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High corrosion resistance of electroless Ni-P with chromium-free conversion pre-treatments on AZ91D magnesium alloy

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Abstract: Phosphate-manganese, tannic acid and vanadium conversion coatings were proposed as an effective pre-treatment layer between electroless Ni-P coating and AZ91D magnesium alloy substrate to replace the traditional chromate plus HF pre-treatment. The electrochemical results show that the chrome-free coatings plus electroless Ni-P coating on the magnesium alloy has the lowest corrosion current density and most positive corrosion potential compared with chromate plus electroless Ni-P coating on the magnesium alloy. These proposed pre-treatment layers on the substrate reduce the corrosion of magnesium during plating process, and reduce the potential difference between the matrix and the second phase. Thus, an electroless Ni-P coating with fine crystalline and dense structure was obtained, with preferential phosphorus content, low porosity, good corrosion-resistance and strengthened adhesion than the chromate plus electroless Ni-P.

Key words: magnesium alloy; corrosion resistance; electroless; chromium-free pre-treatment

1 Introduction

Magnesium alloys with low density have distinctive properties which make them promising for several industrial applications. They have the advantages of high specific strength and excellent anti-shock resistance. Therefore, they are indispensable for aerospace and automotive industries and also for manufacturing electrical equipment such as cellular phones, television sets, and sporting industries[1]. Due to their heat conductivity and electromagnetic shielding effectiveness, they also have attractive features for IT industry and communication satellites[2]. However, they have poor atmospheric corrosion resistance and are very reactive in air, which means that the magnesium oxide film will be corroded easily. It is also difficult to do electro-chemical treatment on them because of its high chemical affinity to aqueous solutions. Therefore, they are not suitable to be used without any protective layer, especially in a humid environment. Hence, it is necessary to do surface treatment properly onto the surface to improve the adhesion, wear and corrosion resistance[3-4].

There are many surface treatment techniques that have been proposed, such as conversion treatment, electroplating/electroless and anodic treatment[5]. Conversion coatings are produced by chemical or electrochemical treatment of a metal surface to make a superficial layer of substrate metal oxides, chromates, phosphates, or other compounds that are chemically bonded to the surface[6]. There are different types of conversion coatings including chromate, phosphate/ permanganate[7-9], stannate-based[10] and ceriumbased treatment[11-13] and fluorozirconate treatments processes. Electroplating or electroless is one of the most cost effective and simplest techniques for introducing a metallic coating to a substrate. In both cases, a metal salt in solution is reduced to its metallic form on the surface of the work piece. Electroless deposition is a more suitable method to deposit metal alloys compared with electroplating, involving the deposition with uniform, crack-free and good adhesion onto magnesium alloy, without applying an external electrical circuit. The most difficult process of plating magnesium is developing a

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suitable pre-treatment part. Once a suitable pre-treatment is in place many desired metals can be deposited. Traditionally, the magnesium alloy was etched in a solution of chromium oxide plus nitric acid and soaked in HF solution to form a conversion film (MgF) before electroless plating. Due to high toxicity on environment, the hexa-valent chromium compounds are restricted and HF also exhibits strong corrosive nature. But it could not be completely eliminated from the process until now.

Phosphate-manganese, vanadium and tannic-based conversion (TBC) coatings were proposed as an effective pre-treatment layer between electroless and AZ91D magnesium alloy substrate to replace the traditional chromium oxide plus HF pre-treatment. These proposed pre-treatment layers on the substrate reduce the corrosion of magnesium during plating process and reduce the potential difference between the matrix and the second phase. Thus, an electroless Ni-P coating with fine crystalline and dense structure was obtained, with preferential phosphorus content, high density, low porosity, good corrosion-resistance and strengthened adhesion than the Ni-P with chromium oxide plus HF as pre-treatment. The microstructures and the electrochemical properties of the coatings on the AZ91D magnesium alloy substrate were studied by SEM, EDX and electrochemical measurement.

