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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 °C, 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

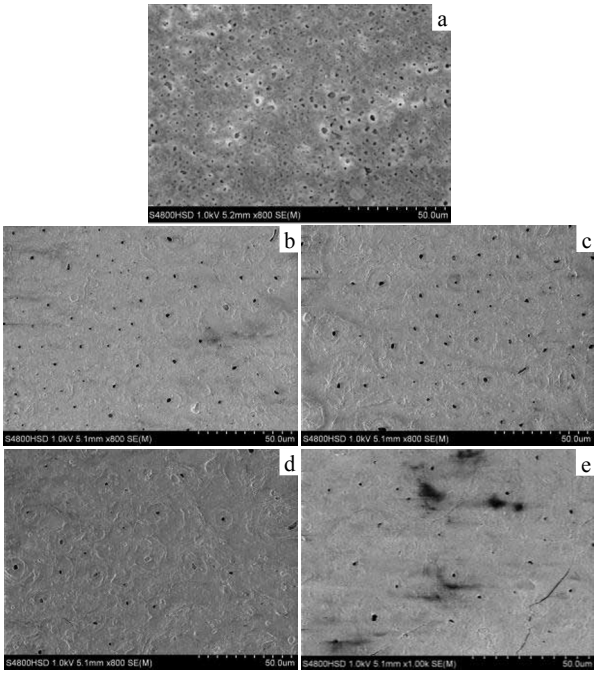

Fig.1 Surface morphologies of the anodic films unsealed (a) and sealed in silica sol with different time: (b) 1.5 min, (c) 2 min, (d) 3 min, and (e) 30 min