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Characterization and corrosion resistance of duplex electroless Ni-P composite coatings on magnesium alloy

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Three different types of electroless nickel (EN)-phosphorus plating were applied on AZ31 wrought magnesium alloy. The first type was plain mid-phosphorus coating, the second one was duplex, with the first layer having a mid-phosphorus content and the upper one consisting of high-phosphorus whereas the third type of coating was also duplex with a first mid-phosphorus layer and a second high-phosphorus one with incorporated ceramic TiO_2 and ZrO_2 microparticles. Characterization of deposits by means of scanning electron microscopy and X-ray diffraction analysis proves the production of adherent, defect free coatings with differences in crystallinity depending on P content. Surface roughness was maintained at acceptable levels while a great increase in microhardness was observed that was further enhanced by ceramic microparticles incorporation. Electrochemical testing, that was performed by Tafel polarization in 3.5% NaCl solution, show that all the coatings effectively protect the Mg alloy substrate. Additionally, the composite coatings exceptionally enhance the protective capability of the system after heat treatment at 200 °C.

1. Introduction

In various fields of industry, where light weight is a prerequisite, such as automobile, aerospace, aeronautics, telecommunications, electronics, magnesium and its alloys are predominant materials. They combine excellent physical and mechanical properties, such as electrical and thermal conductivity, high specific strength, excellent anti-shock resistance, vibration absorption and good electromagnetic shielding effectiveness. All of the above, as well as the fact that magnesium alloys are easy to cut, form, of low cost and recycle are more than enough to be characterized as green engineering materials and of great importance for the 21st century. However, these significant advantages are overshadowed by one major drawback that becomes an obstacle for developing new applications and improving the existing ones. Their high chemical and electrochemical reactivity make them prone to oxidation and corrosion in humid atmosphere, fresh water, seawater and most of organic and inorganic acids and their salts [1]. This highly reactive nature is enhanced by alloying constituents which introduce electrochemical heterogeneity, hence microgalvanic corrosion [2].

Therefore, appropriate methods that improve the corrosion resistance are highly recommended. Electroless nickel-phosphorus (EN) plating is considered one of the most effective surface treatment techniques due to its perfect comprehensive properties, such as good corrosion and wear resistance, deposit uniformity over complex geometries and solderability [3]. However, magnesium alloys are challenging materials as far as plating is concerned, mainly because of MgO that can be formed on their surface, which causes the deterioration of the coatings adhesion. Furthermore, the inhomogeneous microstructure consisting of the primary phase and the second phase can be the reason of non-uniform coatings. Additionally, since magnesium is one of the most electrochemically active metals, EN coatings are cathodic to the alloy substrate so they can only provide a physical barrier against corrosion attack. The considerable potential difference between the substrate and the coating will result in pitting corrosion when cracks and pores are present, a fact that highlights the importance of defect-free coatings [4,5].

The ability to co-deposit fine particulate matter within an electroless metal matrix has led to a new generation of composite coatings. Successful co-deposition is dependent on various factors including particle catalytic inertness, particles charge, electroless bath composition, bath reactivity, compatibility of the particles with the metallic matrix, plating rate and particle size distribution [6]. Composite coatings have been a source of disagreement among many researchers. According to one group, the corrosion resistance of electroless Ni-P coatings is believed to be significantly less than that of the electroless Ni-P composite coatings [7]. Dehghanian et al. reported that the electroless deposited Ni-P-nano-TiN coating on low carbon steel displayed very weak corrosion properties [8]. Zang et al. have found that co-deposition of either SiC or PTFE particles slightly decreased corrosion resistance of the coatings on mild steel in 3% NaCl aqueous solution but had insignificant effects on their corrosion resistance in 1 N H_2SO_4 [9]. On the other hand, electrochemical, salt spray and immersion tests have proved that the corrosion resistance of Ni-P-ZrO_2 composite coating was superior to

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that of Ni-P coating on AZ91D magnesium alloy in the study of Han et al. [10]. Furthermore, Ni-P-CeO_2, Ni-P-TiO_2 and Ni-P-Si_3N_4 composite coatings offer better corrosion protection on medium carbon steel, according to Balaraju et al. [11].

In the present study, electroless Ni-P composite duplex coatings with the upper coating containing crystalline TiO_2 and ZrO_2 microparticles on AZ31 wrought magnesium alloy were prepared. Their physical properties, surface roughness and microhardness, as well as their corrosion behavior were tested and compared to those of duplex and plain coatings.

2. Experimental

The substrate for this work was AZ31 wrought magnesium alloy, whose composition is presented in Table 1. Rectangular coupons (30 × 20 × 4 mm) were gradually ground down from 1000 to 2000 grit using silicon carbide papers to achieve similar surface roughness, and they are then subjected to the pretreatment process (Table 2). Alkaline cleaning removes oils and greases from the coupons surface whereas acid pickling creates an oxide-free substrate. To minimize air contact and thus atmospheric oxidation, coupons are rinsed thoroughly with deionized water and as quickly as possible after each step of the pretreatment process. Ethanol rinses were also applied before water rinses to assure that each specimen would be wetted equally by the solutions, i.e. ethanol was employed as a wetting agent. The weight loss during pretreatment was negligible.

