

# Improving the Corrosion Resistance of Az91d Magnesium Alloy by Electroless Plating

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**Abstract** -This paper presents an experimental study on the influence of four different types of surfactants namely sodium trimethyl ammonium bromide (CTAB), sodium lauryl sulphate (SDS), N- Dimethylmyristylammonio and polyethylene glycol hexadecyl ether on the micro hardness and wear resistance of electroless nickel phosphorus (Ni-P) coatings using electroless coating method. Corrosion performance of the electroless Ni-P coatings was evaluated by Potentiodynamic Polarization technique. The results showed that SDS anionic surfactant causes increasing of corrosion resistance.

## 1 INTRODUCTION

Usage of magnesium and its alloy in industry has been gradually increasing because of their high strength to light weight ratio with a density one fourth that of iron and two third that of aluminum. Magnesium and its alloy have low corrosion resistance and wear resistance value because it's high chemical and electro chemical reactivity which resulting in formation of porous oxide carbonate film on the surface 1.

To improve the corrosion resistance and wear resistance of magnesium alloy electroless nickel plating method is used because of its good property and uniform coverage in surface 2. Direct plating on Mg is a challenge because of highly chemically active alloy. Hence Mg alloys needs special bath formulation and pretreatments process 3. Chromium-free pre-treatments for the electroless nickel phosphorous (Ni-P) deposit are always desirable, as it is environment friendly 1. The pretreatment steps included degreasing, alkaline cleaning, acidic cleaning, activation and electroless nickel plating, with a fluoride layer formed after activation between substrate and coating 3. According to electrochemical mechanism, electroless deposition was resulted from mixed anodic and cathodic reactions. By using hypophosphite as reducing agent, anodic partial process was the oxidation of reducer with water, and the electrons generated in the anodic reaction were utilized in the coupled cathodic processes for deposition of Ni and P. Meanwhile, the evolution of hydrogen gas was account for a result of the secondary reaction of hydrogen ions 2. Electroless plating deposition process is based on a redox reaction, in which the reducing agents are oxidized and Ni<sup>2+</sup> ions are reduced on the substrate surface 5.

By adding surfactant in the bath improves the deposition rate and its properties. Surface active agents having both hydrophobic and hydrophilic structural units; the adsorption generally results in the modification of the surface

or interfacial properties of the system. A surfactant can be classified by the presence of formally charged groups in its head. A non-ionic surfactant has no charge groups in its head and an ionic surfactant carries a net charge. If the charge is negative, the surfactant is called anionic; if the charge is positive, it is called cationic 4. Hence, this study mainly focuses on surfactants influence on the micro hardness and wear properties of the electroless Ni-P deposits on magnesium substrate. However, there was no such investigation on magnesium alloy and moreover it is complicated because of corrosive nature in the electrolyte bath. Hence, in this investigation, four types of surfactants namely sodium trimethyl ammonium bromide (CTAB), sodium lauryl sulphate (SDS), N-Dimethylmyristylammonio and polyethylene glycol hexadecyl ether used in the electrolyte for electroless Ni-P deposit on magnesium alloy, which affects the surface tension forces between solid/liquid interfaces 4. By adding surfactant in the bath solution deposition rates, surface morphology, surface topography and micro hardness are investigated in this study.

## 2 EXPERIMENTAL DETAILS

### 2.1 Sample and bath preparations

Circular shaped AZ91D die cast magnesium alloy with a size of 30 mm × 7 mm used as a substrate material in the present investigation 1. Samples were mechanically polished with emery paper (400,600, 800, 1000 and 2000 size) and then surface pretreatment is to be done. Samples should be transferred as quickly between surface treatments process. The bath composition and all the operation parameters for the electroless Ni-P deposition are reported in Table 1

### 2.2 Steps for Surface Preparation

All the samples were subjected to the following pre-treatment procedure:

1. Ultrasonic cleaning in absolute acetone for 2 min.
2. Alkaline cleaning in sodium hydroxide and tri-sodium orthophosphate at 65 OC for 20 min.
3. Rinsing with tap water at room temperature (RT) for 2 min.
4. Acid pickling in chromic-nitrate for 10 sec.
5. Rinsing by immersion in tap water at RT for 2 min.
6. Activation in 16 vol. % HF at RT for 1 min.
7. Rinsing with distilled water at RT for 2 min.
8. EN plating process
9. Rinsing by immersion in 60 OC water for 1 min.

