Improvement of Corrosion Resistance of AZ91D Magnesium Alloy by Nickel Plating

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Abstract

The demand of lightweight structural materials is growing in automobile industry for energy saving. Magnesium alloy is one of the best candidates due to its low density. However, its low thermal stability and poor corrosion-resistant property against wear and environment limit applications of magnesium alloy. The main object of this investigation is to improve corrosion resistance of magnesium alloy, AZ91D, by nickel coatings. The nickel coatings protect the magnesium substrate by providing a barrier layer between the substrate and its environment. After suitable pretreatment procedures and copper strike on AZ91D surface, nickel coatings were obtained by successive electroless and electrical nickel platings with thickness of 18 μm and 10 μm, respectively. The microstructural analyses were performed by field-emission scanning electron microscope (FE-SEM) with elemental mapping. The uniform deposition of nickel was observed from the cross-sectional SEM micrograph. Local compositions were studied with energy dispersive analysis using X-ray unit attached to the SEM. Linear polarization curves were measured by potentiostat and neutral 3.5% NaCl aqueous solution was adopted as electrolyte for electrochemical study at room temperature. The measured corrosion potentials were −1.49 V and −0.79 V (vs. Ag/AgCl) for AZ91D and nickel-coated samples, respectively. The measured corrosion current densities were 5.03 μA/cm² and 0.67 nA/cm² for AZ91D and nickel-coated samples, respectively. Pitting corrosion of AZ91D was found from the anodic polarization curve. The results of present study are promising for the improvement of corrosion prevention of AZ91D material by nickel plating methods.

Keywords: Corrosion resistance; nickel coating; magnesium alloy; surface treatment

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1. Introduction

Magnesium (Mg) has the lowest density, 1.7 g/cm³, of all the structure metals. Its alloys are used where light weight is an important consideration such as aircraft, mobile phone, and vehicle. However, magnesium and its alloys (Mg-Li, Mg-Al-Zn) are highly unstable and especially susceptible to corrosion in moist or saltwater environments [1, 2]. Therefore, a uniform, good adhesion with pore (or crack) free deposition is the key point for the surface coating on Mg alloys. Recently, many kinds of surface treatment are developed for the protection of Mg alloys such as micro-arc oxidation, organic coating, conversion coating, anodizing or metal coatings [2-11].

The micro-arc oxidation (MAO) treatment has been popularly applied on Ti, Al and Mg alloys [12, 13]. The ceramic coatings formed by MAO technology provided good corrosion, wear resistance, insulation and cohesiveness with the Mg alloy substrate. However, the electric power consumption of MAO treatment is very large and the coatings are always of porous microstructure. Electroless nickel-phosphorus (Ni-P) plating method is a well established surface protective technique. The coating of electroless Ni-P possesses many interesting properties such as uniform thickness, good corrosion resistance and hardiness [14, 15]. In this research, electroless Ni-P plating and further electrolytic nickel plating were deposited on the surface of Mg alloy (AZ91D) with suitable surface pretreatment. The microstructure, chemical composition, adhesion strength of the coatings and corrosion resistance properties were then of interest to study.

2. Experimental

In this investigation, electroless Ni-P plating was coated on AZ91D magnesium alloy by using copper as interlayer for corrosion resistance. Firstly, the sample was cleaved into small piece (2 x 2 cm²) and surface cleaning by isopropyl alcohol (IPA) with ultrasonic agitation at room temperature for 10 min. The specimen was then degreased by alkaline solution at 60 °C for 2 min. After acid pickling, surface activation and zincating treatments, the sample was immersed in copper strike solution for copper coating with pure copper (99.9%) as an anode. The current density was 5 A/dm² (ASD) and the plating time was 10 min at room temperature. The Cu layer provided the under layer for further electroless Ni-P plating. The composition of plating solution is listed in Table 1. The plating time was 40 min and the ratio of solution volume to surface area was 10 mL/cm². The pH value and operating temperature of the Ni-P plating solution were 4.8 and 80 °C, respectively. The Ni-P deposition was successfully coated on magnesium alloy by electroless Ni-P plating. Finally, electrolytic Ni was then performed on the top of electroless Ni-P plating to improve the brightness of coatings. The pretreatment solutions and electroless Ni-P plating solution for Mg alloy were supplied by Kwo-Huah Company. Field-emission scanning electron microscopy (FE-SEM, ZEISS Ultra-plus) with energy dispersive X-ray analysis was used to observe the cross-sectional morphology and the elemental mapping, respectively. The phase identifications of Mg alloy, electroless Ni-P coating, and electrolytic Ni top coating were studied by high resolution X-ray diffractometer (BRUKER, D8-SSS) with Cu Kα radiation. The electrochemical behavior of corrosion resistance in 3.5 wt. % NaCl solution was evaluated by potential polarization test (JIEHAN 5600 Electrochemical station).
Table 1. Chemical composition of electroless nickel and nickel electroplating solutions.

