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Original Research

The enhanced corrosion resistance of UMAO coatings on Mg by silane treatment

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Abstract

The surface silanization was carried out on ultrasonic micro-arc oxidation (UMAO) coatings on pure magnesium using KH550 as silane coupling agent (SCA). The surface morphology, chemical bonds and corrosion resistance of the silane films were investigated by scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR) and electrochemical workstation, respectively. The results showed that hybrid coatings were successfully prepared on pure magnesium by UMAO-NaOH (1 mol/L, 2 mol/L, 3 mol/L)-SCA processing. The organic films with Si–O–Mg bonds are helpful for the reduction of the pores in UMAO coatings. The pores decreased with increasing NaOH concentration. Compared with single UMAO treatment, the corrosion potentials (E_{corr}) of magnesium plates with UMAO-NaOH (1 mol/L, 2 mol/L, 3 mol/L)-SCA treatment increased by 29 mV, 53 mV and 75 mV, respectively, meanwhile the corrosion current density (I_{corr}) reduced one to two orders of magnitude. It indicated that the corrosion resistance of the coatings was improved by silane treatment.

Keywords: Pure magnesium; Ultrasonic; Micro-arc oxidation; Silane treatment; Corrosion resistance

1. Introduction

Magnesium and magnesium alloys have a good application prospect due to their small density, high specific strength and similar modulus of elasticity to human body. However, as biodegradable bone fixation materials, too quick degradation limits their clinical application in the body [1–3]. After the implant materials are implanted into the body, their biological properties depend on the interaction of their surface with human tissue and body fluid. Therefore, the surface modification treatment on magnesium and magnesium alloys can make them apply in the field of medicine better. Among the surface modification techniques, the micro-arc oxidation (MAO) exploits high temperature and pressure caused by micro-arc discharge on the surface of nonferrous metal, which makes the metal atoms on the surface of samples react with the activated oxygen ions in the electrolyte, forming dense oxide ceramic layer to improve the corrosion resistance [4]. However, the MAO ceramic layer on magnesium exists a lot of pores and some pores penetrate the substrate where the corrosive medium accelerates the corrosion of the metals [5–6]. Therefore the silane treatment is carried out on the MAO coating of pure magnesium in order to improve the corrosion resistance of the coating.

Silane treatment on the metal surface has a broad development prospect owing to its non-toxic, non-pollution, simple operation and low cost. Silane film as preservative coating can improve the corrosion resistance of the metal [7]. According to chemical bond theory [8], the silanization process can be divided into the following steps: (1) the hydrolyzation of silane, namely the –Si–OR linking to the silicon substrate hydrolyzes to form –Si–OH; (2) the silanol absorbs on the silane base, then the dehydration between the –Si–OH synthesizes the –Si–O–Si– and –Si–OH which combines with the –OH on the substrate surface to form hydrogen bonds; (3) heating curing is accompanied by dehydration reaction resulting in the covalent bond of –Si–O–Mg with the substrate. Only one silicon hydroxyl at the interface combines with the substrate surface, while the residual two

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–Si–OH condense with –Si–OH in other silanes or stay as free state. Whether in the solid or liquid phase, silane is difficult to produce oxidation–reduction reaction, which provides a very good protection for the metal surface. Zucchi [9] applied the silane treatment technology to WE43 magnesium alloy and found that the long-chain silane protected the magnesium alloys better. Domestic researchers used silane solution to prepare protective film on AZ31B magnesium alloy to control the corrosion of the magnesium alloy [10]. The water-soluble amino-silane of KH-460 was used on magnesium alloy for electrophoresis treatment, making the coating achieve an excellent corrosion resistance [11]. Many investigations show that silane treatment can enhance the corrosion resistance of magnesium alloy [12].

