

Ni-B Coating Production on Magnesium Alloy by Electroless Deposition

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Abstract—The use of magnesium alloys is limited due to their susceptibility to corrosion although they have many attractive physical and mechanical properties. To increase mechanical and corrosion properties of these alloys, many deposition method and coating types are used. Electroless Ni-B coatings have received considerable interest recently due to its unique properties such as cost-effectiveness, thickness uniformity, good wear resistance, lubricity, good ductility and corrosion resistance, excellent solderability and electrical properties and antibacterial property. In this study, electroless Ni-B coating could be deposited on AZ91 magnesium alloy. The obtained coating exhibited a harder and rougher structure than the substrate.

Keywords—Amorphous, electroless Ni-B, magnesium, X-ray diffraction.

I. INTRODUCTION

MAGNESIUM and its alloys have received great attention because of their superior properties, such as low density, high specific strength/stiffness, excellent dimensional stability and electromagnetic shielding property, superior damping capacity, high creep strength, good machinability, weldability, high impact resistance, high recyclability, as well as thermal and electrical conductivities etc. [1], [2]. Several techniques have been applied in order to improve the surface properties of magnesium alloys. Anodizing is among the promising techniques for surface protection of Mg alloys; however, most existing anodizing processes use toxic chromate, harmful phosphate or/and fluorides. In recent years, electroless plating has attracted attention due to its virtues. Electroless plating refers to the autocatalytic or chemical reduction of aqueous metal ions plated to a base substrate. In the process, a sharp edge receives the same thickness of deposit as a blind hole does [3]-[5]. Electroless nickel is well known for its corrosion resistance and hardness [6]-[11]. The available information on electroless nickel-coating of magnesium alloys is generally about Ni-P, however, on nickel-boron is very limited. This paper reports the work carried out on electroless nickel-boron of AZ91 magnesium alloy, and an attempt has been made to evaluate the influence of the electroless nickel boron on the microhardness and surface roughness of the magnesium alloy.

II. EXPERIMENTAL METHOD

A. Materials

The die-cast Mg alloy AZ91, whose chemical composition is shown in Table I, was prepared as circular discs of 20 mm

diameter and 3 mm thickness. Fig. 1 shows the undeposited magnesium alloy substrates. The surface of the substrates was ground to a roughness value of almost $Ra \approx 0.8 \mu m$ by using SiC emery paper with 1200 mesh grit. Before deposition, they were rinsed in distilled water, supersonic degreasing in acetone and finally dried in air. Then substrates became brighter than in step one because Mg is passive in alkaline media (a mixture of 50 g/L NaOH and 10 g/L Na_3PO_4) for 10 min so that dust, grease... etc. were removed from the surface of magnesium alloy. After alkaline cleaning, gross surface scale or oxides are removed and replaced by preferred oxides to be removing later by acide etching (a mixture of 125 g/L CrO_3 and 110 ml/L HNO_3) for 45 sn. Etching treatments also provide surface pits to act as sites for mechanical interlocking to improve adhesion. Then flouride activation (385 ml/L HF) was applied for 10 min. Removing residual oxides, that created in the above step and replacing it with a thin layer of MgF_2 .

TABLE I
CHEMICAL COMPOSITION OF AZ91 MG ALLOY (WT%)

Al	Zn	Mn	Si	Cu	Fe	K	Mg
9.09	0.88	0.45	0.11	0.00	0.01	0.01	89.45

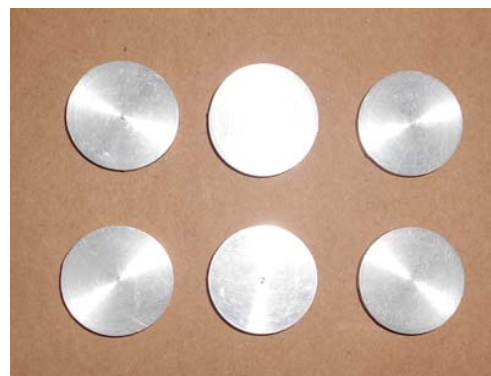


Fig. 1 The Undeposited Magnesium Alloy Substrates

B. Experiment

Table II shows bath composition and operating conditions of the reference bath. The substrates were mounted in this deposition bath and kept at a bath temperature of 95°C for 60 min. Figs. 2 (a) and (b) show the equipment used for electroless Ni-B deposition on AZ91 magnesium alloy substrates. The surface and cross-section morphologies and thickness of the treated coating were observed by scanning electron microscopy (SEM-Jeol 6400).

