Electroless Ni–P deposition plus zinc phosphate coating on AZ91D magnesium alloy


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Received 12 May 2005; accepted in revised form 11 September 2005

Available online 24 October 2005

Abstract

An electroless Ni–P deposition process has been developed to treat the AZ91D magnesium alloy surfaces against corrosion. Magnesium alloy AZ91D was first phosphatized in a zinc phosphating bath containing molybdate. Then an electroless Ni–P deposition was carried out on the phosphate coating from a sulfate solution. The phases in the phosphate coatings were analyzed by XRD. Microstructures of phosphate coatings and electroless Ni–P depositions were observed by SEM and EDS. It was found that there was metallic zinc in the phosphate coating and the addition of Na2MoO4 in the phosphating bath resulted in the increase of zinc in the coating. A lot of disperse metallic zinc particles acted as the catalyst nuclei for the succeeding Ni–P deposition. Consequently, the Ni–P depositions with dense and fine microstructure were obtained on the phosphate coatings gained from the phosphating bath wherein 2.0∼2.5g/L Na2MoO4 was added. The Ni–P plus phosphate coatings on the AZ91D magnesium alloy exhibited acceptable corrosion resistance as shown by the results of the Salt Spray Corrosion Test.

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Keywords: Magnesium alloy; Phosphating; Electroless deposition; Corrosion resistance

1. Introduction

Magnesium alloy has low density, high strength-to-weight ratio and other good physical and mechanical characteristics, which makes it possible for structural applications in the aerospace, electronics and automobile fields. However, the use of magnesium alloys has been limited due to their undesirable properties that include poor corrosion and low wear resistance. Thus, formation of anticorrosion and high wear-resistance coatings on the surface of Mg or Mg alloys is necessary in practical applications [1–3]. Since magnesium is one of the most electrochemically active metal, ordinary coatings, such as nickel, copper and zinc coatings, can only provide a physical barrier against the corrosion attack of magnesium substrate. So, any coatings on magnesium alloys should be uniform, adherent and porosity free as possible.

Electroless deposition technique of Ni and Ni–P alloy coatings has been a well-known commercial process that has found numerous applications in many fields due to its production of excellent coatings that are corrosion-resistant, high wear-resistant and possess good lubricity, high hardness and acceptable ductility [4–8]. There were some reports on the electroless plating Ni and Ni–P on magnesium alloys [9–14]. However, it is noted that in these reports on the electroless plating on magnesium, the nickel ions were provided by basic nickel carbonate in the plating bath. Also, in the electroless Ni plating process on magnesium alloy [13], the samples were etched first in a solution of chromate and nitric acid and then soaked in HF solution to form a conversion film before electroless nickel deposition took place. But chromium compounds are carcinogenic substances that should be used with caution.

In our previous work, an electroless Ni–P deposition on AZ91D magnesium alloy from a plating bath containing sulfate nickel was proposed [15]. In this study, AZ91D magnesium alloy samples were first pretreated in a zinc phosphating bath to obtain a phosphate coating. Then, the electroless Ni–P deposition on the phosphate coating was undertaken by using the plating bath containing sulfate nickel. The influences of molybdate (Na2MoO4) in the phosphating bath on the microstructure of phosphate coating and the microstructure and corrosion resistance of the final electroless Ni–P deposition were studied.
2. Experiments

The AZ91D magnesium alloy samples with the size of 50 × 50 × 3 mm were used in the experiments. The chemical composition of the alloy is given in Table 1. The combinatorial technology for obtaining phosphate layer plus Ni–P layer on magnesium alloy is shown in Table 2. The samples were abraded with No. 1500 SiC paper before the processes. Alkaline cleaning was used to remove soils or greases on the surface of magnesium alloy. Then magnesium alloy samples were treated in the zinc phosphating bath for 2–3 min to obtain the phosphate coating. After being rinsed in distilled water, the samples were dipped in the electroless plating bath to obtain the Ni–P deposition layer. The thickness of Ni–P deposition is nearly linear with the plating time (about 27 μm/h).