The pretreatment of magnesium alloys is very important throughout the process of silane films deposition because it will influence on the quality of the silane film directly. Li [13] considers that the industrial alkali washing is the most important step during the process of silane treatment for the metal. Correa [14] believes that alkaline cleaner can keep a large amount of alkaline hydroxyl groups on the surface of the magnesium alloy which provides additional attachment points for the deposition of the silane film on the substrate to react with the acid silane-hydroxy, resulting in stronger Si–O–Mg bond.

In this study, ultrasonic micro-arc oxidation and immersion processing were exploited on pure magnesium in the silicate electrolyte system. Firstly, ultrasonic micro-arc oxidation treatment was carried out, followed by alkali heat treatment with different concentration and silane treatment at last to prepare composite coating. The influence of silane treatment on the surface morphology, bond and corrosion resistance of the micro-arc oxidation coating on pure magnesium was investigated in order to solve the problem of transfixion pores and improve the corrosion resistance.

2. Materials and methods

2.1. Pretreatment of substrate material

The starting materials were 99.9% pure magnesium plates with a size of 10 × 10 × 1.5 mm^3. The surface of samples were mechanically polished by waterproof abrasive paper, rinsed with acetone and distilled water, and then air-dried for use.

2.2. Ultrasonic micro-arc oxidation and immersion processing

2.2.1. Ultrasonic micro-arc oxidation treatment

The UMAO parameters were set up as follows: voltage of 300 V, frequency of 500 Hz, duty cycle of 2.5%, duration time of 10 min, ultrasonic frequency of 60 kHz, electrode distance of 40 mm. The cathode was stainless steel and the anode was magnesium plate. The silicate electrolyte system was selected and worked under ultrasonic condition. The prepared samples were washed with distilled water.

2.2.2. Silane treatment

(1) Hot alkali pretreatment

The above UMAO plates were put into NaOH solution with different concentrations (1 mol/L, 2 mol/L, 3 mol/L), and heated at 60 °C for 1 h. After that, the samples were rinsed with DI water and dried in the air, and labeled as UMAO–NaOH.

(2) Silane treatment

In this work, KH550 (γ-aminopropyl triethoxysilane) was used as silane coupling agent (SCA) with a hydrolysis ratio of 1:9:1 to ethanol and water by volume. The pH of solution was adjusted 4.0 by the addition of acetic acid slowly. The solution was sufficiently stirred. The alkali treated samples were immersed into the silane hydrolysis, and then heated in an oven to form the final cured film. These samples were labeled as UMAO-NaOH-SCA.

2.3. Surface characterization

2.3.1. Scanning electron microscope

The surface morphologies of the coating were examined by scanning electron microscope (SEM, JSM-6360LV).

2.3.2. Fourier transform infrared spectroscopy

The chemical bonds of the coating were analyzed by Fourier transform infrared spectroscopy (Bruker Germany). The powders peeled from the coating were mixed with KBr and pressed into tablets. The scanning wavelength is 400–4000 cm^{-1}, using resolution accuracy of 4 cm^{-1}.

2.3.3. Electrochemical tests

Princeton IM6e 400 electrochemical workstation made in German was employed to evaluate the corrosion resistance of coatings. During this course, a three-electrode system was used with magnesium plate as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode (Hg/Hg_2C1_2 saturated KCl solution) as the reference electrode. 0.9% NaCl solution was used as electrolyte.

3. Results and discussion

3.1. Surface morphology of coatings

Fig. 1 shows the surface morphologies of magnesium plates after treatment by UMAO and UMAO-NaOH (1 mol/L, 2 mol/L, 3 mol/L)-SCA processes. As shown in Fig. 1a, there exist unequal-sized pores on the surface of the UMAO coating, which can be acted as a passageway for corrosive medium to reach the substrate, and consequently impair the corrosion resistance of the coating. After the UMAO coating was immersed in NaOH solution, the diameter of pores on the surface of coating decreased with increasing NaOH concentration, as shown in Fig. 1b, c and d. It can be observed from Fig. 1e, f and g that the surface morphologies can be influenced by alkali and SCA treatments. The higher concentration of alkali heat treatment, the better pores fill. When the

