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ARTICLE

Effect of SiO_2 Sol Sealing on Corrosion Resistance of Anodic Films of AZ31 Mg Alloy

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Abstract: Silica sol was used to seal the pores of anodic oxide film of AZ31 magnesium alloy. The effect of the immersion time, the calcinating temperature and the immersion times on morphology and corrosion resistance of the film was discussed. Scanning electron microscope (SEM) was employed to characterize the surface morphology of the composite film, and potentiodynamic polarization curves were used to analyze the corrosion behaviors. The surface composition of the sealed anodic films was studied by energy dispersion spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). It has been found that the corrosion resistance of anodic film is improved by sealing by silica sol. When the dipping time is 1.5 min and the calcination temperature is 350 ℃, the corrosion resistance of the film is the best. Times of dipping and calcination have a greater influence on the performance of the film. When the dipping-calcination is 7 times, the film has a good corrosion resistance. After sealing, silica sol is adsorbed on inner pores and outside pores of the anodic oxidation film.

Key words: AZ31 Mg alloy; sealing; anodic film; SiO_2 sol; corrosion resistance

Due to light weight, high specific strength and stiffness, high damping and easy recovery, magnesium alloys has been used in many fields, such as aerospace, automotive, cellular phones and computer industries[1]. However, the poor corrosion resistance of magnesium alloys has restricted their further applications. In order to improve the corrosion resistance of magnesium alloys, surface treatment is a kind of available and effective method, including microarc oxidation[2], electroless plating[3], diamond-like carbon coating[4], conversion coatings[5], vapor-phase process[6], organic treatment and laser surface modification technique. Compared with other treatments, anodizing is a proper way to coat magnesium alloys. Nevertheless, for industrial applications, the corrosion resistance of anodized coatings is not sufficient, because the coatings are normally porous and contain many cracks and defects. Sealing treatment can improve the mechanical and protective properties of anodic films, which is considered to be an essential step to improve the surface morphology and corrosion resistance of the film.

As sealing strongly recommended for the coatings, the process condition is required to be discussed urgently. The influence of sol in electrolyte on the morphology and the corrosion resistance was studied in some anodizing process; however, few researches about the sealing of anodic film with sol were reported. Song[7] reported that an E-coatings pre-film could be deposited in the pores or cracks of an anodized coating on a ZE41 magnesium alloy which sealed the defects of the coatings. After curing, the insulating sealants would become insoluble, permanently filling in the defects of the coatings. Guo [8] studied the effects of titania sol on anodizing AZ31 Mg alloy in borate and aluminate electrolyte. TiO_2 was deposited in the anodic film. The addition of titania sol could improve the uniformity and enhance the corrosion resistance of the anodic film. Li[9] investigated that anodic films were prepared on the AZ91D magnesium alloy in Na_2SiO_3 electrolyte with addition of silica sol under the constant current density of $20mA/cm^2$. The addition of silica sol increased the thickness of the anodic film and improved the

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roughness of the film surface.

In the present paper, we focused on finding the best sealing process condition of the anodic film on AZ31 Mg alloy.

1 Experiment

AZ31 magnesium alloy was used for this study. The samples of AZ31 magnesium alloy were prepared with the size of 2.0 cm×2.0 cm×0.2 cm.

Prior to formation of anodic film, specimens were polished with $200^{\#}$, $500^{\#}$, $800^{\#}$, $1000^{\#}$, and $1200^{\#}$ grit SiC paper to obtain even surfaces, and pretreated with alkaline solution degreasing and acid pickle polishing, and then were anodized in electrolyte solution, rinsed twice in flowing distilled water as quickly as possible between each step to remove all the salts. Alkaline cleaning was conducted at 55±5 °C for 5 min in the following solution composed of 60 g/L sodium carbonate, 30 g/L sodium silicate and 60 g/L trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$). Acid pickling was conducted at room temperature for 20~30 s in the following solution composed of 195 mL/L CH_3COOH and 45 g/L $NaNO_3$.