| Electroless nickel | Nickel electroplating |
|--------------------|-----------------------|
| NaH₂PO₂· H₂O       | NiSO₄· 6H₂O           |
| 27 g/L             | 240 g/L               |
| Succinic acid      | NiCl₂                 |
| 16 g/L             | 45 g/L                |
| NiSO₄· 6H₂O        | H₃BO₃                |
| 20 g/L             | 30 g/L                |
| Stabilizer         | Brightener            |
| 0.54 ppm           | 10 mL/L              |
| pH                 | Current density       |
| 4.80               | 1.0 A/dm²             |
| Temp.              | Temp.                 |
| 80°C               | 55°C                  |

3. Results and discussion

Figure 1 shows the optical microscopy (OLYMPUS, BX51M) of the multi-layer (Ni/Ni-P/Cu/Mg alloy) structure obtained by Cu strike, electroless Ni-P coating and electrolytic Ni plating. The coatings seem to be very uniform and the total thickness of the coatings is about 28.6 μm. The standard oxidation potentials for magnesium, zinc, and copper are given as the following:

\[
\begin{align*}
\text{Mg} & \rightarrow \text{Mg}^{2+} + 2e^{-}, E^0 = 2.37 \text{ V}. \\
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^{-}, E^0 = 0.76 \text{ V}. \\
\text{Cu} & \rightarrow \text{Cu}^{2+} + 2e^{-}, E^0 = -0.34 \text{ V}.
\end{align*}
\]

During zincating process, zinc is deposited on the surface of magnesium alloy by displacement reaction. Copper is one of the easiest metals to electrodeposited on the zincated substrate. For copper striking, copper is deposited on zincated magnesium alloy by initially chemical displacement and followed by electrodeposition. Copper is not catalytic to the chemical reduction of electroless nickel. A method of activating copper layer in electroless plating solution is to contact with a piece of steel after immersing in a plating bath. Once a layer of nickel atoms is deposited, the autocatalytic reaction of electroless nickel plating is continuing to the desired thickness. The reaction mechanism of electroless nickel plating is proposed as the following [16]:

\[
\begin{align*}
\text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \xrightarrow{\text{cat.}} & \text{HPO}_3^{2-}\text{-H}^+ + \text{H}^- & (1) \\
\text{Ni}^{2+} + 2\text{H}^- \xrightarrow{\text{cat.}} & \text{Ni} + \text{H}_2 & (2) \\
\text{H}_2\text{PO}_2^- + \text{H}^+ + 2\text{H}^+ \xrightarrow{\text{cat.}} & \text{P} + 2\text{H}_2\text{O} + \frac{1}{2}\text{H}_2 & (3)
\end{align*}
\]

