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Surface protection method for magnesium alloy based on using organic coating and electroless plating

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ABSTRACT

Aimed at the traditional surface treatment technology failing to conduct the electrochemical protection for the magnesium alloy, the paper proposed a novel method of the surface protection for the magnesium alloy based on using the organic coatings and electroless plating. In this method, firstly the organic coating is coated on the surface of magnesium alloy, secondly then chemical copper plating for the magnesium alloy was carried out. Therefore, during the chemical plating, copper will be deposited on the organic coating surface. The organic coating enable the substrate can not directly contact copper coating so as to avoid the occurrence of galvanic corrosion. The metallized films-ray diffraction and scanning electron microscope analysis were used to research the morphology of the interlayer and plating film. The research results showed that the films have a rather perfect compact structure. The potentiodynamic polarization curves for corrosion study of the coated magnesium alloys were also performed in a corrosive environment of NaCl solution. Polarization curve test results verified that comparing with the substrate, the corrosion resistance of coated magnesium alloys increases greatly. In addition, the environmental pollution can be avoided because of using the sodium hypophosphite instead of formaldehyde as the reducing agent.

KEYWORDS

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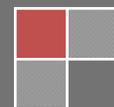
INTRODUCTION

The magnesium alloy is the lightest metal among the structural materials and has many excellent properties, such as high tensile strength, high specific strength and excellent performance in the shock absorption, noise reduction and electromagnetic shielding. Magnesium alloy which can be widely used in military, automobile, aircraft, mobile phone, computer, electrical and other industrial products, known as the twenty-first century green engineering material. However, magnesium and magnesium alloy is a kind of the very active metals, its standard electrode potential is lower than the potential of iron, aluminum, zinc, copper and other metals, in the air it is susceptible to oxidation so as to form a film on the surface of magnesium alloy. This kind of the film is usually sparse porous, not only can not protect the substrate, but also will cause substrate to react corrosive pitting so as to accelerate corrosion rate of the substrate, so the corrosion resistance of the magnesium and magnesium alloy is low. The poor corrosion resistance of magnesium and magnesium alloy greatly limits their application scope. To improve the corrosion resistance of magnesium and magnesium alloys, it is necessary to carry on processing on them. The simplest method is the surface processing on magnesium alloy [1-3]. At present, the common surface processing methods mainly are chemical plating, anodizing, chemical conversion film, organic coating, and so on. Among the methods the surface protection, chemical plating has been favored because of its simple operation, uniform and compact coating, good profiling, and other advantages [4-6]. The chemical copper plating process has low cost, less pollution, less side reaction, easy wastewater treatment and other advantages. The plating layer itself has good corrosion resistance, anti-electromagnetic interference performance and decorative performance. However, because the electrode potential of magnesium and its alloys is lower than copper, the capper plating layer on the surface of magnesium and magnesium alloy plating layer is difficult to be obtained. In view of this phenomenon, this paper developed a new chemical plating process with introducing the organic coating. The characteristic of this process is that the alloy surface was coated with a layer of organic film before chemical plating. The paper used this new technology to process the surface of AZ31 magnesium alloy and got compact copper plating layer [7-8]. And the corrosion resistance performance of the alloy surface after treatment was also conducted a preliminary study.

EXPERIMENT METHOD

Experiment material

AZ31 magnesium alloy was used as the substrate sample. Its chemical composition was shown in TABLE 1. The size of the sample sheet is 1.2 mm × 30mm × 50mm. The organic coating been used was 8604 organic silicone heat-resistant paint which had good water resistance and heat resistance.