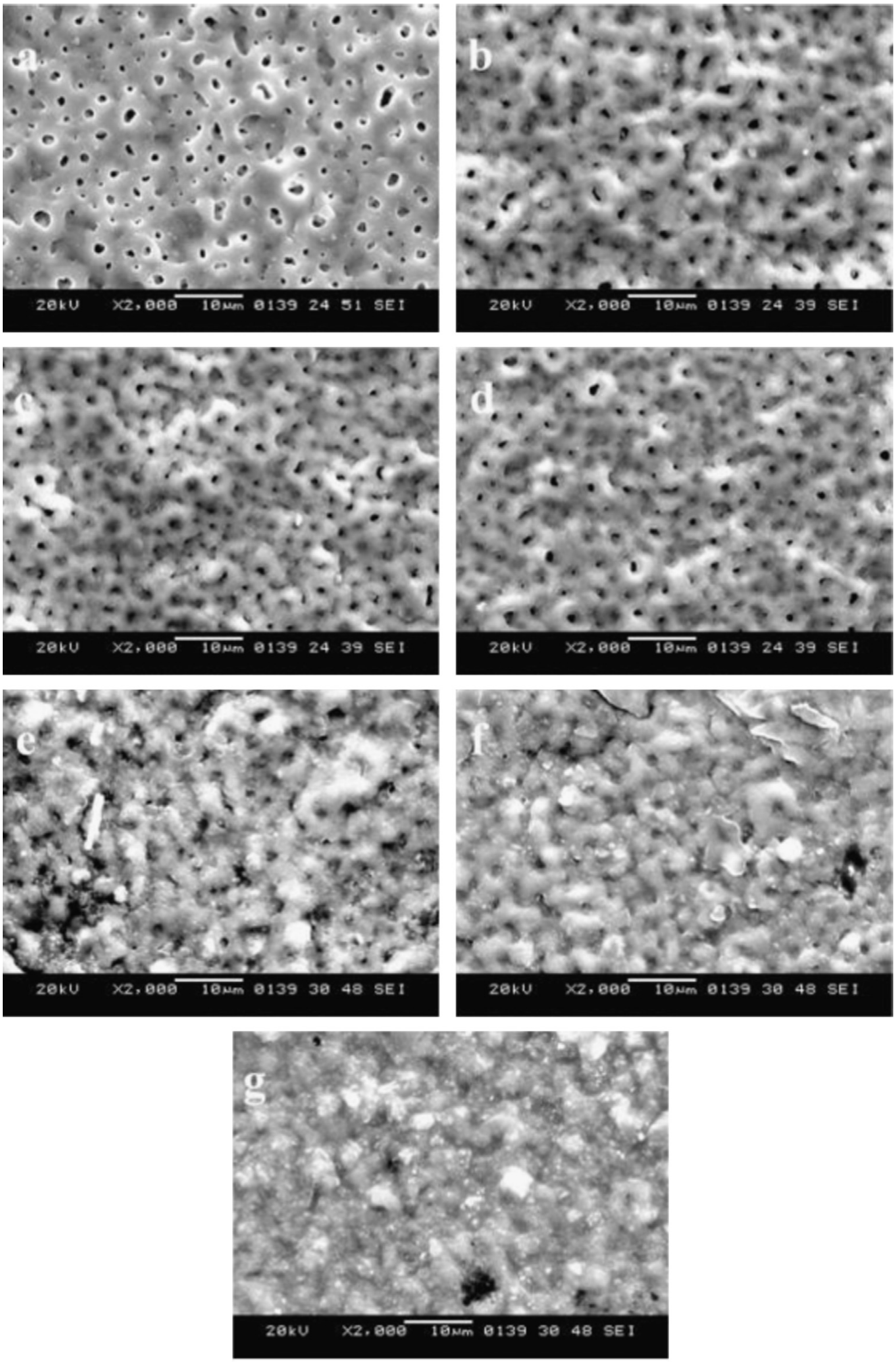

Fig. 1. Surface morphologies of magnesium plates with different treatment: (a) UMAO; (b) UMAO-NaOH (1 mol/L); (c) UMAO-NaOH (2 mol/L); (d) UMAO-NaOH (3 mol/L); (e) UMAO-NaOH (1 mol/L)-SCA; (f) UMAO-NaOH (2 mol/L)-SCA; (g) UMAO-NaOH (3 mol/L)-SCA.

