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Homogenization pretreatment and electroless Ni−P plating on AZ91D magnesium alloy

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Abstract: Electroless nickel plating on AZ91D substrate with a new and eco-friendly pretreatment process based on tuning an electrochemical homogeneous surface was investigated. The morphology, deposition process, chemical composition and microstructure of Ni−P coating were studied. It is indicated that β phases are selectively removed, producing a microstructural homogeneous surface and the subsequent uniform and compact Zn immersion layer. A defect-free and well adhesive Ni−P coating can be successfully obtained due to its uniform nucleation and growth based on such pretreatment. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests reveal that Ni−P coating could significantly improve the corrosion resistance of AZ91D substrate.

Key words: AZ91D magnesium alloy; homogenization pretreatment; electroless nickel plating; corrosion

1 Introduction

Magnesium alloys are increasingly used in various industries, e.g., automotive, aerospace and portable electronics. However, the widespread application of Mg alloys is largely limited by their poor corrosion and wear resistance. Electroless nickel plating is considered to be an efficient way to improve the surface properties of Mg alloys [1−4].

Electroless nickel plating on magnesium alloys has many challenges in the process of plating [5−7]. As a highly chemically active alloy, Mg is quite sensitive to galvanic corrosion and severe pit corrosion on the metal results in unexpected appearance and poor mechanical properties [8]. The most difficult and critical part of plating magnesium alloy is how to develop a suitable pretreatment process to obtain high performance plating coating with superior anti-corrosion resistance, adherence performance and mechanical properties. Nowadays, there usually exist two plating techniques [9]: 1) zinc immersion and 2) direct nickel plating procedures. The zinc layer obtained by zinc immersion could equalize the surface potential and reduce potential difference between the Mg alloy substrate and subsequent nickel deposit. Once a suitable undercoating is available, many desired metals can be plated easily [10].

In practice, the process of plating on AZ91D is rather complicated. AZ91D alloy is chemically and electrochemically heterogeneous due to the heterogeneous distribution of Al in the three constituent phases (primary α phase (i.e., matrix), eutectic α phase (i.e., Al-rich α) and β phase (i.e., $Mg_{17}Al_{12}$ intermetallic)). β phase is more cathodic than eutectic α and primary α phase [11]. Several prior studies have shown that the deposition of Ni−P coating is preferentially nucleated on the position of β phases and spread to eutectic-α and primary-α phase in the plating process. In the electroless plating bath, the initial deposition is seriously affected by the galvanic couple between β phase and adjacent α phase. The anodic dissolution of magnesium from α phase provides electrons which are consumed by the cathodic deposition of electroless nickel on β phase [5]. However, the coating on β phases was discontinuous and grew slowly, leading to non-uniform coating growth

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[12], which would cause coating defects and coating failure. It should be noted that in many reports on electroless nickel plating, Mg alloy was etched in a solution of chromium oxide, phosphorous acid and nitric acid and soaked in HF or NH_4HF_2 solution in order to form a conversion film [5−7]. The use of these chemicals introduced strong damage to the environment and was progressively restricted due to their high toxicity [13]. Therefore, an environment-friendly pretreatment is in need to be developed.

Previous pretreatment processes mainly focused on providing a thin layer on the surface to improve homogeneity [14,15]. In previous work, YANG et al [16] developed a novel and eco-friendly pretreatment process called homogenization pre-treatment (HP) which could effectively enhance the homogeneity of microstructure on AZ91D surface by controlling the β phase amount. Noticeably, the HP was totally environment-friendly, avoiding the use of hexavalent chromium and fluoride, etc, compared with the conventional pretreatment process. Hence, it was anticipated that HP could be a suitable approach to obtain a resultant uniform, compact and defect-free Ni−P coating on AZ91D substrate.

Herein, electroless nickel coating upon AZ91D magnesium alloy based on HP process was studied. The deposition process, morphology, chemical composition and microstructure of Ni−P coating were investigated by SEM/EDS and XRD measurements. The corrosion resistance of the obtained coating was evaluated by electrochemical measurement including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests, and also the adhesion was examined by thermal shock test.

2 Experimental

2.1 Materials and procedure

The substrate material was die-cast AZ91D magnesium alloy (15 mm × 15 mm × 3 mm) with a nominal composition of 8.9% Al, 0.89% Zn (mass fraction) and balanced Mg. Specimens were mechanically ground with #1500 SiC papers before the pretreatment process. The HP process tuning of β phases on the AZ91D surface was used according to our previous work [16], which mainly consisted of acid pickling in $C_6H_8O_7$ solution, conditioning in NaOH solution and dilute $C_6H_8O_7$ acid cleaning. The detailed procedure of electroless nickel plating on AZ91D magnesium alloy is listed in Table 1. All the chemicals were analytical reagents and used as received without further purification.

Table 1 Process flow of electroless Ni−P plating on AZ91D magnesium alloy

Process	Bath composition	Condition
Grinding		No. 2000 SiC sandpaper
Activation	100 g/L $C_6H_8O_7$	Room temperature, 45 s
Conditioning	200 g/L NaOH	65 °C, 30 min
Dilute acid cleaning	10 g/L $C_6H_8O_7$	Room temperature, 10 s
Zinc immersion	30 g/L $ZnSO_4·7H_2O$, 120 g/L $Na_4P_2O_7·10H_2O$, 5.5 g/L NaF, 5.5 g/L Na_2CO_3	(80±2) °C, pH=11.7, 6 min
Electroless Ni−P plating	15 g/L $NiSO_4·6H_2O$, 13 g/L $NaC_2H_3O_2$, 8 g/L NH_4HF_2, 1 mg/L Thiourea, 14 g/L $NaH_2PO_2·H_2O$, 12 mL/L HF (40% V/V)	(80±2) °C, pH=6.4±0.2, 60 min

2.2 Characterization

The surface, cross-section morphologies and chemical compositions of the zinc immersion layer and Ni−P coating were observed using scanning electron microscopy (SEM, NOVA NanoSEM 230, USA) with energy-dispersive X-ray spectroscopy (EDS) system. The crystallographic structures of the samples were measured by X-ray diffractometer (XRD, D/MAX255ovl/84) with Cu target and a monochromator at 35 kV and 200 mA with scanning rate of 4 (°)/min and step of 0.01°. The corrosion resistance of Ni−P coating was evaluated by electrochemical measurements including potentio-dynamic polarization and electrochemical impedance spectroscopy (EIS) using a PARSTAT 2273 advanced electrochemical system from Princeton Applied Research. All the electrochemical tests were performed in 3.5% NaCl (mass fraction) solution at (25±2) °C. A classical three-electrode cell was used, with the sample as working electrode, a platinum plate as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. The specimen area exposed to test solution was 0.5 cm^2. Prior to each test, samples were immersed into electrolyte for 30 min to stabilize the open-circuit potential (φ_{OCP}). EIS tests were conducted at φ_{OCP} and the measuring frequency was ranged from 100 kHz down to 100 mHz, with a sinusoidal signal amplitude of 10 mV. The impedance data were further interpreted to study the corrosion mechanism on the basis of an equivalent circuit through fitting by ZsimpWin program. The potentiodynamic polarization curves were measured at a scanning rate of 0.5 mV/s. The hardness of Ni−P coating was evaluated using a HX-500 microhardness tester with Vickers indenter applying a load of 0.98 N for 15 s. The