TABLE 1: Quality percentage of chemical composition of AZ31 magnesium alloy

element	Al	Zn	Mn	Si	Cu	Ca	Mg
content	2.9	1.3	0.6	0.03	0.02	0.03	95.12

Technological process

Technological process of the surface protection method is surface treatment→unoiling（4～10g/L Na2SiO3, 2～7g/L NaCO3, 0.5～2g/L NaOH, 0.1～1g/L KCrO3, room temperature, 10min）→water washing→pickling neutralization (60ml/L HNO3, room temperature, 3min)→desiccation→coating film→desiccation→coarsening（400～600g/L NaOH, 50℃, 30min)→water washing→sensibilization（5～10g/L SnCl2, 1～16ml/l HCl, moderate deionized water)→water washing→activation 10～15g/L AgNO3, 10～15g/L NaOH, moderate deionized water)→water washing→chemical copper plating→water washing→desiccation.

The composition and content of chemical copper plating Liquid is 8g/L CuSO4·5H2O, 20 g/ L NaH2PO3, 32g/L Na3C6H5O7, 0.5g/L NiSO4·6H2O, 45g/L H3BO3, 0.2 mg/L stabilizer, pH10.1, temperature 50℃, 100min.
The main equipment and instruments: electric thermostatic water bath pot, the blast drying box and digital display acidity agent.

Test

The cross cutting method was used to observe the combination situation of the coating and substrate (execute GB/T 9286-1998). The SS-550 scanning electron microscope (SEM) was used to observe the micro-morphology of the film and chemical plating layer. Energy dispersion coating composed of random with the spectrum determination. The composition of coating layer was determined by the energy dispersive X-ray analyzer (EDX). The structure of coating layer was determined by the X-ray diffraction (X'Pert Pro MPD). Autolab PGSTAT 302 electrochemical testing system was used to carry out the comparison test on the sample and magnesium alloy. The medium was the neutral NaCl solution. Test temperature was the room temperature. A standard three electrode system was used as the electrolytic cell. The sample tested was used as the working electrode. In order to calculate conveniently, the working surface area of the sample is 1cm2. The silica gel was used to seal the non-working face of the sample. The reference electrode was a saturated calomel electrode. The auxiliary electrode was a platinum sheet. To use potentiodynamic scanning way to scan AZ31 magnesium alloy and the sample whose

surface was treated, in a relatively open circuit potential range from -1800mV to 250mV. The scanning speed is 1mv/s. This paper also used immersion corrosion way to investigate the corrosion resistance of the sample after plating. The immersion solution was 3.5%NaCl solution.

RESULT AND DISCUSSION

Organic film of substrate surface

As shown in Figure 1, the organic coating film thickness is approximately 50 μm, there are not the cracks, holes and other defects in the inner of the coating layer. There is not the situation of the separation and peeling between the coating film and substrate interface, which indicates that the combination of both is good. According to the results of cross cutting method and referencing the regulations in the GB/T9286-1988 (equivalent to ISO2409-1972), the combination between the coating film and substrate has reach level 2 which can meet the conventional requirements. Figure 2 is the micro-morphology of the surface of the sample before and after coarsening. As you can see in Figure 2a, the film surface is flat and smooth, and the film surface is hydrophobic, which is very detrimental to the subsequent sensitization, activation and chemical plating process, thus the specimen surface after coating must be treated. The essence of coarsening treatment is to etch the surface of the coating film to make the surface form numerous grooves and pores to increase the area of the contact surface, which makes it easy that the copper particles deposit on the surface of the coating layer to form the locking effect during the chemical plating so as to improve the combination strength between the plating layer and coating. In addition, the coarsening treatment on the film surface also improves the wettability of subsequent sensitizing solution, activation solution and chemical plating solution and to make the surface of the coating film change from hydrophobic to hydrophilic so as to form the catalytic active center of the uniform distribution as much as possible during the activation, which facilitates the rapid deposition and rapid solidified membrane of the subsequent copper particles. Repeated experiments verified that coarsening effect is best when the controlled the coarsening time is 30 min. As seen from figure 2b, compared with before the coarsening, the concave and convex uneven degree and micro-roughness of the coating surface after the coarsening increased significantly.
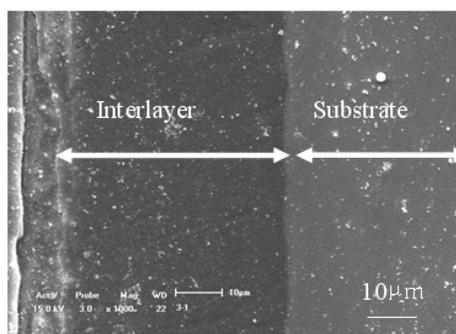