5 mm. The alloy mainly contained about 9.1% Al, 0.64% Zn, 0.17% Mn, 0.001% Fe and Mg balance (mass fraction). The substrate was ground with 2000 SiC paper. After grinding, the sample was rinsed with deionized water, cleaned in acetone ultrasonically for 30 s and finally dried, before being taken into the process. The technical flow chart of the electroless nickel with chromate pretreatment on the AZ91D magnesium alloy is shown in Fig.1(a) and that with chrome-free pretreatments on the AZ91D magnesium alloy is also shown in Fig.1(b). The samples were cleaned thoroughly with de-ionized water as soon as possible between any two steps of the treatments. After being pretreated in chromate (Fig.1(a)) and chrome-free (Fig.1(b)) pretreatment bath, the sample was immersed in the same electroless bath solution for plating Ni-P deposition layer. The electroless solution was put in a 1 000 mL glass beaker, which was kept at a constant temperature by a thermostat. The bath composition and all operation parameters for the electroless Ni-P deposition are reported in Ref.[14]. After Ni-P deposition, the three different chrome-free pretreated electroless samples were compared with the chromate pretreated sample. The thickness of Ni-P deposition is nearly linear (about 20 µm).

2.2 Coating characterization

2 Experimental

2.1 Sample preparation

The substrate material used was AZ91D die cast magnesium alloy with dimensions of 20 mm \times 20 mm \times

The surface of the chromate and chrome-free coatings and the cross-section morphology observations were studied under the light of a scanning electron microscope (SEM, JEOL JSM-5310, Japan) and an EDX attachment was used for qualitative elemental chemical analysis.



Fig.1 Technical flow chart of electroless nickel with chromate pretreatment (a) and with chrome-free pretreatments (b) on AZ91D magnesium alloy

Electrochemical measurements were performed on an electrochemical analyzer (CHI800, Shanghai, China), which was controlled and supported by a computer software system. All experiments were carried out in a classic three-electrode cell with a platinum plate (Pt) as counter electrode and a saturated calomel electrode (SCE) as reference electrode at room temperature. Polarisation experiments were carried out in a 3.5% (mass fraction) NaCl aqueous solution using a three-electrode cell with a platinum plate (Pt) as counter electrode and an Ag/AgCl electrode as reference electrode. The exposed area for testing was obtained by thick coating with epoxy resin leaving an uncovered area of approximately 1 cm². The reference and platinum electrodes were fixed near to the working electrode (\sim 0.5 mm), which could minimize the errors, due to instrument reading(IR) drop in the electrolytes. During the potentiodynamic sweep experiments, the samples were first immersed into 3.5% NaCl solution for about 10 min to stabilize the open-circuit potential. The $\lg J - \varphi$ curves were measured and plotted after the above plot electrochemical measurements. Tafel was transformed from the recorded data and the corrosion current density (J_{corr}) and corrosion potential (φ_{corr}) were determined directly from these $\lg J - \varphi$ curves by tafel region extrapolation. The salt spray tests were conducted in a SF850 salt spray cabin (Atlas Electric Devices) and ASTM B117-03 standard was adopted for the salt spray test[15].

3 Results and discussion

3.1 Phosphate-manganese conversion coating

The early studies[16] showed that the phosphatemanganese conversion coating can be used as the pretreatment layer for the electroless Ni-P alloy on the AZ91D magnesium alloy substrate and its corrosion potential was -1.442 V. In the present work, it has been further improved by the addition of Na₂MoO₄. This sodium molybdenum can disintegrate into MoO₄²⁻ ions, which could absorb to the anode sites or combine with Mg²⁺to form MgMoO₄:

$$Mg^{2+} + MoO_4^{2-} \longrightarrow MgMoO_4$$
 (1)

The MoO_4^{2-} or $MgMoO_4$ then behaves as the cathode sites (similar to Mg matrix) and makes easier to coat the phosphates-manganese. This is alike to the case of phosphating on steel, where MoO_4^{2-} ions coupled with Fe²⁺ to form FeMoO₄ and that is absorbed onto the iron substrate to behave as nuclei to stimulate the growth of phosphates[17]. Hence, the addition of Na₂MoO₄ could create more suitable cathode sites for facilitating the growth of phosphate film. As a consequence, a fine and fully covered phosphate film was formed on the magnesium alloy substrate.

