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A novel process for electroless nickel plating on anodized magnesium alloy

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Abstract

In this paper, a novel palladium-free activation electroless nickel (EN) plating process, by which a TiB_2 powders contained intermediate film was used as catalyst, was introduced for anodized magnesium alloy AZ91D. The corrosion behavior of AZ91D without and with coating was compared and the bonding strength of the EN plating to the substrate was also measured. The results showed that the EN plating could easily take place on the intermediate catalytic layer, directly on which a smooth and compact Ni–P alloy layer without obvious flaws, about 20 μm thickness, was successfully deposited. The catalytic function was principally from TiB_2 powder. The adhesive tensile test indicated a good bonding strength of about 11 MPa between the substrate and the catalytic layer. An obvious passivation range and higher E_{corr} (−0.323 V) for the EN plating during anodic polarization in 3.5 wt.% NaCl solution, implied a typical character of a compact Ni–P alloy layer, with an effective protection for the substrate.

Keywords: Magnesium alloy; Electroless nickel plating; Palladium-free activation; Catalytic; Corrosion resistance

1. Introduction

Magnesium alloys have a number of desirable properties, such as high specific strength and stiffness, but the poor corrosion resistance restricted their large-scale application in industries [1]. This makes protective surface treatment an essential and practicable part of the manufacturing process for Mg alloys. Among various surface treatments, anodic oxidization, or plasma electrolytic oxidation (PEO), was widely adopted to enhance the corrosion resistance of Mg alloys [2–5]. But a single anodized film generally was not adequate for protection of magnesium alloys. So electroless nickel (EN) plating was adopted as a protective top layer on the anodized film [6,7], due to its special advantages of EN coatings, such as uniform deposition, good corrosion and wear resistance, good electrical and thermal conductivity, and good solderability [8], as well as that other metallic plating might further be deposited onto the EN plating [9]. Traditionally an EN plating on an anodized film may become a self-sustaining process only if the so called Pd-activation technique is adopted [6,7]. However, the Pd-activation technique was inconvenient in practice due to the strictly prolix operation process and a high material cost [10].

It was reported that a Pd-activation process was also adopted for electroless plating of Ni–B alloy on TiB_2 powders to improve its spraying performance [11]. However EN plating of TiB_2 powders was found to be an autocatalytic process in our study. The fact clearly implies that TiB_2 may act as a catalyst for the EN plating process.

Therefore, this paper dealt with a novel palladium-free activation process for EN plating on anodized magnesium alloy with a thin intermediate layer containing TiB_2 powders, which could provide a good autocatalytic function for EN plating and a seal function for anodized film. This novel process achieved acceptable bonding strength and corrosion resistance of a composite coating for the Mg alloy substrate.

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Table 1
Nominal composition of AZ91D (in wt.%)

Al	8.5–9.5
Zn	0.50–0.90
Cu	<0.30
Mn	0.17–0.27
Ni	<0.002
Fe	<0.005
Si	<0.1
Mg	Balance

Table 4
The bath composition and plating parameters

Bath species and parameters	Quantity
Basic nickel carbonate (g/l)	10
Citric acid (g/l)	5
Ammonium bifluoride (g/l)	10
Sodium hypophosphite (g/l)	20
Ammonium hydroxide 25% (ml/l)	30
pH	4.5–6.8

2. Experiment

2.1. Specimen preparation

Specimens were cut from die cast magnesium alloy AZ91D with a size of 25 mm × 25 mm × 10 mm. The specific composition of the test materials was listed in Table 1. A hole of 2 mm in diameter was drilled in the middle of one edge of each specimen for convenient hanging up in the solution during treatments. The surfaces of the specimens were polished by emery papers up to 1000 grit before the pre-treatment processes. The EN plating process used in this work was a four-stage procedure (shown in Table 2).

2.2. Anodizing

The Dow17 process was adopted to produce anodized film for magnesium alloy specimens, its detailed operation processes could be found elsewhere [2]. The bath composition and operation parameters were given in Table 3.

2.3. Catalytic layer application

The catalytic powder of TiB_2 was mixed completely with epoxy resin and curing agent to form a dilute solution with solvent addition. The weight ratio of TiB_2 with organic adhesive was 1.5:1. The anodized specimens were dipped in the solution for certain period and then lift out to form a thin film on the surface. The specimens were finally cured at 343 K for 30 min. The thickness of catalytic layer film was about 10–15 μm.

Table 2
Procedures of EN plating

Pre-treatment	Ultrasonic degreasing using acetone 10 min, alkaline cleaning in 10% NaOH at 333 K for 5 min
↓	
Anodizing	
↓	
Catalytic layer	Dipping and curing
↓	
EN plating	

Table 3
Anodizing process for magnesium alloys

Process	Electrolyte constituents	Operation conditions
Dow17	Ammonium bifluoride Sodium dichromate	Temperature 343 K Voltage 90 V, current density 1 A/dm^2, time 15 min

2.4. Electroless plating

After the catalytic film was applied, the specimens were put to the EN plating bath for desired time, then rinsed and dried. The bath composition and operation parameters were given in Table 4.

2.5. Analysis methods

The surface and cross-sectional morphologies and chemical composition of powder, intermediate catalytic film, anodized film, EN plating were examined by SSX-550 scanning electron microscopy (SEM) equipped with energy dispersive analysis of X-rays (EDAX). Specimens were coated with gold prior to analysis. The tensile test was employed to study the adhesion between EN plating and the substrate according to GB 5210-85 (eqv ISO 4624) standard [12] and the schematic illustration of the test was shown in Fig. 1. Test specimens and two loading fixtures were attached to the face of the plated coatings using special adhesive with an adhesive strength of about 60 MPa.

The electrochemical measurements were performed using a Princeton Applied Research (PAR) EG&G potentiostat/galvanostat model 273 with model 352 corrosion software. All electrochemical measurements were conducted using a three-electrode electrochemical cell with the samples as the working electrode, a platinum plate as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference. All experiments were carried out at room temperature. Potentiodynamic polarization at scan rate of 0.5 mV/s was used to evaluate the corrosion resistance of the bare AZ91D, anodized film, catalytic layer and the EN plating on AZ91D, respectively.

3. Results and discussion

As shown in the SEM image (Fig. 2(a)), the anodized film on Mg alloy had relatively high porosity with different size pores randomly distributed in the film. The pores were formed by the molten oxide and gas bubbles thrown out of discharge channels during the anodizing process. Those pores lead to poor corrosion resistance of the anodized film when exposed in corrosive