Figure 1: Section morphology of test sample after coated with organic coating
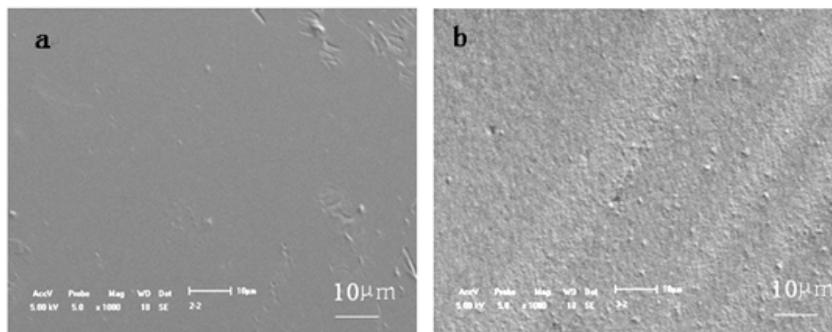

Figure 2: Micro-morphology of coating surface before coarsening (a) and after coarsening (b)
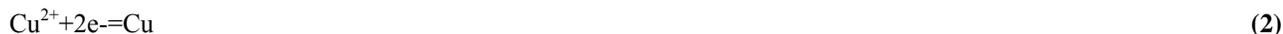
Principle of chemical copper plating

In this paper, the basic composition of chemical copper plating bath was copper salt, reducing agent, complexant, reactivation agent and so on. In order to avoid the pollution of the environment, the experiment the sodium hypophosphite which has no pollution to the environment was used as a reducing agent in the experiment. Therefore, the main redox reactions in the plating liquid were that Copper ion was transformed into metallic copper and hypophosphite ion was transformed into phosphite ion[9-10]. However, because the organic coating itself has no catalytic properties, it can not induce sodium hypophosphite to release electron, copper ion can not be reduced to copper particles because of not enabling to get

electronics. Therefore, before the chemical plating, sensitization and activation processing on the specimen surface must be carried out to induce the deposition of the copper particles. During the sensitization, because the micro-roughness of the film surface after coarsening is larger, the sample will adsorb a large number of stannous ions. Those stannous ions have strong reducing property. They are easy to be oxidized. After sensitization, thrown this test sample was thrown into the activation solution. The surface of the test sample can soon adsorb silver particles with the catalytic activity. The reaction was shown in Eq. 1.

$$2Sn^{2+} + Ag^{+} \rightarrow Sn^{4+} + Ag \tag{1}$$

These silver particle acts as the catalytic active center at the surface of the test sample. They enable the chemical copper plating on the surface of the test sample to be carried out smoothly. According to the electrochemical mixed potential theory, the anode reaction and reaction cathode on the same surface of the substrate occur concomitantly at the same time. They can be described by two half cell reactions [11-13]. Therefore, in the alkaline chemical copper plating process with using sodium hypophosphite as reducing agent, two electrode reactions were shown in Eq.2 and Eq.3.
The cathode reaction:

$$Cu^{2+} + 2e{-} = Cu \tag{2}$$

The anodic reaction:

$$H_2PO^{2-} \rightarrow HPO^{2-} + HHPO^{2-} + OH^- \rightarrow H_2PO^{3-} + e\text{-}H + H \rightarrow H_2\uparrow \tag{3}$$

As shown in Eq.4, the total reaction is the redox cell reaction which is composed of two half reactions:

$$2H_2PO^{2-} + Cu^{2+} + 2OH^- \rightarrow Cu + 2H_2PO^{3-} + H_2\uparrow \tag{4}$$

The test sample after the activation of the surface be put into the chemical copper plating solution, Copper ions are reduced as elemental Cu by using sodium hypophosphite. Along with the continuous deposition of elemental Cu, the coating surface has been covered by the deposition copper plating layer. When the sodium hypophosphite is used as reducing agent, the metal catalytic activity sequence is Au>Ni>Pd>Co>Pt>Cu.