The phosphate ion, hydrogen ion and hydride ion are formed by hydrolysis of hypophosphite in the acidic electroless plating solution at pH 4.8 as shown in equation (1) where the nickel layer behaves as catalyst of reaction. The nickel ion is reduced to metallic nickel by hydride ion as shown in Eq. (2). Furthermore, phosphorus is co-deposited in the electroless nickel coating as indicated in Eq. (3). The Ni-P coating was deposited on the surface of Mg alloy substrate.
The FE-SEM surface morphology of the sample after electroless Ni-P plating is shown in Fig. 2. Electroless Ni-P coating surface is with nodule structure. The surface roughness (Ra) is about 2.3 μm. The cross-sectional view of the multiple layers observed by FE-SEM is shown in Fig. 3. The EDS results for element composition (wt. %) of the regions from A to D are listed in Table 2. The analytical results showed that the regions A, B, C and D are electrolytic Ni, electroless Ni-P coating, Cu layer and Mg alloy, respectively. Those coatings were directly deposited on the surface of the Mg alloy (AZ91D) one by one.

The GIAXRD patterns of the Mg alloy substrate with multi-layer coatings, as shown in Fig. 4. The diffraction peaks of the Mg alloy substrate were disappeared after Cu strike and followed by electroless Ni-P plating. The broad peak at about 46° shows the presence of amorphous structure in Ni-P coating. The amorphous structure is responsible for the increase of corrosion-resistant ability [17, 18]. The XRD pattern also indicates the pure Ni was coated on the surface of the Ni-P/Cu/Mg alloy after electrolytic Ni plating.

Table 2. Elemental percentages of regions A, B, C and D as shown in Fig. 3.

| Element (wt.%) | Region | A   | B   | C   | D   |
|---------------|--------|-----|-----|-----|-----|
| Ni            |        | 100 | 91.32 | 11.53 | -   |
| P             |        | -   | 8.68 | -   | -   |
| Cu            |        | -   | -   | 35.32 | -   |
| Mg            |        | -   | -   | 35.04 | 89.06 |
| Al            |        | -   | -   | 2.95  | 10.35 |
| O             |        | -   | -   | 15.16 | -   |
| Zn            |        | -   | -   | -   | 0.59 |
The result of adhesion test of deposited multi-layer on Mg alloy is shown in Fig. 5. The adhesion strength of directly deposited coating was 115.4 kgf/cm². The measured polarization curve of surface-treated Mg alloy in the neutral 3.5wt. % NaCl solution is shown in Fig. 6. There are significant changes of the corrosion potential ($E_{corr}$) and corrosion current ($I_{corr}$) after Ni-P deposition. The values of $E_{corr}$ and $I_{corr}$ are listed in Table 3. The Ni-P coating shows a higher corrosion potential (-0.78 V vs. Ag/AgCl) and a lower corrosion current (0.70 nA/cm²). The corrosion potential moving from active region to more noble region indicates that the corrosion resistance is increased. Therefore, electroless Ni-P coating can greatly improve the corrosion-resistant ability of Mg alloy (AZ91D). The corrosion current is slightly decreased to 0.67 nA/cm² for the dual nickel coating: with electroplated nickel as the top layer and with electroless-plated nickel as the bottom layer.

Table 3. Values of corrosion potential ($E_{corr}$) and corrosion current ($I_{corr}$) of samples.

| Samples                  | $E_{corr}$ (V vs. Ag/AgCl) | $I_{corr}$ (nA/cm²) |
|--------------------------|----------------------------|---------------------|
| Mg alloy substrate       | -1.49                      | 5.03 μA/cm²         |
| NiP/Cu/Mg alloy          | -0.78                      | 0.70 nA/cm²         |
| Ni/NiP/Cu/Mg alloy       | -0.79                      | 0.67 nA/cm²         |

4. Conclusions

The electroless Ni-P and electrolytic Ni coating can be deposited on the surface of Mg alloy (AZ91D) after suitable surface pretreatments. The Cu coating was electrodeposited on Mg alloy substrate and acted as an activated and protective inter-layer between Ni-P and AZ91D substrate. The total thickness of multi-layer structure Ni/Ni-P/Cu/Mg alloy was about 28.6μm with surface roughness (Ra) 2.3 μm. The corrosion potential was -0.78 V (vs. Ag/AgCl) and corrosion current was 0.70 nA/cm² for Ni-P coated AZ91D. The amorphous Ni-P coating could enhance the corrosion resistance of Mg alloy significantly.
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