AZ31 Mg alloy was anodized in alkaline borate electrolyte containing 110 g/L $Na_2B_4O_7$, 50 g/L $NaAlO_2$, 40 g/L NaOH, and 10 g/L sodium citrate. The anodic film was formed under constant current density of 2.0 A/cm^2 for 10 min at room temperature. The AZ31 Mg alloy sample was used as anode, and the stainless steel plate as cathode. The formation of anodic film was observed by the change of voltage and spark discharge during the process. The voltage began to rise from 0 V to 80 V (about 2 min), then the spark discharge was visible, and the relatively thick oxide film was produced.

In the investigation, the colorless and transparent silica sol was prepared by adding 4 mL tetraethoxysiliane to 35 mL ethanol with stirring for 20 min at room temperature (as solution I), and then slowly dripping the mixture solution (35 mL ethanol, 2 mL distilled water and 0.2 mL ammonia solution) into the solution I for 1 h. Then the silica-sol was aged for 24 h at room temperature for using.

After anodizing, selected specimens were sealed in silica sol under vacuum state for several minutes with different times, and then exposed to air. The sealed samples were calcinated at a certain temperature for 0.5~2 h. After sealing, the samples were cooled down to room temperature.

The morphologies of the conversion coating were observed using scanning electron microscope (JSM-6480) equipped with energy dispersion spectroscopy (EDS).

The chemical composition of the coating was investigated using physical electronics, PHI 5700 EICA XPS with Al Kα (1486.6 eV) monochromatic source. All energy values were corrected according to the adventitious C 1s signal, which was set at 284.62 eV. The data were analyzed with XPSPEAK 4.1 software.

The corrosion resistance of the coating was measured by electrochemical tests. Potentiodynamic polarization tests were conducted using a commercial Model CHI760B electrochemical workstation in a three-electrode system with the sample as working electrode, saturated calomel electrode as reference electrode and platinum sheet with 1cm×1cm surface area as counter electrode. The corrosive medium was 3.5 wt% NaCl solution. The potentiodynamic polarization curves were tested with a scan rate of 0.01 V/s from –500 to 500 mV (SCE) vs open circuit potential. The polarization tests were carried out in triplicate to evaluate the reproducibility of the results. All of the measurements were carried out at room temperature.

2 Results and Discussion

2.1 Effect of immersion time on morphology and corrosion resistance of the film

Fig.1 shows the surface morphologies of anodic films before and after sealing in silica for different time. Fig.1a shows the anodic film surface with pores which were about a few of microns in size and evenly distributed over the surface. After sealing in silica sol, a smooth white coating is formed on the anodic film surface. From Fig.1b~1e, it can be obviously observed, with the increasing of immersion time, the number of pores decreases and the size of pores declines gradually. The results show that longer immersion time can form a more compact and denser film.

In order to study the relationship between immersion time and the corrosion resistance, potentiodynamic polarization curves of anodic films after sealing in silica sol were measured in 3.5 wt% NaCl solution as shown in Fig.2. The results of corrosion potential (E_{corr}) and corrosion current

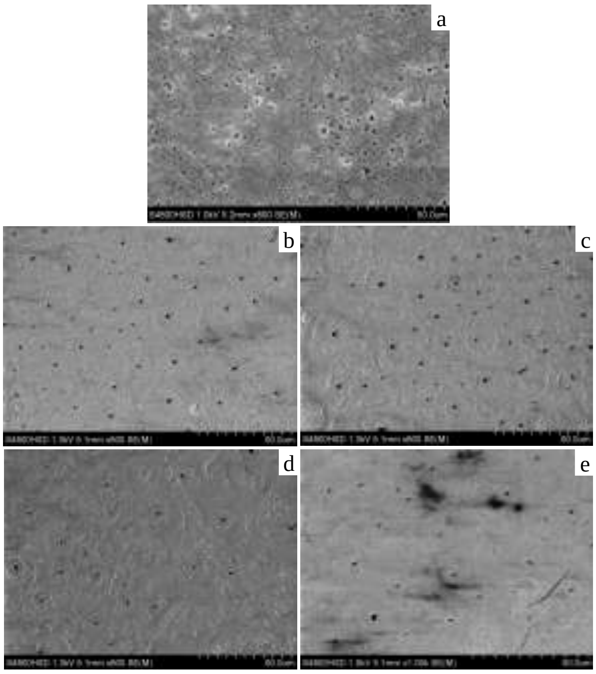

Fig.1 Surface morphologies of the anodic films unsealed (a) and sealed in silica sol with different time: (b) 1.5 min, (c) 2 min, (d) 3 min, and (e) 30 min

