5.85E-8 | 5.3E+4 | 1.21E+5 | 6.49E-3 |
| 36       | 37.01               | 1.78E-7 | 0.7563              | 4.16E+5 | 5.38E-7 | 1.96E+5 | 0.013 | 4.43E+4 | 7.99E-3 |
| 48       | 48.07               | 1.95E-7 | 0.7637              | 6.83E-5 | 7.05E-7 | 4.55E+4 | 0.029 | 1.44E+4 | 5.83E-3 |
| 72       | 45.24               | 1.94E-7 | 0.812               | 2.91E+5 | 3.72E-7 | 1.93E+4 | 0.069 | 2.04E+5 | 9.57E-3 |
| 96       | 73.27               | 3.24E-7 | 0.8336              | 1.74E+5 | 4.39E-6 | 4.13E+4 | 0.171 | 9.88E+3 | 8.24E-3 |

Fig.12 exhibits the experimental and fitted electrochemical impedance spectra (EIS) of PEO coatings obtained in silicate electrolyte with the addition of 10 g/L PEG6000 at high voltage. The equivalent circuit of Fig.11 (a) are chosen to fit the coating's EIS obtained when immersion time is from 0.5 to 36 h, while the coating's EIS corresponded to the immersion of 48 to 96 h needs to be fitted by Fig.11 (b).

The fitted results based on Fig.11(a) and (b) are presented in Tables 4 and 5. Apparently, the higher $R_i$ value manifests that the inner layer of the coating exerts a main influence in protecting the substrate against the erosion from corrosive media. The $R_i$ value of the coating gradually decreases with the immersion time prolonging from 0.5 to 36 h. When the immersion time reaches 48 h, the $R_i$ value of the coating is remarkably reduced, and the pitting corrosion occurs on the surface of the coating. After that, $R_i$ value increases again with further extension of immersion time because of the formation of corrosion products and the blocking effect of micropores, meaning that the coating can still provide an effective protection for the substrate in the later stage of the immersion.

Comparing Fig.10 with Fig.12 as well as Tables 2 to 5, it can be seen that the coating prepared in the silicate electrolyte containing 10 g/L of PEG6000 possesses a higher impedance modulus and better corrosion resistance, specifying that the addition of PEG6000 improves the resistance to corrosion of the coating. This is consistent with the result of the potentiodynamic polarization curve test.
Fig. 12. Experimental and fitted (a and b) Bode and (c) Nyquist plots of synthesized coatings in electrolytes with 10 g/L of PEG6000 at high voltage.

Table 4. Fitted EIS data of PEO coatings immersed in 3.5 wt.% NaCl corrosive media for 0.5 to 36 h.

| Time / h | $R_s$ / ($\Omega\cdot$cm$^2$) | $CPE_{s}$ | $R_e$ / ($\Omega\cdot$cm$^2$) | $CPE_{e}$ | $R_i$ / ($\Omega\cdot$cm$^2$) | $\chi^2$ Value |
|----------|--------------------------------|-----------|----------------------------|-----------|-----------------|----------------|
| 1        | 100.1                          | 1.42E-8   | 0.9199                     | 3.68E+3   | 7.99E-9         | 0.8971         | 9.31E+7        | 6.35E-3        |
| 6        | 90.1                           | 2.12E-7   | 0.9999                     | 1.22E+4   | 7.32E-8         | 0.808          | 6.22E+7        | 1.13E-3        |
| 10       | 60.54                          | 8.16E-8   | 0.7914                     | 2.45E+5   | 3.88E-8         | 0.9121         | 1.59E+7        | 4.19E-3        |
| 24       | 90.03                          | 6.54E-8   | 0.817                      | 1.61E+6   | 5.22E-8         | 0.7226         | 1.20E+7        | 3.35E-3        |
| 36       | 84.69                          | 6.91E-8   | 0.8143                     | 2.09E+6   | 7.66E-8         | 0.7158         | 7.47E+6        | 1.14E-3        |

Table 5. Fitted EIS data of PEO coatings immersed in 3.5 wt.% NaCl corrosive media for 48 to 96 h.

| Time / h | $R_s$ / ($\Omega\cdot$cm$^2$) | $CPE_{s}$ | $R_e$ / ($\Omega\cdot$cm$^2$) | $CPE_{e}$ | $R_i$ / ($\Omega\cdot$cm$^2$) | $L$ / H | $\chi^2$ Value |
|----------|--------------------------------|-----------|----------------------------|-----------|-----------------|---------|----------------|
| 48       | 52.95                          | 1.77E-7   | 0.7079                     | 1.00E+5   | 2.88E-9         | 9.31E+5 | 6.83E+5        | 1.81E+6        | 7.28E-3        |
| 72       | 70.78                          | 1.49E-7   | 0.791                       | 1.03E+6   | 4.51E-7         | 7.28E+5 | 0.008          | 1.97E+6        | 2.56E-3        |
| 96       | 84.23                          | 1.59E-7   | 0.817                      | 2.59E+6   | 1.88E-6         | 3.19E+6 | 6.22E+5        | 9.85E+4        | 1.68E-3        |
4. Discussion

Lots of factors dominate the corrosion resistance of PEO coatings, which contain the thickness of the coating, chemical composition, phase composition, surface defects and coating's compactness like size and number of micropores, surface porosity, and morphology of micropore in the coating. In addition, hydrophobic surface is also favoured for strengthening the anti-corrosion performance of the coating. During preparing PEO coating, PEG6000 and voltage influence the anti-corrosion property of the coating by affecting these factors.