The polarization curves of AZ91D magnesium alloy substrate treated in the phosphate-manganese conversion coating with varying Na_2MoO_4 concentrations of 0, 2.5, 5.0 g/L are shown in Fig.2. From the results, the corrosion current densities obtained are 940.8, 181, 40.4, 484 μ A/cm² for the specimens untreated and treated in 0, 2.5, 5 g/L Na₂MoO₄ solutions, respectively. Figure 2 reveals that phosphate-manganese coating with 2.5 g/L Na₂MoO₄ has the most positive corrosion potential of -1.368 3 V and the smallest corrosion current density of $40.4 \ \mu A/cm^2$ in comparison with other cases. The results of the salt spray test of Ni-P plus Mn-phosphate coating with the different concentrations of Na2MoO4 on AZ91D Mg alloy (present) are shown in Fig.3, where the previous Ni-P plus Zn-phosphate coatings were added for comparison. This reveals that the sample from the Ni-P plus Mn-phosphate bath without the addition of molybdate withstands only 22 h in the salt spray without rusting. On the other hand, the Ni-P coating samples with $2.0 \sim 2.5$ g/L Na₂MoO₄ in the phosphating bath withstand about 160 h in salt spray and this is in agreement with our previous work of Zn-phosphating. The reason is because the addition of molybdate increases the fine crystalline flower-like structure in Mn-phosphate film (the SEM images were well explained in our previous work on Zn-phosphate-molybdate coating), this will induce the nickel during the electroless process and hence fine porous-free, good adhesion electroless Ni-P is obtained. This improved Mn-phosphate-molybdate chemical conversion treatment has potential alternative for the chrome-based conversion coating treatment. So, the addition of Na₂MoO₄ can improve the corrosion performances of phosphating conversion coating and the succeeding Ni-P coating and the specific concentration 2.5 g/L is an appropriate one. Hence, this optimum new phosphate-manganese-molybdate conversion coating was



Fig.2 Polarization curves for untreated magnesium AZ91D substrate (a), and treated in phosphate-manganese conversion coating with Na_2MoO_4 of 0 g/L (b), 2.5 g/L (c) and 5.0 g/L (d)



Fig.3 Effect of Na_2MoO_4 concentration in phosphate bath on corrosion resistance of electroless (Ni-P) coatings on AZ91D Mg alloy in salt spray test

selected as a pretreatment layer for further electroless process.

3.2 Vanadium-based conversion coating

Vanadium solution is usually used as the corrosion resistant inhibitor for the paint or pigment these application[18]. However, vanadium-based conversion coatings on magnesium alloys are scanty. Surface morphology, and composition as well as the immersion time are briefly studied to facilitate the electroless Ni-P process. The polarization curves of AZ91D magnesium alloy substrate treated in the conversion coating solution 30 g/L NaVO₃ for 10, 20, 40 and 60 min are shown in Fig.4(a). From the results, the corrosion current densities obtained are 940.8, 63, 19, 34, $170 \ \mu\text{A/cm}^2$ for the specimens untreated and treated for 10, 20, 40, 60 min, respectively. The results indicate that the conversion coating by vanadium bath provides a good corrosion resistance than the untreated one. Figure 4(b) shows the effect of the treatment time on the corrosion potential (φ_{corr}) and corrosion current density (J_{corr}) measured from Fig.4(a). It reveals that 20 min of treatment time greatly increases φ_{corr} and decreases J_{corr} and further increase of immersion time does not improve the corrosion resistance.

Figures 5(a) and (b) show the SEM images of AZ91 substrate after immersion in vanadium solution for 10 and 20 min, respectively. In 10 min of immersion in the conversion solution vanadium nucleation was just beginning and the coating thickness was not enough to cover the entire surface of the substrate as the mechanically polished scratches was still observed. From SEM, it is clear that mechanically polished scratches were decreased with the increase of immersion time from 10 min to 20 min. However, the distribution of cracks increased on the surface when the immersion time