2.3 Surfactant added

Surfactant is necessary in the chemical baths to stabilize the dispersion and improve the deposition of Ni-P coatings. In addition, anionic surface activator sodium lauryl sulphate (SDS), cationic surface activator cetyl tri-methyl ammonium bromide (CTAB), Zwitterionic surface activator N-Dimethylmyristylammonio and non-ionic surface activator polyethylene glycol hexadecyl ether were used in this study as a surface activator in the electrolyte bath and to enhance the properties of the deposits 1.

The surface and cross-section micrographs of the coatings were investigated by scanning electron microscope (SEM) and then their hardness was measured using a Vickers diamond indenter under a 200 g load for 10 s 5.

Wear tests were conducted under dry condition using a JM-IV tribometer .The coated sample was placed onto a disc which was rotated at a constant speed of 70 rev min<sup>21</sup>, and two wheels of w50612 mm hard material (HRC 62) with a load of 1 kg which rotated in opposite direction were inflicted on the coated sample. The wear tests were conducted with different cycles and the wear resistance was calculated by the weight loss measurement using electronic balance with precision of 0.01 mg 5

Electrochemical polarization measurements were performed by an electrochemical analyzer, which was controlled by a computer software system. Potentiodynamic experiments were conducted at ambient temperature. The experiments were carried out in a 3.5 wt% NaCl aqueous solution using a three-electrode cell with a platinum plate as counter electrode and a saturated calomel electrode was fitted through the rubber stopper and used as a reference electrode and scan rate of 5 mV/s was used 1.

3 RESULTS AND DISSCUSION

3.1 Corrosion properties of electroless Ni P deposits with surface activator

The corrosion properties of the electroless Ni P deposition were improved by using surfactant. Figures 1, 2, 3, 4 and 5 shows the Potentiodynamic polarization curves obtained from a coated AZ91 alloy and as-plated EN samples. In order to avoid the negative effects of the porosity in the coating that causes extra galvanic corrosion during the polarization testing, a simple porosity test was performed by immersing the as-plated samples into 3.5 % NaCl solution. Any samples failing this test were removed from subsequent polarization testing. After these tests, it was found that the anionic surfactant coatings remained bright in appearance of Ni plating. According to the potentiodynamic curves in as shown in Figure the anionic surfactant coatings exhibited much higher positive corrosion potential  $E_{corr}$  and lower corrosion current density  $I_{corr}$  than that of other surfactant used magnesium substrate, showing that the coatings can completely protect the substrate material from corroding. In the anodic region of every curve, an activation control dominated the anodic reaction, and the corrosion current increased quickly with the increasing anodic potential.

The corrosion rate (CR) can be determined using the Faraday law

$$E_{COR} = K \quad EW$$

Where  $E_{CR}$  is given in mm/year,  $K = 3.27 \times 10^{-3}$  mmg/Acm year,  $\rho$  the density of the substrate (g/cm<sup>3</sup>) and EW the equivalent weight of the substrate. Similar evaluation of corrosion rate has been reported in the literature. The corrosion potential ( $E_{corr}$ ) and corrosion current density ( $i_{corr}$ ) calculated with Tafel extrapolation method are given in Table 5.1 for plated EN and uncoated AZ91 samples. The corrosion potential ( $E_{corr}$ ) of the as-plated EN coatings show a significant shift to the positive direction, and the corrosion current density ( $i_{corr}$ ) decreases to a certain extent, which indicates that the EN coatings have corrosion resistance.