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TABLE II
BATH COMPOSITION AND DEPOSITION CONDITIONS

Bath composition	g/l
Concentration of NaBH_4	1.2
Concentration of NiCl_2	10
Concentration of ethylenediamine	90
Concentration of sodium hydroxide	90
Concentration of lead nitrate	0.0145
<i>Conditions</i>	
Temperature= 95°C; pH=13.5; Deposition time=60min	

TR-200 Roughness tester was used to characterize the surface roughness. The XRD pattern of the coating was determined by XRD (Rigaku D-Max 2000), and the coating was analyzed with $\text{CuK}\alpha$ ($\lambda = 0.154 \text{ nm}$) radiation with 2θ between 10° and 100° (with a step size of 0.1°). Buehler Micromet 2001 Microhardness tester ($\text{HV}_{0.01}$) was used to determine hardness.

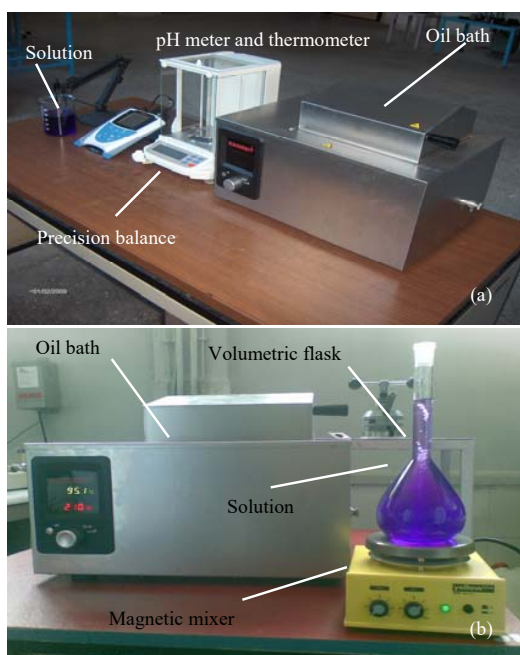


Fig. 2 The equipment for electroless Ni-B deposition

III. RESULTS AND DISCUSSION

A. The Imaging of Etched Substrate

Etching treatments provide surface pits to act as sites for mechanical interlocking to improve adhesion [12]. Therefore, alkaline cleaning, oxides were removed by acid etching using the acids such as CrO_3 , HNO_3 and HF . Fig. 3 shows the optical microscopy image of the etched AZ91 magnesium alloy before electroless deposition.

B. Thickness and Morphology of Electroless Ni-B Coating on the Substrate

Fig. 4 shows the SEM image of cross section view of electroless Ni-B coating which has a thickness of about $6 \mu\text{m}$. The deposited coating was a colonial and uniform structure.

Fig. 5 illustrates that the coating has a cauliflower-like morphology. This result confirms the typical Ni-B coating mentioned in the literature [13]-[15].

Krishnaveni et al. [13], Anik et al. [14], and Dervos et al. [15] reported that a typical cauliflower-like type structure is responsible for the lubricious characteristics of Ni-B films. Almost all researchers have arrived at the same conclusions regarding the effects of these cauliflower-like structures on tribological properties, without making any distinction between them. However, the different resultant structures based on the size, geometry, and distribution of grains and/or nodules comprising the cauliflower-like structures can provide different coating properties [16].