PEG6000 is a nonionic surfactant with the hydrophobic group (-CH$_2$-) and the hydrophilic group (-OH), which is also often used as a dispersant [32]. When it is added into the aqueous silicate electrolyte, the C atom at the hydrophobic group of PEG6000 can preferentially attaches on the substrate surface by physical adsorption due to the higher surface activity, while the hydrophilic group orient toward the electrolyte, which will reduce the substrate/electrolyte interfacial tension and make the electrolyte fully spread on the surface of the substrate. On one hand, the adsorptive capacity of anions on the surface of the substrate increase. This can be confirmed from Figs. 2 and 4, after adding PEG6000 into electrolyte, although the coating thickness reduces slightly, the content of MgO and MgSiO$_4$ phases deposited in the coating increases somewhat, which will promote the enhancement of the corrosion resistance of the coating. On the other hand, the adsorptive uniformity of anions on the substrate surface also increases, leading to the more even discharge points of foreign particles. Hence, the surface of the substrate can also uniformly react with the adsorptive anions to increase the homogeneity of the coating, making the subsequent breakdown discharge evenly occur on the surface of the coating. This will inhibit large-arc discharge and decline the energy of the single spark discharge, which can be confirmed by the lower current value presented in Fig.1. In consequence, after PEG6000 being added into the electrolyte, the pore size of micropores and surface porosity are reduced, the compactness of the synthesized coating is improved, and further the corrosion resistivity of the coating is significantly enhanced.

Voltage also exhibits a great influence on the thickness, microstructure and corrosion resistance of the coating. Higher voltage provides the more powerful electric field. This will give rise to the greater driving force for plasma electrolytic oxidation, and so the coating possesses a higher thickness under high voltage. However, it will also result in larger pore size and a large number of large-size micropores, which can be proved by comparing Fig.5 (a$_i$) with (b$_i$), and comparing Fig.7 (a$_i$) with (b$_i$). Accordingly, the corrosion resisting performance of the coating prepared in the electrolyte without PEG6000 under high voltage is inferior.

To decrease the size of micropores and the number of large-size micropores, and improve the compactness of the coating, it may be necessary to add more PEG6000 into the electrolyte under the condition of high voltage. Thereby, at high voltage, when the added amount of PEG6000 is 10 g/L, the diameter of micropores are the smallest, and the number of the large-size micropores is the least, and so coating possesses the lowest surface porosity and the densest microstructure, as shown in Fig.5 (b$_3$), Fig.6, and Fig.7 (b$_3$). Finally, the coating exhibits the highest hydrophobicity and the best anti-corrosion performance (Figs. 8 and 9 and Table 1). But in the case of low voltage, due to weaker breakdown discharge, only adding 5 g/L of PEG6000 into electrolyte can effectively inhibit large arc discharge, reducing the pore size, the number of large-size micropores, together with the coating’s surface porosity, and thus it enhances the resistant to corrosion of the coating to
the maximum extent. The possible mechanism of the influence of PEG6000 on the coating during plasma electrolytic oxidation process under high and low voltages is illustrated in Fig.13.

It should be noted that, under high and low voltages, as the concentration of PEG6000 continues to increase, too much PEG6000 may reduce its adsorption ability on the surface of the coating, which affects the surface roughness and microstructure of the coating and declines slightly the resisting corrosion property of the coating, as shown in Fig.5 (a3, a4, b4), Fig.7 (a3, a4, b4), Figs. 8, 9 and Table 1.

![Fig. 13. Schematic picture of working principle of PEG6000 during PEO process under high and low voltages.](image)

5. Conclusion

After adding PEG6000 into the electrolyte, the thickness of the coating decreases slightly, chemical and phase compositions of the coating nearly keep invariant, but the content of the deposited phases increases somewhat. Moreover, the number of the large-size micropores and surface porosity decrease, and the compactness of the coating augments, which may be due to the more uniform adsorption of anion ions on the interface between sample and electrolyte. Hence, corrosion resistance of the coating enhances attributed to the denser and more compact structure, and more hydrophobic surface.

As the concentration of PEG6000 increases, the resistance to corrosion of the coating increases firstly and then decreases owing to the difference in absorptive ability of PEG6000 on the surface of the coating. The best coating is obtained under 5 g/L of PEG6000 at low voltage. Its corrosion current density decreases by 74 % than that without additive, and its polarization resistance is approximately 6 times of the base electrolyte. While in the case of high voltage, the optimum coating is attained when PEG6000 is 10 g/L, whose corrosion current density is 36 % of that prepared in the base electrolyte, and the polarization resistance is about one order of magnitude higher than the latter.

Voltage exhibits an evident impact on the thickness and hydrophobicity of the coating. The
thickness of the coating prepared using low voltage is much lower in comparison with that under the high voltage, but its hydrophobic performance is stronger. Meanwhile, compared to the high voltage, the coating prepared at low voltage under the addition of less amount of PEG6000 (0 and 5 g/L) exhibits more excellent corrosion resistance, attributed to coating's lower surface porosity, denser microstructure and more hydrophobic surface.

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