concentration is 3 mol/L, the pores almost seem invisible. It can be explained that the silanol from the hydrolysis of silane molecules reacts with the metal oxide and hydroxyl of the ceramic layer as well as the self-condensation of the silane molecule to form film, which improves surface morphologies of the coating.

3.2. The FTIR analysis of coatings

Fig. 2 presents the FTIR results of the coating with UMAO-NaOH (1 mol/L)-SCA treatment. The 562 cm^{-1} indicates the Mg–O stretching vibration. The 876 cm^{-1} and 1028 cm^{-1} present the Si–O stretching vibration. The 3452 cm^{-1} and

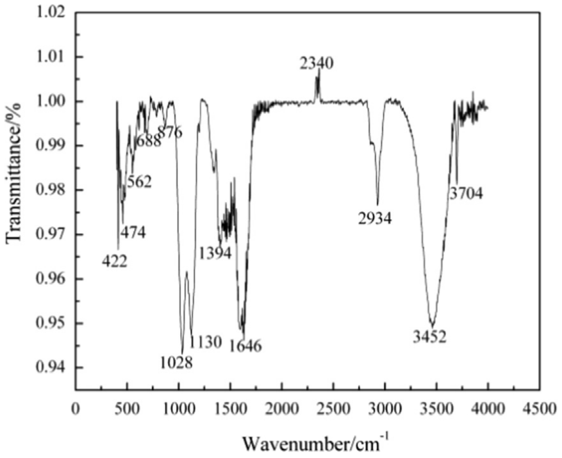

Fig. 2. FTIR of magnesium plate with UMAO-NaOH (1 mol/L)-SCA treatment.

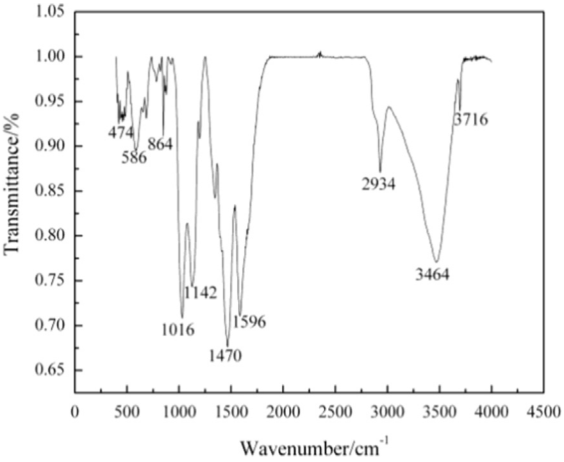

Fig. 3. FTIR of magnesium plate with UMAO-NaOH (2 mol/L)-SCA treatment.

1192 cm^{-1} correspond to the stretching vibration of N–H and C–N, respectively. The 474 cm^{-1} was the O–Mg–O stretching vibration. The 876 cm^{-1} was the –Si–OH stretching vibration resulting from hydrolyzed silane hydrogen bond. The 3704 cm^{-1} presents the hydroxy from unreacted silanol.

Fig. 3 shows the FTIR results of coatings with UMAO-NaOH (2 mol/L)-SCA treatment. The 586 cm^{-1} presents the Mg–O stretching vibration. The 864 cm^{-1} and 1016 cm^{-1} exhibit the Si–O stretching vibration. The 3464 cm^{-1} indicates the N–H stretching vibration. The 1192 cm^{-1} was the C–N stretching vibration. The 474 cm^{-1} was the O–Mg–O stretching vibration. The 864 cm^{-1} was the –Si–OH. The 3716 cm^{-1} presents the hydroxy from unreacted silanol.