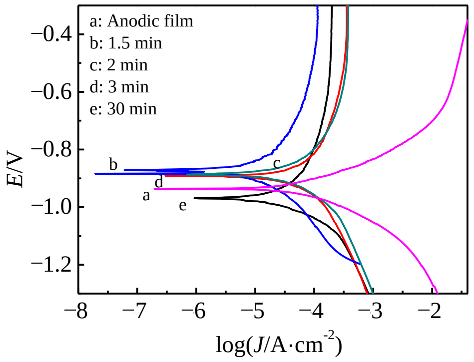

Fig.2 Potentiodynamic polarization curves of unsealed and sealed anodic films with different immersing time in 3.5% NaCl solution

Table 1 Parameters of polarization curves for anodized film in Fig.2

Sample	a	b	c	d	e
$J/\times10^{-5}$A cm^{-2}	40.37	1.301	4.092	7.637	3.430
E/V	–0.929	–0.865	–0.888	–0.892	–0.969

density (J_{corr}) are listed in Table 1. The corrosion resistance of sealed film is improved compared with the anodic AZ31 Mg alloy.

From these curves in Fig.2, it can be clearly observed that, with the increasing of the immersion time, the corrosion current density of the composite film increases. When the immersing time was 1.5 min, the silica sol can be absorbed on the film surface and inner pores, forming a compactly protective layer on anodic film. The OH^- ions of silica sol can erode the anodic film for a longer immersion time. With the increasing of immersion time, the corrosion resistance decreases. When the dipping time increases to 30 min, the silica sol on the surface is so much that leads to the film loosing; therefore, its cohesion with the substrate is bad, and the corrosion current density is higher, resulting in the worst corrosion resistance. It is necessary to roast after immersion which can achieve more strong cohesive force.

2.2 Effect of calcinating temperature on corrosion resistance of the film

Fig.3 shows the potentiodynamic polarization curves of sealed anodic film after immersion in the silica sol for 1.5 min at different calcinating temperatures for 1 h. The results of electrochemical parameters are listed in Table 2. Compared with the curves in Fig.2, the corrosion current density of the composite film after calcinating (in Fig.3) is lower than that uncalcinated. The results show that calcinating can increase the corrosion resistance of the sealed film. The lower the corrosion current density of the film, the better the corrosion resistance. When the calcinating temperature is 350 ℃, the corrosion current density is the minimum (8.815×10^{-6}A/cm^2) and the corrosion resistance of the anodic film is the best.

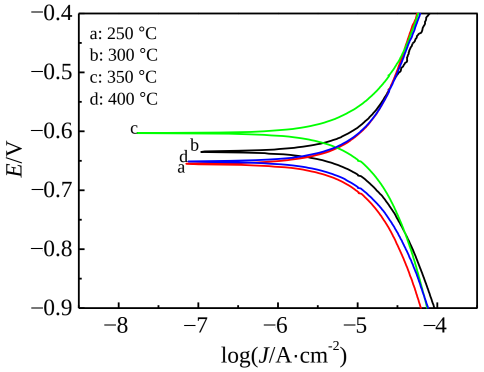

Fig.3 Potentiodynamic polarization curves of sealed anodic film (sealed 7 times) at different calcinating temperatures for 1 h in 3.5% NaCl solution

Table 2 Parameters of polarization curves for composite film in Fig.3

Sample	a	b	c	d
$J/\times10^{-6}$ A cm^{-2}	9.042	10.64	8.815	96.66
E/V	–0.655	–0.685	–0.603	–0.651

2.3 Effect of immersion times on morphology and corrosion resistance of the film

After immersion and calcination, a smooth white coating is formed on the anodic oxide film surface. Fig.4 shows the surface morphologies of the anodic films after immersing in the silica sol for 1.0 min with different times followed by calcinating at 300 ℃ for 0.5 h. With the increase of times of dipping, the pores become smaller and the surface becomes more compact, as shown in Fig.4. When the immersion number reaches 7 times, the number of pores on the anodic film declines greatly.