Fig.4 Polarization curves (a) and effect of treatment time on corrosion potential and corrosion current density (b)

was beyond 20 min. The coating thickness was measured to be $0.5-0.8 \mu m$. Figure 5(c) shows the EDX spectrum of the film composition containing the vanadium signals after immersion in the solution for 10 min and the vanadium concentration further increases with increasing immersion time. The detection of vanadium signal by EDX suggested that the conversion coating can be accomplished on the AZ91 alloy in the bath. The vanadium coating formation process is gelatin of hydrated vanadium oxide[18]. The formation of pentavalent vanadium oxides by condensation and polymerization has been described thoroughly and the elements in this process appear to be functioning in vanadium coating formation. Vanadium oxide gel formation includes a long octahedral coordinated $VO(OH)_3(OH_2)_2$. The existence of cracks in the vanadium coating might be the oxide deposition in hydrated form, which is susceptible to dehydration after removal from the coating bath.

Various concentration of phosphoric acid (H_3PO_4) has negative impact on the formation in the vanadium coating and decreases the corrosion resistance. YANG et al[19] developed the vanadium based conversion



Fig.5 Surface morphologies of AZ91D alloy immersed in vanadium solution for 10 min (a), 20 min (b) and EDX spectrum showing vanadium signals after immersion in solution for 10 min (c)

coating on the AZ61 magnesium alloy and reported that the corrosion resistance of vanadium coating is better than that of cerium and phosphate, and in addition, this vanadium chemical conversion treatment has potential to replace the chrome-based conversion coating treatment. Therefore, the conversion coating by vanadium bath provided a good corrosion resistance than the untreated one. In addition, it reveals that the sample with 20 min immersion has good corrosion potential and corrosion current density value, and above which, the corrosion performance becomes worsening and it is evident from Fig.4. Hence, this optimum vanadium based conversion coating with 20 min immersion time was selected as a pretreatment layer for further electroless process.

3.3 Tannic-based conversion coating

Early studies[19] showed that the tannic acid based conversion coating can be formed on AZ91D magnesium alloy through a solution containing C76H52O46 (tannic acid), NH₄VO₃, K₂ZrF₆ and H₃PO₄. Pentahydroxy benzamide-magnesium complex is the main component of the coating, which is succeeding in two steps. $Zr(HPO_4)_2 H_2O(\alpha - ZrP)$ forms first at immersion time of 70-120 s, which behaves as a catalyst to activate the main reaction. The oxidization of gallic acid into pentahydroxy benzoic acid is the second reaction, as well as the formation of pentahydroxy benzamidemagnesium complex, which takes place in the time interval of 120–300 s. The reactions take up first on β phases and then spread to α phase. The coating thickness is about 1.6 µm when the treatment time is 10 min, and above which the coating surface is coarse and uneven, leading to the reduction of corrosion resistance of the conversion coating.

Our previous work explained the surface morphologies and XPS spectra of the tannic based conversion (TBC) coating[19]. In the present work, this TBC has been used as a pretreatment for the further electroless process. This TBC provided good corrosion resistance in electroless bath. At present, the tannic based conversion coating with 5 min immersion time was selected as a pretreatment layer for further electroless process and further research is in progress.

Figure 6 shows the polarization curves of as-received AZ91D alloy, and the specimens after the optimized pretreatment of phosphate-manganesemolybdate, vanadium bath and tannic acid conversion coatings. For the pretreatment samples, the corrosion potential was shifted positively about 220 mV for the phosphate-manganese-molybdate coating, 420 mV for vanadium coating and 470 mV for TBC conversion coatings, respectively. The corrosion current density was decreased significantly from 940.8 µA/cm² of the substrate to about 40.4 µA/cm² for phosphate-manganesemolybdate, 19.8 µA/cm² for vanadium and 15.6 µA/cm² for TBC of the various chrome-free pre-treatment layers, respectively. Table 1 lists the values of corrosion potential and corrosion current density obtained from the electrochemical polarization curve in Fig.6. The results indicate that the conversion coating by tannic acid provides better corrosion resistance than others and further research is in progress to improve this TBC-based conversion coating. The surface and corrosion properties of this optimum phosphate-manganese-molybdate, vanadium and TBC based conversion coating (chrome-free) plus electroless Ni-P are compared with chrome plus electroless Ni-P.