Surface observations of phosphate coating and electroless Ni–P coating were realized with SEM (JSM-5310, Japan Electronics) and EDS (INC250). The phases in phosphate coatings were analyzed by XRD (D/max-2500PC, CuKα). Salt spray exposure of about 40 μm Ni–P coating based on phosphate coating was carried out in a SF850 salt spray cabinet (Atlas Electric Devices Company) according to ASTM B117 standard. A 5 wt.% NaCl solution was used to create a salt fog within an enclosed chamber. Test temperature of 35 °C was maintained.

The deposition coating of electroless Ni–P is generally not very dense. There are micro-holes or gaps between the micrometer clusters (which are consisted of amorphous or nanocrystalline grains). Therefore, a porosity test was proposed to evaluate the porosity of the Ni–P coating on magnesium alloy. That is, a filter paper was soaked in a reagent solution of 10 g/L NaCl, 106 g/L ethanol and 0.1 g/L phenolphthalein dissolved in distilled water. Then the filter paper with the reagent solution was pasted onto the nickel coating for 10 min. After taking the filter paper away, red spots or red areas were noted on the surface of the coating. The porosity of coating is evaluated relatively by the ratio of red spot area to the zone area previously pasted by the filter paper. The principle of the method is that, if there are microwaves on the coating penetrating to the base alloy, magnesium in the magnesium alloy is being eroded by the NaCl solution. At the same time hydrogen gives out on the surface and H⁺ ions are consumed, a lot of OH⁻ ions accumulate in solution of the filter paper, which makes the phenolphthalein in the solution turn red.

3. Results and discussion

3.1. Zinc phosphating bath and the microstructure of the phosphate coating

In the present zinc phosphating bath ZnO and H₃PO₄ are the main constituents, see Table 2. They create soluble Zn²⁺ and H₂PO₄⁻ in the solution. Unsolvable PO₄³⁻ was deposited onto the surface during the phosphating process. Their optimal concentrations were shown in Table 2.

A magnesium alloy has high chemical reactivity, so fluoride activation of magnesium alloy in a HF solution is generally used before chemical treatment [16,17]. The formation of MgF film on the surface can restrain the corrosion of the Mg matrix. In the present experiment, a mixture of sodium fluoride and organic amine (NaF: organic amine = 8.5:1 in weight) was used as anticorrosion agent and was directly added into the phosphating bath. Tartaric acid was employed to reduce the production of the sludge in the phosphating bath. If no tartaric acid was added in the phosphating bath, some insoluble phosphate will precipitate out as sludge in the bath. The sludge in the bath would influence the coating quality. Tartaric acid can combine with some insoluble phosphate to form a solvable complex compound that will stabilize the bath.

Phosphate coating is generally used as pretreatment or base coating for further surface treatment. Short phosphating time is an advantage for its application in industrialization. Therefore, an accelerator should be used. In previous studies [18,19], it was found that nitrate and nitrite were effective to accelerate the formation of phosphate coating. In the phosphating bath, the nitrate and nitrite ions are strong oxidizing agents. During phosphating, the reduction of nitrate and nitrite resulted in the increase of local pH at metal–solution interface, which facilitated
the precipitation of insoluble phosphate [18]. With the addition of nitrate in the phosphating bath, full phosphate coating on the AZ91D magnesium alloy formed in about 2–3 min.

SEM micrograph of the phosphate coatings formed on AZ91D alloy is shown in Fig. 1. EDS analysis on different micro regions indicated that the clusters were the complex of hopeite (Zn₃(PO₄)₂·4H₂O) and metallic zinc particles. There are some micro cracks (Fig. 1 (a)) in the phosphate coating that was obtained from the bath without Na₂MoO₄. And the phosphate coating obtained from the bath containing Na₂MoO₄ has less micro cracks, see Fig. 1 (b)–(f).