According to the above metal catalytic activity sequence, the sodium hypophosphite reduction catalytic activity of Cu is small. Because the reaction can not be catalyzed by copper deposition, the reaction will stop when the catalytic surface is completely covered by copper deposition. In order to make the chemical plating reaction be carried out smoothly, usually the reactivation agent is added into the plating solution. A small amount of Ni2+ being added into the plating solution, Ni2+can be reduced into metal nickel with very high catalytic activity to make the catalytic reaction continue. After the chemical plating of 100min or so, the test sample was analyzed. EDX energy spectrum of copper plating layer was shown in Figure3. EDX energy spectrum analysis showed that the chemical composition elements of the plating layer are copper and phosphorus. Among them, the phosphorus content in the plating layer was 0.319%, which showed that a small amount of phosphorus in chemical reaction process was reduced and deposited on the sample surface together with the copper. However, there was not Ni in the EDX. This was because when it the metal nickel catalyzed the oxidation reaction of sodium hypophosphite, it and the copper ion in the solution generated the reaction as shown in Eq.5.

$$Ni + Cu^{2+} \rightarrow Ni^{2+} + Cu \tag{5}$$

The reaction equation (5) showed that the metal nickel entered into the solution again, which ensured that the reaction equation (3) existed so as to make the chemical plating process continue.
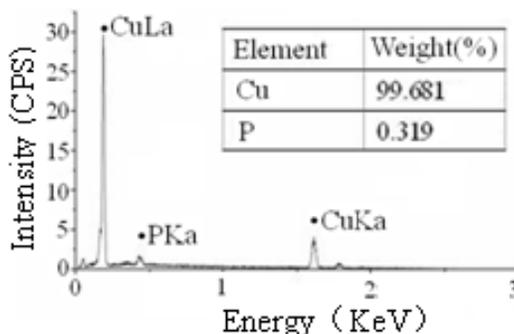

Figure 3: EDX energy spectrum of copper plating layer
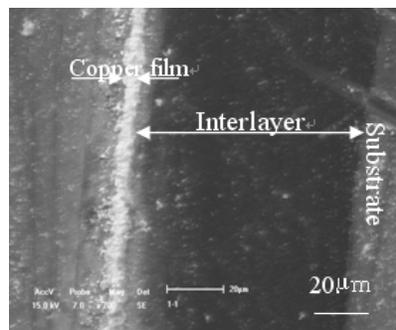
Surface morphology of the plating layer

The EDX analysis results showed that the surface of the test sample had been deposited copper plating layer. Figure 4, Figure 5 and Figure 6 were the surface and section morphology of the plating layer after the sample surface had been carried out the chemical plating for 100 min. As shown in Figure4, the copper plating layer was dense and had not cracks, holes and other defects. Under a high-powered microscope, it can be seen in Figure5 that the copper particle on plating layer surface was nearly spherical, uniform in the size and dense in the arrangement. Figure 6 is a sectional chart of the test sample. As can be seen in Figure6, the thickness of the copper plating layer is uniform, about $7 \sim 8$ μm thick, distribution along the substrate surface. The combination of the plating layer and coating film was good, with coating not cracking and not spalling.
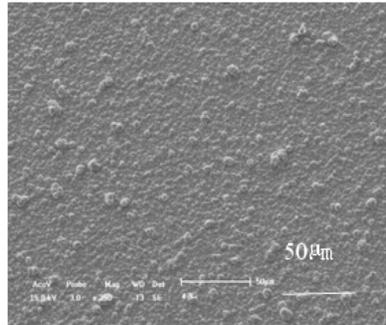
**Figure 4: Chemical copper plating layer surface morphology**
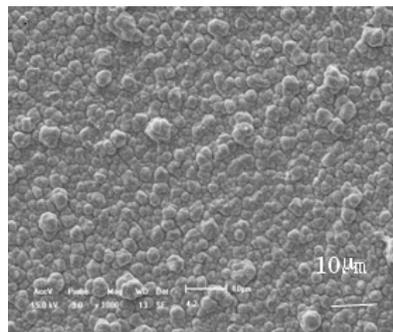
Figure 5: Chemical copper plating layer surface morphology under high-powered microscope