Fig. 4 shows the FTIR results of coatings with UMAO-NaOH (3 mol/L)-SCA treatment. The 574 cm^{-1} indicates the Mg–O stretching vibration. The 876 cm^{-1} and 1028 cm^{-1} present the Si–O stretching vibration. The 3464 cm^{-1} was the N–H stretching vibration. The 1192 cm^{-1} was the C–N stretching vibration. The 486 cm^{-1} presents the O–Mg–O stretching vibration. The 870 cm^{-1} was the –Si–OH. The 3704 cm^{-1} presents the hydroxy from unreacted silanol.

In summary, the silane coupling agent of KH550 has entered the micro-arc oxidation coating and the silicon layer reacts with the alcohol moiety by hydrolysis of the silane molecule to produce Mg–O–Si combination.

3.3. The electrochemical corrosion of coatings

Fig. 5 shows the tafel curves of the coatings with UMAO and UMAO-NaOH (1 mol/L, 2 mol/L and 3 mol/L)-SCA treatment on pure magnesium. Table 1 presents the electrochemical corrosion parameters of magnesium plates with different treatment.

Compared with the UMAO treatment, the corrosion potential (E_{corr}) of magnesium plates with UMAO-NaOH (1 mol/L, 2 mol/L, 3 mol/L)-SCA treatment increased by 29 mV, 53 mV

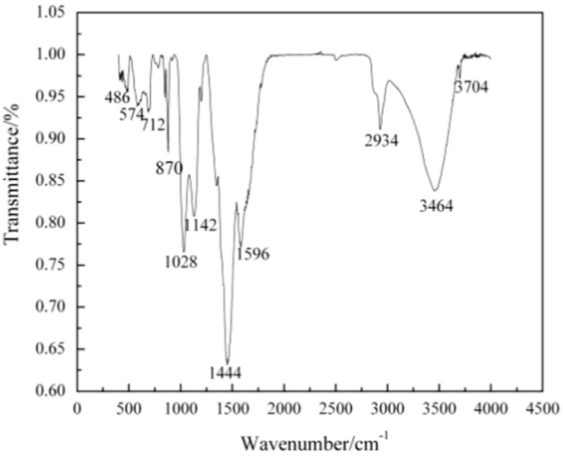

Fig. 4. FTIR of the coating with UMAO-NaOH (3 mol/L)-SCA treatment.

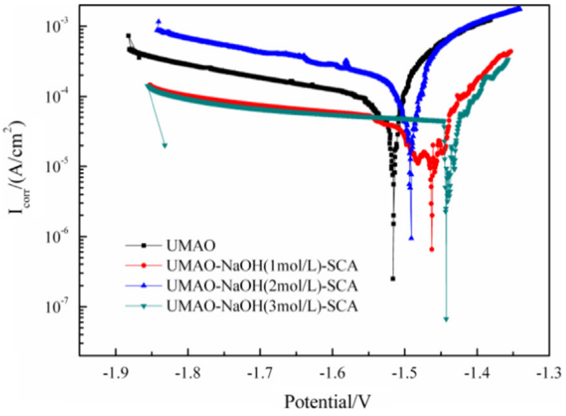

Fig. 5. Tafel polarization curves of magnesium plates with different treatment.

Table 1
E_{corr} and I_{corr} of magnesium plates with different treatment.