Fig. 1 shows that the addition of Na₂MoO₄ in the bath results in the refinement of the phosphates and full coverage of the substrate by the phosphate coating. Fig. 2 shows both the weight of the phosphate coating and the porosity (red area) of the phosphate coating. This coating, which was measured by the porosity test, decreases as the concentration of Na₂MoO₄ in the bath increases. Therefore, it can be confirmed that a dense and fine phosphate coating was obtained with the addition of Na₂MoO₄ in the phosphating bath.

In the phosphating bath, the adjacent micro areas of metal surface can be divided into micro anode sites (lower electron density sites) and micro cathode sites (higher electron density sites). The reactions on the surfaces should be considered to have taken place on different local polarization sites. As to the AZ91D magnesium alloy, the β phase in the magnesium alloys is regarded as the micro cathode sites and the magnesium matrix.

![Fig. 1. SEM micrographs of the phosphate coatings on AZ91D magnesium alloy formed in the baths with different Na₂MoO₄ concentration: (a) 0.0; (b) 0.5; (c) 1.0; (d) 1.5; (e) 2.0; (f) 2.5 g/L.](image)

![Fig. 2. Effects of Na₂MoO₄ concentration in the phosphating bath on the weight and red area percentage by porosity test of the phosphate coating on AZ91D magnesium alloy.](chart)
as the micro anode sites [18]. At the anode sites, some magnesium ions that dissolved in to the solution leave electrons on the surface, which will benefit the deposition of metallic zinc. It has been reported that there are a lot of magnesium atoms and some aluminum atoms that resolved at the micro anode sites in the Mg–Al–Zn alloy surfaces and there are no resolved zinc atoms [20]. Therefore, the following reactions can occur at micro-anode sites. Magnesium dissolved and releases metal ions at the micro anode sites:

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e \]  
(1)

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3e. \]  
(2)

Some Zn\(^{2+}\) ions reduce near the surface to Zn deposited on the surface on the micro anode sites and become the composition of the phosphate coating:

\[ \text{Zn}^{2+} + 2e \rightarrow \text{Zn}. \]  
(3)

Hence, the replacement reactions take place as follow.

\[ \text{Mg} + \text{Zn}^{2+} \rightarrow \text{Zn} + \text{Mg}^{2+} \]  
(4)

\[ 2\text{Al} + 3\text{Zn}^{2+} \rightarrow 3\text{Zn} + 2\text{Al}^{3+}. \]  
(5)

At micro cathode sites hydrogen ions were reduced simultaneously:

\[ 2\text{H}^+ + 2e \rightarrow \text{H}_2. \]  
(6)

The reduction of hydrogen ions results in the increase of local pH at the metal–bath interface, which facilitated the precipitation of insoluble zinc phosphate. The formation of insoluble phosphate film may follow the reaction:

\[ 3\text{Zn}^{2+} + 2\text{H}_2\text{PO}_4^- + 4\text{H}_2\text{O} + 4e \rightarrow \text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2 \]  
(7)

\[ \text{Al}^{3+} + \text{H}_2\text{PO}_4^- \rightarrow \text{AlPO}_4 + \text{H}_2. \]  
(8)

\[ \text{Na}_2\text{MoO}_4 \] decompose to give out MoO\(_4^{2-}\) ions, which would absorb to the anode sites or combine with Mg\(^{2+}\) to form MgMoO\(_4\).

\[ \text{Mg}^{2+} + \text{MoO}_4^{2-} \rightarrow \text{MgMoO}_4 \]  
(9)

The MoO\(_4^{2-}\) ions or MgMoO\(_4\) then act as the cathode sites (in comparison with Mg matrix) facilitating the deposition of zinc phosphates as well as metallic zinc. This is similar to the case of phosphating on steel, where MoO\(_4^{2-}\) ions combined with Fe\(^{2+}\) to form FeMoO\(_4\) that is absorbed on to the iron substrate to act as nuclei to accelerate the growth of phosphates [21,22]. As a result, the addition of Na\(_2\)MoO\(_4\) would create more suitable cathode sites for the formation and growth of phosphate film. As a result, a fine and fully covered phosphate film was formed on the magnesium alloy substrate.