For the present study two different EN plating baths were prepared (Tables 3–4). Their common compounds are nickel sulfate and sodium hypophosphite which serve as the source of nickel cations and metal reducing agent respectively. Thiourea in the first bath and Pb^{2+} in the second one serve as stabilizers in order to prevent bath decomposition, whereas the complexing agents are sodium acetate for the first EN plating process and propionic and lactic acids for the second one. After pretreatment, the specimens were immersed in the first EN plating bath for 1 h at 90 °C. They were then removed, dried and weighed before their subsequent 1-h immersion in the second EN plating bath, that contained microparticles of TiO_2 or ZrO_2, and was kept under stirring by a rotating stirring rod with a rate of 250 rev/min. The grain size of TiO_2 was 0.3–0.5 μm and that of ZrO_2 powder was up to 5 μm. Afterwards the coupons were once more dried and weighed. For comparison, plain Ni-P deposits by immersing coupons in the 1st EN plating bath for 2 h and duplex Ni-P deposits by immersing coupons in the 1st EN plating bath for 1 h and then in the 2nd EN plating bath without microparticles were also prepared. The total thickness of the deposits was estimated at approximately 50 μm for each specimen. The microhardness of the substrate and of the coatings was calculated as the average of five measurements taken on each side of the coupons with a load of 150 g for 10 s using a Leitz Wetzlar tester with a Vickers diamond indenter. The surface morphology of the specimens was examined by means of Siemens X-ray diffractometer 5000 (XRD) equipped with a Cu Kα X-ray source and FEI QUANTA 2000 scanning electron microscopy (SEM) along with EDS analysis in order to determine the chemical composition of the deposits. The latter was also used to study cross-sections of the specimens for possible defects of coatings as well as for an estimation of the adhesion of the coatings. Surface roughness test was also conducted with a Talysurf instrument and the average of five measurements on each side of the coupons was recorded.

Table 1
Composition of AZ31 wrought magnesium alloy.

Alloy	Mg	Al	Zn	Mn	Si	Cu	Ni	Fe
AZ31	Balance	3.0	1.0	0.44	<0.1	<0.01	<0.003	<0.005

Table 2
Pretreatment of coupons to be electroless nickel plated.

Pretreatment		
Stage	Solution	Parameters
Alkaline cleaning	NaOH 45 g/L	10 min, 65 °C
Acid pickling	HNO_3 (65% w/w) 100 mL/L CrO_3 125 g/L	1 min
Fluoride activation	HF (50% w/w) 280 mL/L	10 min

Tafel electrochemical tests were carried out in a three-electrode cell, having a saturated calomel electrode (SCE) as reference, a platinum sheet as counter electrode and the tested specimen as a working electrode, exposed in a 3.5% NaCl aqueous solution at room temperature in the range of −0.25 to 0.25 V vs. open circuit potential and at a constant scan rate of 1 mV/s. The instrumentation was a CMS 100 Gamry potentiostat, computer controlled, with commercial software for the obtained data process.

Thermal treatment of the system was also tried to test cracking and the overall behavior of the coatings in high temperatures. The heat treatment was carried out in a furnace with constant airflow, at 200 °C for 2 h, and then the coupons were left to cool at room temperature. This level of temperature was selected, as it is the average operating temperature of many helicopters engine. The heat treated coupons were then studied for any changes in microhardness and their surface roughness as well as for the effect of temperature in the crystallinity of deposits and their overall corrosion behavior by XRD and Tafel analysis respectively. Cross-sections of heat treated specimens were examined for cracks by means of the aforementioned scanning electron microscope.

3. Results and discussion

3.1. Characterization of the as-plated specimens

The surface roughness of the specimen to be plated should be considered before the beginning of any other plating procedure. The initial roughness plays an important role in the thickness and adhesion of the deposits as well as in their wear properties. In a polished substrate with a very low surface roughness, a thinner, less adherent coating will develop in contrast with a rougher substrate that favors an enhanced interlocking force. On the other hand, on a rough substrate, coatings of high friction coefficient will be produced [12]. Therefore, the coupons of this study were grinded down to 2000 grit, so as their average surface roughness (R_a) reached 0.1 μm (Fig. 1).

The pretreatment process is the key to successful EN plating on magnesium alloys. Their high chemical reactivity with air will result in the formation of an oxide film on their surface that has a detrimental effect on the coatings adherence and uniformity. Therefore, air contact of specimens must be minimized during this process. The acidic solution corrodes the surface, making it rougher but more

Table 3
Composition of the first, medium-phosphorus EN plating bath.

1st EN plating bath	
$NiSO_46H_2O$	15 g/L
$NaC_2H_3O_2$	13 g/L
NH_4HF_2	8.5 g/L
HF (50% w/w)	10 mL/L
NaH_2PO_2	14 g/L
CH_4N_2S	1 mg/L
NaOH(aq) for adjusting pH	
T = 90 °C, pH = 6.2, t = 60 min	