Fig.6 Polarization curves of as-received AZ91D alloy (a), optimized pretreatment of phosphate-manganese-molybdate (b), vanadium (c) and tannic (d)

 Table 1 Corrosion potential and corrosion current density

 obtained from electrochemical polarization curves in Fig.6

Sample	φ _{corr} (vs SCE)/V	$J_{\rm corr}/$ ($\mu {\rm A} \cdot {\rm cm}^{-2}$)
AZ91D alloy substrate (a)	-1.590 2	940.86
AZ91D/phosphate-manganese- molybdate (optimized) (b)	-1.368 3	40.40
AZ91D/vanadium bath (optimized) (c)	-1.171 2	19.80
AZ91D/tannic acid (d)	-1.119 2	15.60

3.4 Surface and corrosion properties of various chrome-free films as pre-treatment for electroless

Phosphate-manganese-molybdate, vanadium-based and TBC conversion coatings have been successfully used as a pre-treatment for electroless Ni-P alloy on the AZ91D alloy substrate. The phases in the pretreatment layer cannot be detected by XRD. The pale colored surface may imply the presence of passive film on the substance and XRD pattern of electroless Ni-P is explained elsewhere in our previous work. Figure 7 shows the SEM images of phosphate-manganesemolybdate plus electroless Ni-P and TBC plus electroless Ni-P coating on the AZ91D substrate. All the chrome-free samples are fine and compact structure, moreover, some porosity is found on the surface Fig.7(b). The results from EDX analysis show the same tendency, and the concentrations in the layer were analyzed and it is found to be medium phosphorus.

Figure 8 shows the electrochemical polarization curves for the untreated, chrome pre-treatment plus electroless Ni-P, phosphate-manganese-molybdate pre-treatment (optimized) plus electroless Ni-P, vanadium pre-treatment (optimized) plus electroless Ni-P and TBC pre-treatment plus electroless Ni-P on the magnesium AZ91D substrate in a 3.5% NaCl solution at room temperature. All the corrosion potential (φ_{coor}) of the substrate with 20 µm electroless Ni-P layer is shifted positively. From the results, the corrosion potentials (φ_{coor}) are shifted positively about 870 V for chrome plus Ni-P, 850 V for Phosphate-manganese-molybdate plus Ni-P, 930 V for vanadium plus Ni-P, 1 070 mV for TBC plus Ni-P compared with those of the substrate, and the corrosion current density is decreased predominately from 940.8 µA/cm² of the substrate to about 3.6 µA/cm² for chrome plus Ni-P, 2.91µA/cm²



Fig.7 SEM images of phosphate-manganese-molybdate plus electroless Ni-P (a) and TBC plus electroless Ni-P (b)



Fig.8 Polarization curves of as-received AZ91D alloy (a), pretreatment with chrome plus electroless (b), with phosphate-manganese-molybdate plus electroless (c), with vanadium plus electroless (d) and with TBC plus electroless (e)

for Phosphate-manganese-molybdate plus Ni-P, 5.4 μ A/cm² for vanadium plus Ni-P and 12.71 μ A/cm² for TBC plus Ni-P.

As the cathode reaction in the polarization curves coupled with the evolution of the hydrogen, the anodic polarization curve is the most important features related to the corrosion resistance. When the applied potential increased into the anodic region, an obvious passivity occurred for all chrome and chrome-free treatment plus electroless Ni-P. For the electrochemical polarization curve of the substrate with chrome plus electroless Ni-P, the corrosion potential was shifted positively to -0.717V and the corrosion current density was 3.6 µA/cm². Between the potential of -0.556 6 and -0.131 4 V, the formation of a thin passive film occurred and broke down beyond this value, further the Ni dissolution would occur through the pores of coating. For the substrate with phosphate-manganese-molybdate (chrome-free) plus electroless Ni-P, the corrosion potential was shifted positively to -0.733 4 V and the corrosion current density was only 2.91 µA/cm². Between the potential of -0.563 9 and 0.029 V, the formation of a thin passive film involved ovation than other and above which, Ni dissolution occurred. This one has better passive film, which indirectly means porosity is less than chrome treated electroless. The reason is because the addition of molybdate increases the fine crystalline flower like structure in Mn-phosphate film, this enhances fine porous-free, good adhesion electroless Ni-P. For the substrate with vanadium (chrome-free) plus electroless Ni-P, the corrosion potential was shifted positively to -0.658 9 V and the corrosion current density was 5.4 μ A/cm². The passive film formed between -0.461 and -0.190 V. For the substrate with TBC (chrome-free) plus electroless Ni-P, the corrosion potential was shifted more positively to -0.518 6 V and the corrosion current density was increased to 12.71 µA/cm². This indicates that the film has porosity; hence the passive film could not form ovation in this case. But, the corrosion potential of the TBC (chrome-free) plus Ni-P coating was more positive (-0.518 6 V) than that (-0.717 0 V) of the Ni-P coating plus chrome as a pre-treatment. From Fig.8, it is evident that all of the Ni-P coatings show great positive shifts in corrosion potential and decrease in corrosion current density in comparison with their magnesium alloy substrate. Furthermore, Table 2 lists the corrosion potential and corrosion current density obtained from the electrochemical polarization curve (Fig.8).