![Fig. 3. XRD patterns of the phosphate coatings on the magnesium alloy AZ91D from the phosphating bath with different concentration of Na\(_2\)MoO\(_4\) (g/L).](image-url)

The XRD traces (I-2\(\theta\)) of the coatings come from the bath with the addition of different concentration of Na\(_2\)MoO\(_4\) were shown in Fig. 3. It is seen that the phosphate coatings consists of mainly Zn\(_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O},\) crystal Zn, AlPO\(_4\) and MgMoO\(_4\). There was considerable metallic zinc in the zinc phosphating coating on magnesium alloy, which is different from the zinc phosphate coating on steel and casting iron [21,22]. The forming of metallic zinc is mainly due to the replacement reaction. It can be seen that the addition of Na\(_2\)MoO\(_4\) resulted in the increases of
metallic Zn concentration in the coating as shown by the diffraction peaks of zinc (Fig. 3). But there is no further increase when the concentration of Na$_2$MoO$_4$ was increased from 1.0 to 2.0 g/l. It may be explained by Eqs. (4) and (9), that the reaction of Eq. (9) reduced Mg$^{2+}$ to MgMoO$_4$, which facilitated the reaction of Eq. (4) to the right side. In any case, the existence of considerable metallic zinc makes the phosphate coatings possible to be the base for further electroless Ni or Ni–P deposition, as metallic zinc in the phosphating coating can act as the catalyzer particles for nickel deposition. And it can be seen that A peaks ($2\theta = 9.60^\circ$) of phosphate coating are relative higher when the phosphating bath contains 1.0 to 2.0 g/L Na$_2$MoO$_4$ in Fig. 3. In the phosphating process, the Mg$_2$MoO$_4$ concentration in the coating increases when Na$_2$MoO$_4$ in the phosphating bath increases, shown by the diffraction D peaks (Fig. 3).

3.2. Electroless Ni–P deposition on the phosphating coating and its performance

A further electroless Ni–P deposition was realized on the phosphate coating on AZ91D alloy through the sulfate bath [15]
shown in Table 2. The influence of Na$_2$MoO$_4$ concentration in the phosphating bath on the microstructures of final electroless Ni–P coatings was shown in Fig. 4. Typical microstructure of electroless Ni–P coating consists of many “nodular-like” clusters. The phosphorus concentration in the Ni–P deposition layer is about 3.7 wt.% and the XRD diffraction taken on the electroless Ni–P coating indicated that the coating was a mixture of amorphous and nanocrystalline grains [15]. It is seen that the cluster size decreased as the Na$_2$MoO$_4$ concentration in the phosphating bath increases. This should be attributed to the increase of zinc concentration in the phosphate coatings with the increase of Na$_2$MoO$_4$ in the phosphating bath. Because Zn$_3$(PO$_4$)$_2$·4H$_2$O is a nonconductor phase, during electroless deposition, nickel should first deposit preferentially on zinc crystals and then extend to zones without zinc crystals. The increase of zinc crystals in the phosphate coating provided more nuclei for the deposition of Ni and growth of Ni–P. Therefore, the cluster size decreases as the Na$_2$MoO$_4$ concentration in the phosphating bath increases. As a result of the decrease of cluster size, more dense microstructures with less micro-holes or gaps were obtained (see SEM micrographs in Fig. 4).