Sample	E_{corr} (V)	I_{corr} (A/cm^2)
UMAO	−1.517	2.135×10^{-2}
UMAO-NaOH (1 mol/L)-SCA	−1.488	2.73×10^{-3}
UMAO-NaOH (2 mol/L)-SCA	−1.464	8.927×10^{-4}
UMAO-NaOH (3 mol/L)-SCA	−1.442	2.383×10^{-4}

and 75 mV, respectively, meanwhile the corrosion current density (I_{corr}) reduced one to two orders of magnitude. Corrosion rate of metals slows down with the decrease of corrosion current density. Thus, the greater self-corrosion potential and the smaller self-corrosion current, which can obtain better corrosion resistance. It is showed that the corrosion resistance of magnesium plates with UMAO-NaOH (1 mol/L, 2 mol/L, 3 mol/L)-SCA treatment was higher than that of single UMAO treatment. Therefore, the silane treatment for the ultrasonic micro-arc oxidation coating can inhibit the cathode and anode polarization reactions effectively, which provides available protection for magnesium and decreases its corrosion rate in human body. It is indicated that after the micro-arc oxidation coatings was treated by silane, the silanol from the hydrolysis of silane molecule reacted with the oxide and the hydroxyl of the ceramic layer, then dehydrated and solidified to form film. This film can prevent the corrosive medium from invading the magnesium, so the corrosion potential was improved.

Fig. 6 shows electrochemical corrosion morphologies of magnesium plates with different treatment. It can be seen that magnesium plate with single UMAO treatment suffered from more serious corrosion, and pitting corrosion linked and spread to ulcer-like corrosion. Corrosive microcracks appeared in some areas. The porous coating provided channels for the Cl^- to penetrate the substrate. Once deep etch pits formed, the film was destroyed. When magnesium plates were treated by

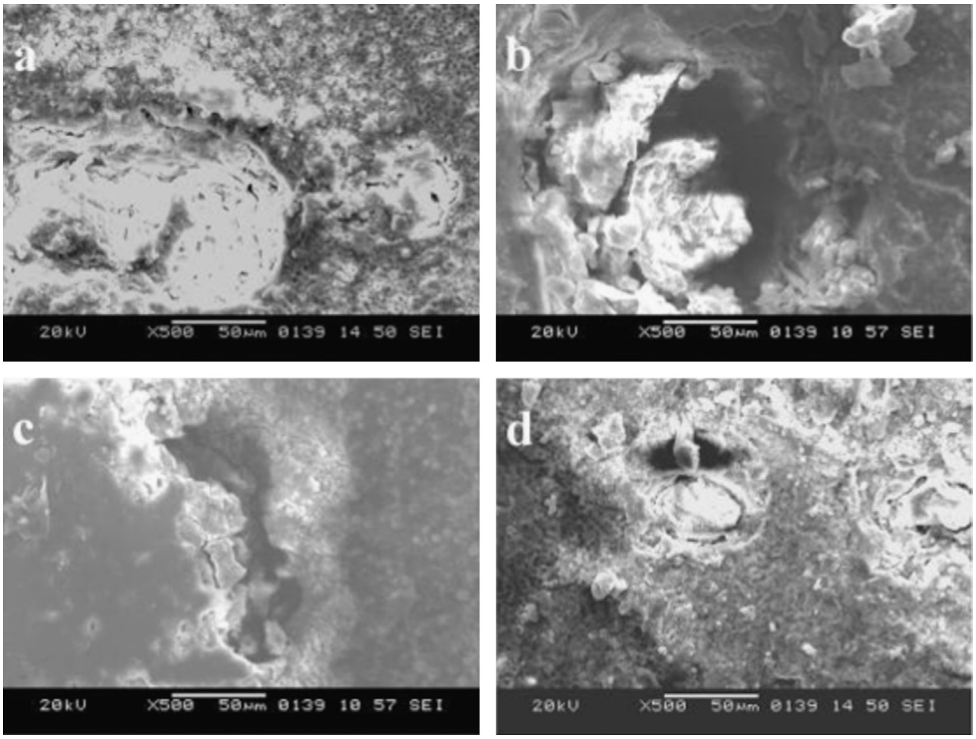

Fig. 6. Electrochemical corrosion morphologies of magnesium plates with different treatment: (a) UMAO; (b) UMAO-NaOH (1 mol/L)-SCA; (c) UMAO-NaOH (2 mol/L)-SCA; (d) UMAO-NaOH (3 mol/L)-SCA.