In conclusion, phosphate-manganese-molybdate and vanadium are potential to replace chrome treatment for electroless coating on magnesium alloy. It further suggests that TBC plus electroless can seal the porosity

 Table 2 Corrosion potential and corrosion current density

 obtained from electrochemical polarization curve in Fig.8

Sample	$\varphi_{\rm corr}({\rm vs~SCE})/{\rm V}$	$J_{\rm corr}/$ ($\mu A \cdot cm^{-2}$)
AZ91D Alloy Substrate (a)	-1.590 2	940.86
AZ91D/chrome/ Ni-P (b)	-0.717 0	3.6
AZ91D/phosphate-Mn- molybdate/ Ni-P (c)	-0.733 4	2.91
AZ91D/vanadium bath/Ni-P (d)	-0.658 9	5.4
AZ91D/tannic acid/ Ni-P (e)	-0.518 6	12.71

by adding proper additives. By increasing the thickness and phosphorous content in the Ni-P coating, higher corrosion-resistance could be obtained without using chrome. In overall, chrome-free treatment scores more than chrome plus electroless, and gives future perspective of research in this field to make them in a profound way.

4 Conclusions

1) The phosphate-manganese conversion coating with the addition of molybdate $(2.0-2.5 \text{ g/L Na}_2\text{MoO}_4)$ enhances the corrosion resistance due to the fine flower-like crystalline structure in phosphate-manganese film. The vanadium-based conversion coating with immersion time of 20 min can significantly improve the corrosion resistance of the AZ91D Mg substrate. The tannic-based conversion coating provides a better corrosion resistance than others. These three conversion coatings have potential alternative for the chrome-based conversion coating.

2) Electrochemical result suggests that phosphatemanganese-molybdate and vanadium are potential to replace chrome treatment for electroless coating on magnesium alloy. It further suggests that TBC plus electroless can seal their porosity by adding proper additives. Phosphate-manganese-molybdate plus electroless have more passive region (good J_{corr} value) and less porosity than chrome plus electroless and φ_{corr} is almost equal. Vanadium plus electroless and TBC plus electroless have high corrosion potential than chrome plus electroless.

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J. SUDAGAR, et al/Trans. Nonferrous Met. Soc. China 21(2011) 921-928

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无铬转化膜预处理提高AZ91D镁合金 化学镀Ni-P的腐蚀性能

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摘要:在化学镀Ni-P层和AZ91D镁合金之间生成磷酸锰、单宁酸或钒转化膜预处理层,以取代传统的铬酸盐加氢氟酸预处理工艺。电化学测试结果表明:与传统的铬酸盐处理加化学镀相比,镁合金上的无铬转化膜加化学镀镍磷具有低的腐蚀电流密度和更正的腐蚀电位,能够减少基体上化学镀层的腐蚀。因此,镀层具有致密的细晶结构,适当的磷含量、低孔隙度和良好的耐蚀性并且和基体结合良好的涂层可以取代传统的铬酐钝化加化学镀的工艺。

关键词: 镁合金; 耐腐蚀性能; 化学镀; 无铬预处理

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928