The porosity (represented by the red area) of about 20, 40, and 60 μm thickness Ni–P coating was estimated by the porosity test proposed in the experiment part and the results were shown in Fig. 5. It is seen that for the 20 μm Ni–P coating the red area decreased rapidly as the concentration of Na$_2$MoO$_4$ in the phosphating bath increased, and relatively dense Ni–P coatings were obtained with the concentration of Na$_2$MoO$_4$ in the phosphate bath being 2.0–2.5 g/L. The porosity of 40 μm Ni–P coating on the phosphate coating rapidly decreases with increasing Na$_2$MoO$_4$ concentration in the phosphating bath (in tenths to 0) when the concentration in the bath is more than 1.0 g/L. Therefore, a thickness of Ni–P coating of about 40 μm is necessary to decrease porosity to zero and to protect the substrate from corrosion.

The cross-section morphology of about 40 μm Ni–P depositions on the phosphate coating formed in the baths with 2.0 g/L Na$_2$MoO$_4$ is shown in Fig. 6. The results of the Salt Spray Test on the Ni–P plus phosphate coatings on AZ91D magnesium alloy were shown in Fig. 7. It is seen that the sample from the phosphating bath without addition of molybdate could withstand only 24 h in the salt spray without rusting. However, the Ni–P coating samples previously phosphated in the phosphating bath with 2.0–2.5 g/L of Na$_2$MoO$_4$ withstood about 150 h in salt spray without experiencing corrosion. The Salt Spray Test was also carried on for two phosphate coatings on AZ91D alloy, the coating from the bath with no Na$_2$MoO$_4$ withstood 8 h and the one with 2.0 g/L Na$_2$MoO$_4$ withstood 11 h without corrosion. There was no great difference in corrosion resistance between the two phosphate coatings. Therefore, the higher corrosion resistance of the final Ni–P coatings with previously phosphated in the bath with addition of Na$_2$MoO$_4$ should be attributed to their fine and dense Ni–P microstructures.

The hardness of the Ni–P coating on the phosphate coating from the phosphate bath with addition of 0 to 2.5 g/L molybdate was about 670 Hv, and the hardness of the Ni–P coating after 2 h heat treatments in 180 °C is about 915 Hv. The
coating hardness values are similar with the Ni–P coating based on chromate coating pretreatments [15].

This heat treatment also offered a benefit effect on the adhesion of the Ni–P coating to the base alloy. The Ni–P coatings with and without the heat treatment were soaked in water (25 °C) for 240 h, some blisters formed on the surface of the coatings. The blister area on the coating surface was used to estimate the adhesion of the Ni–P coating to the base. The results were shown in Fig. 8. It is interesting to see that after the heat treatment, the blister area on the coatings greatly decreased. The separation and diffusion-out of hydrogen atoms from the coatings may take place during the heat treatment at 180 °C, which reduces the tensile or bulging stress of hydrogen in the coating and enhances the adhesion of the coating to the base. The micro blisters formed in the coating were seen in Fig. 6.

4. Conclusions

1. The phosphate coating on the AZ91D magnesium alloy was obtained from the bath containing mainly phosphoric acid and zinc oxide. There was zinc in the phosphate coatings and the addition of Na2MoO4 in the phosphating bath resulted in the increase of zinc in the coating.

2. The existence of metallic zinc in the phosphate coating makes it possible to be as the pretreatment layer for further electroless Ni–P deposition. The Ni–P coatings with dense and fine microstructure were observed on the phosphate coatings on the AZ91D alloy that was obtained from the phosphating bath wherein 2.0~2.5g/L Na2MoO4 was added.

3. The Ni–P plus phosphate coatings on the AZ91D magnesium alloy exhibited good performance. The Salt Spray Test showed that they could withstand about 150 h without corrosion. The surface hardness of the Ni–P coating is about 670 Hv, and its hardness was increased to about 915 Hv through the heat treatment of 2 h at temperature of 180 °C.

Acknowledgements

The authors gratefully acknowledge the foundation of national key basic research and development program No. 2004CB618301 and 985 Project of Jilin University for provided support of this work.

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