Corrosion potential and corrosion current density are used to evaluate corrosion resistance of the conversion coating. Fig.5 shows potentiodynamic polarization curves of anodic

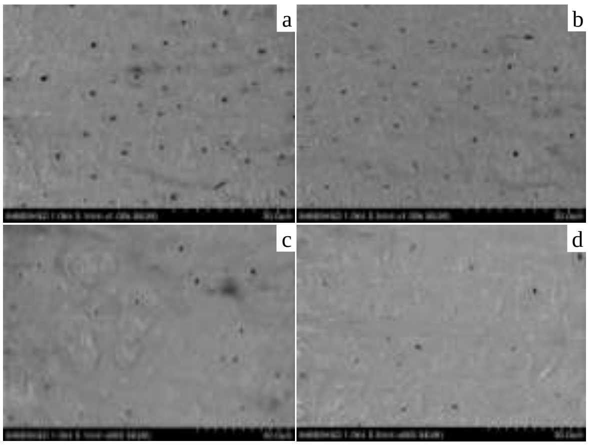

Fig.4 Surface morphologies of anodic films sealed in silica sol with different times, and then calcinated at 300 ℃ for 0.5 h: (a) 4 times, (b) 6 times, (c) 7 times, and (d) 9 times

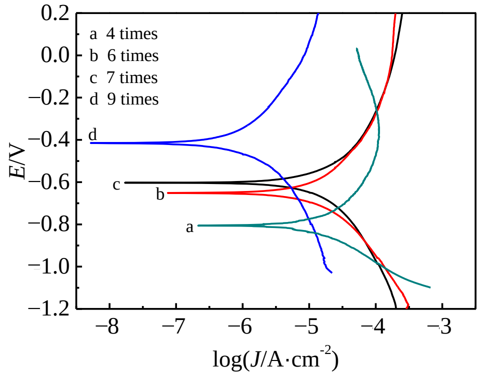

Fig.5 Potentiodynamic polarization curves of anodic films sealed with different immersing times and then calcinated at 300 ℃ for 0.5 h in 3.5% NaCl solution

Table 3 Parameters of polarization curves for composite film in Fig.5

Sample	a	b	c	d
$J/\times10^{-5}$ A cm^{-2}	3.665	2.672	2.118	1.026
E/V	–0.803	–0.644	–0.600	–0.420

films after immersion and calcination with different times in 3.5 wt% NaCl solution. The results are listed in Table 3. From Fig.5 it can be seen that, with the number of dipping and calcinating increasing, the smaller corrosion current density and the higher corrosion potential improve the corrosion resistance of the film. Because each immersion and calcination makes the pores sealed, moreover, calcination can enhance the adhesion of the sol on the membrane surface and in pores. Repeating of immersion and calcination can greatly reduce the number of pores, thereby, the corrosion resistance of the film is improved.

2.4 Morphology and composition of the sealed film

Fig.6 shows the EDS spectra of inner and outer pore (immersion time 1.5 min, 7 times and calcinating temperature 350 ℃ for 1 h).

From Fig.6, it is seen that Si element is located in inner and outer pores. Table 4 shows the element contents of the inner and outer pores after sealing, but the outer deposition of silica sol is higher than that of the inner pore. This is because the sizes of the inner pores are small and sol is difficult to deposit in the pores.

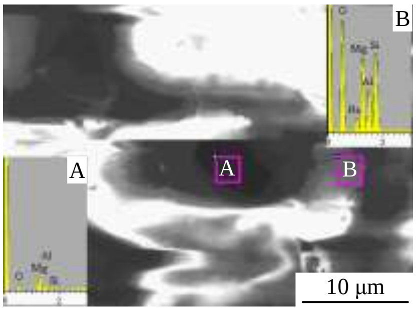

Fig.6 EDS spectra of inner pore (A) and outside pore (B)

Table 4 EDS results of surface element compositions of inner pore and outer pore (at%)

Element	O	Mg	Al	Si	Na
Inner pore	43.23	32.18	12.65	11.94	—
Outside pore	56.89	13.71	8.49	17.95	2.95

XPS is usually employed to identify the specific electron binding energies at the surface of conversion coating and the main reacting products. Fig.7 shows the XPS survey spectra of the anodic film sealed by silica sol. As shown in Fig.7, the composite film is mainly composed of O, Mg, Al and Si elements, but anodic film doesn't have Si element.