Figure 6: Section morphology y of the test sample

Structure of plating layer

Figure 7 is the X-ray diffraction pattern of the test sample before and after the chemical plating. In Figure7, the spectral line a is the diffraction peaks of the coating sample, those diffraction peaks come from the substrate and the coating, the spectral line b is the diffraction pattern of the test sample after chemical plating. As can be seen from the spectral line b, because of the existence of the coating, the intensity of diffraction peak corresponding to the spectral line a in the position greatly reduced, even small completely disappeared, even the diffraction peaks whose intensity was small has completely disappeared. with respectively corresponding to the 111, 200 and 220 crystal surfaces of the copper, the characteristic peak of the copper was enhanced. With having the preferred orientation, the diffraction peak of the 111 crystal surfaces of the copper is the strongest among them. However, there was not the diffraction peak of the phosphorus in this pattern, which may be because the phosphorus content in the coating was very small.
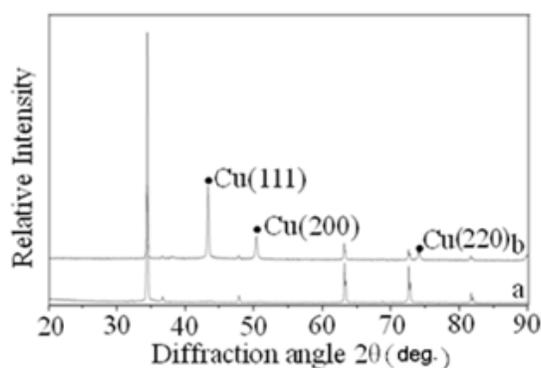
Figure 7 : X-ray diffraction pattern of the test sample before and after chemical plating

Corrosion resistance of the plating layer

The polarization curves in 3.5%NaCl neutral aqueous solution of the test sample was measured experimentally. The test results showed that the self corrosion potentials of the sample after the surface treatment and the substrate was respectively -1.368V and -1.569V, The positive shift of the self corrosion potentials of the sample after the surface treatment is approximately 200mv compared with the substrate. And the self corrosion current of the sample after the surface treatment was decreased by about two orders of magnitude compared with the substrate. The above experiment showed that the sample after chemical copper plating treatment has good corrosion resistance. The plating layer provides good protection to the substrate.

CONCLUSION

This paper developed a new protection method of the magnesium alloy surface method. The experiment research reached the following conclusions: (1) The organic coating film completely isolated the substrate from the plating layer so as to avoid the occurrence of the galvanic corrosion. After the surface of magnesium alloy is coated, it must be carried out the roughening, sensitization and activation treatment. The optimum condition for the coarsening process of the coating film is to immerse the test sample the coating film in the NaOH solution for 30min. At this time, the roughness of the coating film will increase; (2) The plating layer obtained in the experiment is dense, its thickness is uniform, the combination with substrate is good. In addition to containing trace amounts of phosphorus, the rest are all copper, which shows that the copper of the plating layer has high purity. Moreover, the self corrosion potential of the test sample after plating is higher than that of the substrate alloy. The test sample after plating has good corrosion resistance. Therefore, it has the ideal protective effects on the magnesium alloy. (3)In addition to chemical copper plating on the surface of magnesium and its alloys, this technology also can be used to plate a variety of other materials such as silver, nickel and its alloy etc. on the surface of magnesium and its alloys. In addition, in addition to treatment on surface of magnesium and its alloys, this technology is also suitable for other high active materials, such as titanium and its alloys, aluminum and its alloys, zinc and its alloys etc.

ACKNOWLEDGEMENT

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