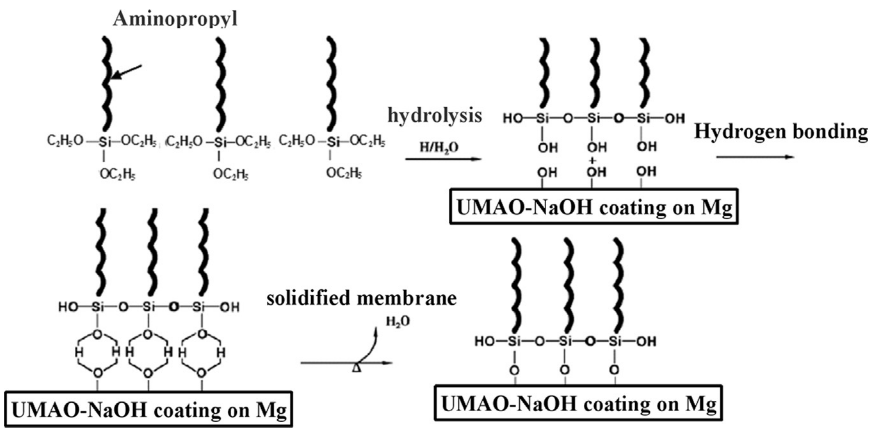

Fig. 7. Mechanism diagram of UMAO-SCA processing.

UMAO-NaOH (1 mol/L, 2 mol/L, 3 mol/L)-SCA, the higher NaOH concentration, the lighter corrosion, and the size of etch pits reduced. The magnesium plates with UMAO-NaOH (3 mol/L)-SCA treatment was damaged minimally and it kept intact. The above analysis showed that the magnesium plates with UMAO-NaOH (3 mol/L)-SCA treatment exhibited the best corrosion resistance in NaCl solution, which is perspective as a biodegradable bone substitute materials for the body.

4. Discussion

KH550 is aminopropyl triethoxysilane whose chemical structure formula is $NH_2(CH_2)_3Si(OC_2H_5)_3$. It molecule comprises two groups, one is aminopropyl and the other is ethoxy. As shown in Fig. 7, in the process of hydrolysis, $-Si-OC_2H_5$ base linking to the silicon hydrolyzed to form –Si–OH. Then the silanol adsorbed on the substrate, and the dehydration condensation between the –Si–OH produced –Si–O–Si and Si–OH which combined with the –OH on the substrate surface to form hydrogen bonds. Heat curing process is accompanied by dehydration reaction which formed covalent bond of –Si–O–Mg with the substrate. At the interface, only one silicon hydroxyl from silane combined with base material surface, and the remaining two –Si–OH condensed with other –Si–OH in other silane or stayed a free state.

Alkali heat treatment is a very important step. Alkaline cleaner can keep large amounts of alkaline hydroxyl groups on magnesium surface to react with acid hydroxyl silane. It is showed that the hydroxy on the substrate surface provides more attachment points for the silane film to deposit which enables the Si–O–Mg to bind stronger.

5. Conclusion

(1) Hybrid coatings were obtained on pure magnesium by UMAO-NaOH (1 mol/L, 2 mol/L, 3 mol/L)-SCA processing. The organic films with Si–O–Mg bonds are helpful for the reduction of the pores in UMAO coatings. The surface layer is compact and uniform. The pores decreased with increasing NaOH concentration.

(2) Compared with single UMAO treatment, the corrosion potential (E_{corr}) of magnesium plates with UMAO-NaOH (1 mol/L, 2 mol/L, 3 mol/L)-SCA treatment increased by 29 mV, 53 mV and 75 mV, respectively, meanwhile the corrosion current density (I_{corr}) reduced one to two orders of magnitude. The corrosion resistance of coating was improved by silane treatment.

Acknowledgments

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