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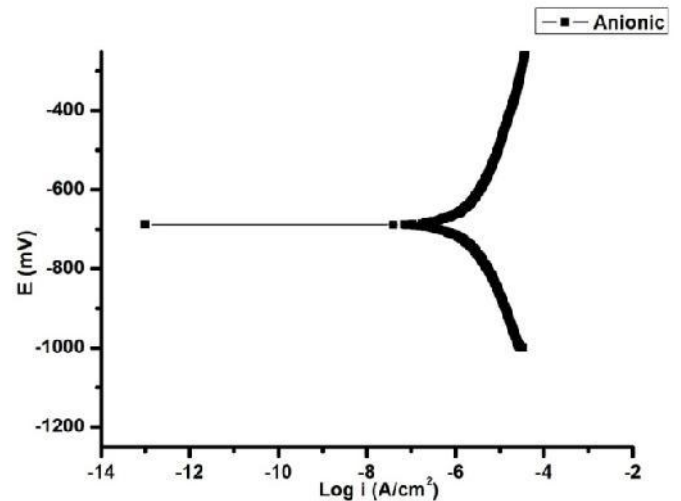


Fig. 1 Potentiodynamic polarization curves for anionic coating

4 CONCLUSIONS

The corrosion resistance was improved by electroless Ni P deposits with surfactants on magnesium alloy. The following conclusion can be drawn from the study that the addition of surfactant significantly improved the corrosion resistance of the electroless Ni P deposit on magnesium substrate (polarization test). The influence of anionic activator is more that cationic, zwitterionic and non ionic in resisting the corrosion. The surfactants increase the smoothness and increased amorphous plus nano-crystalline phases, which were the main reason for the corrosion resistance. On the whole, the study concluded that corrosion resistance was enhanced by adding a surfactant in the electroless Ni P deposits on magnesium alloy

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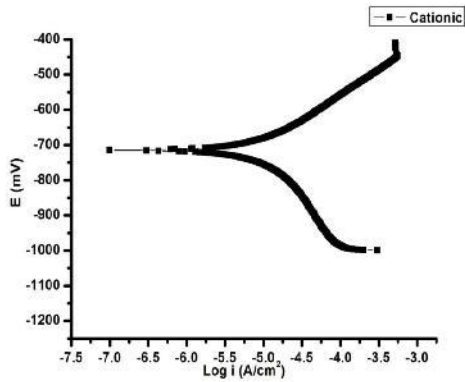


Fig. 2 Potentiodynamic polarization curves for cationic coating

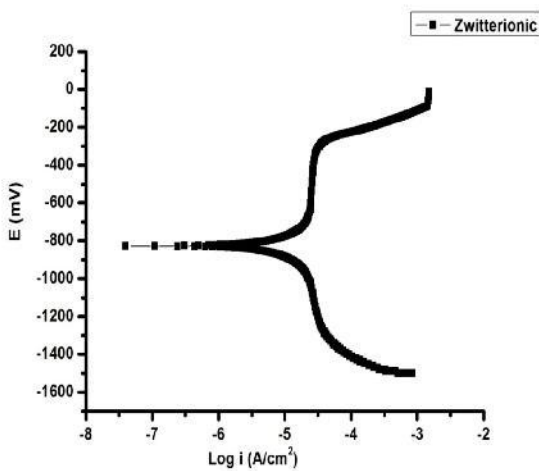


Fig. 3 Potentiodynamic polarization curves for zwitterionic coating

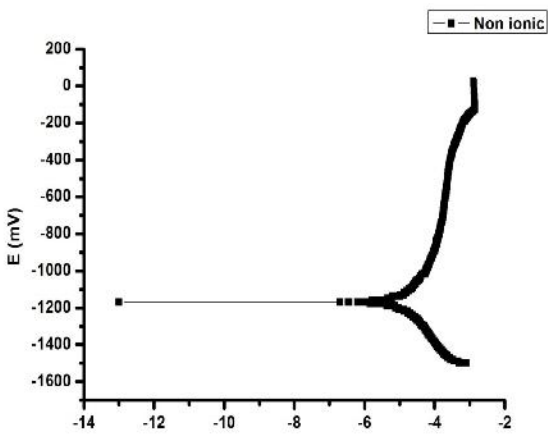


Fig. 4 Potentiodynamic polarization curves for Non ionic coating