The XPS high-resolution scan of Mg 1s and Si 2p spectra are depicted in Fig.8. From Fig.8a, it is seen that the Mg 1s decomposes into three peaks, which were measured at 1303.80, 1303.20 and 1304.00 eV that could be attributed to

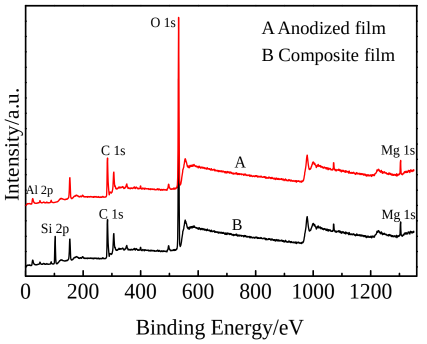

Fig.7 XPS spectra of anodized film and composite film

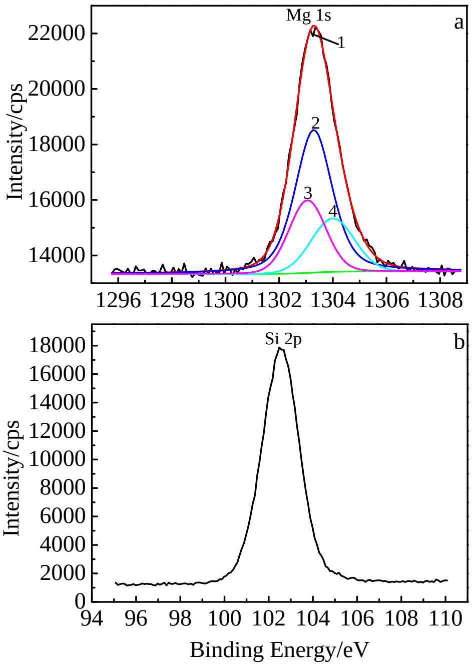

Fig.8 High-resolution XPS spectra of Mg 1s (a) and Si 2p (b) for anodized film after sealing in SiO_2 sol

MgO, Mg and $MgSiO_3$, respectively. The Si 2p peak (Fig.8b) of silica sol sealed film was detected at 103.0 eV, which was assigned to SiO_2. The result shows that the sealed film is mainly composed of MgO, SiO_2 and $MgSiO_3$. After sealing, SiO_2 sol is deposited in the pore and outside the pores, and it can protect the Mg alloy in corrosive media.

3 Conclusions

1) The sealing has a significant effect on the corrosion resistance of composite film.

2) The shorter the immersion time or the more the immersion times, the better the corrosion resistance.

3) When calcinating temperature is 350 ℃, the corrosion current density is reduced and the corrosion resistance of the composite film shows the best corrosion resistance.

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硅溶胶封孔对 AZ31 镁合金阳极氧化膜抗腐蚀性能的影响

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摘　要：采用硅溶胶对AZ31镁合金阳极氧化膜进行封孔处理。分别讨论了浸渍时间、焙烧温度及浸渍焙烧次数对氧化膜形貌及抗腐蚀性能的影响。使用扫描电子显微镜（SEM）分析复合膜的表面形貌，利用动电位极化曲线表征膜的腐蚀性能。采用能谱（EDS）和X射线光电子能谱表征封孔后膜的表面组成。结果表明，硅溶胶封孔可提高阳极氧化膜的抗腐蚀性能；浸渍时间为1.5 min，焙烧温度为350 ℃时，膜的耐腐蚀性能最佳；浸渍-焙烧次数对膜的性能影响也较大，浸渍-焙烧7次时，膜的耐腐蚀性能较好。封孔后，硅溶胶吸附于阳极氧化膜的孔外与孔内。

关键词：AZ31 镁合金；封孔；阳极氧化膜；SiO_2 溶胶；抗腐蚀性能

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