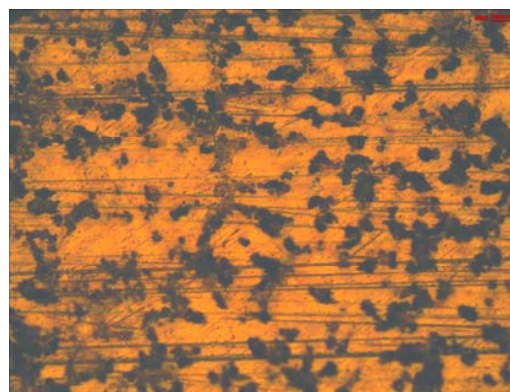


Fig. 3 The optical microscopy image of the etched AZ91 magnesium alloy

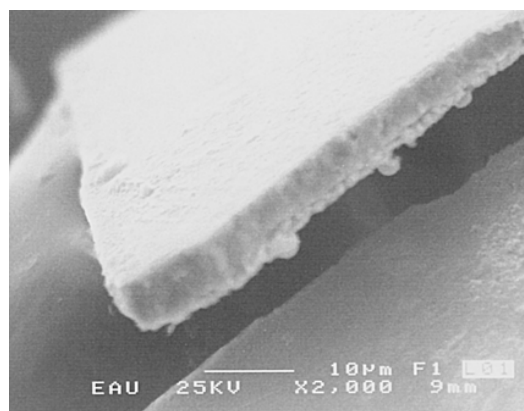


Fig. 4 Cross-sectional SEM image of electroless Ni-B coating

C. The Surface Roughness of Substrate and Coating

The average surface roughness level of the magnesium alloy substrate was $R_a \approx 0.8 \mu\text{m}$. After deposition, the average surface roughness of the electroless Ni-B coating deposited on the substrate was $R_a \approx 1.95 \mu\text{m}$. Surface roughness plays an important role in determining the surface finish of electroless Ni-B coated magnesium alloy substrate. The surface roughness characteristics of the coated substrate dependent on many factors such as bath temperature, pH of coating bath, concentration of reducing agent, plating time, etc. Roughness is sometimes an undesirable property, as it may cause friction,

wear, drag, and fatigue, but it is sometimes beneficial, as it allows surfaces to trap lubricants and prevents them from welding together [17].

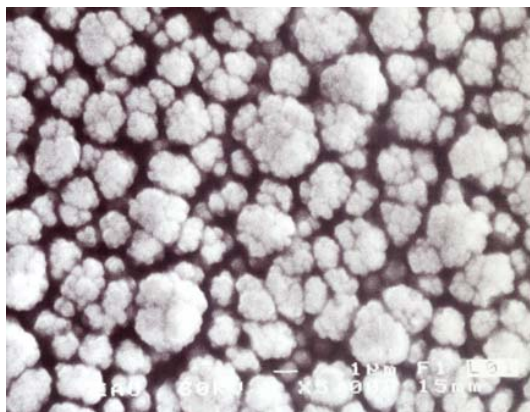


Fig. 5 Cross-sectional SEM image of electroless Ni-B coating having a cauliflower-like morphology

D. The XRD Study of Substrate and Coating

In the coated substrate (Fig. 6), a tendency to broadening between $2\theta=40$ to 50 diffraction angles was found with the development of the Ni_xB_y phases resulting from the electroless Ni-B deposition process. Furthermore, there was a decrease in the intensities of the magnesium alloy-based crystalline phases that came from the substrate. The X-ray diffraction pattern of the electroless Ni-B coating exhibits a broad peak indicative of the amorphous nature of the coating. We found that crystalline stoichiometric nickel boron compounds do not occur in electroless Ni-B coatings if heat treatment is not applied.

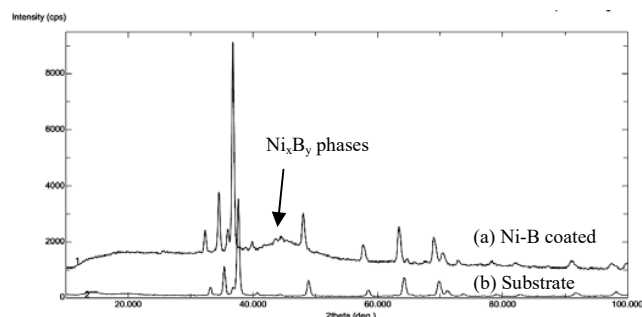


Fig. 6 X-ray diffraction spectra and surface morphologies of (a) the electroless Ni-B coated and (b) the uncoated magnesium alloy specimens

E. The Microhardness of Substrate and Coating

The microhardness value of electroless Ni-B coating was 500 ± 10 HV while the microhardness of magnesium alloy substrate is about 140 HV. Thus the electroless Ni-B coating caused to about a 3.5 fold increase in the hardness (Fig. 7).

The existence of boron in the interstitial solid solution is responsible for the hardness of the coating. In interstitial solid solutions, solute atoms cause a tetragonal distortion. Here, interstitial boron atoms with an atomic radius of less than one angstrom are likely to form interstitial solid solutions. These

atoms occupy an interstitial position among nickel atoms, and thus enhance the microhardness of the coating. We concluded that boron contributes significantly to the hardness of the substrate by interstitial solid solution, since it promotes the formation of a Ni_xB_y amorphous coating [18]. If the heat treatment is applied on the electroless Ni-B coating, the higher hardness values than that of the amorphous condition will be obtained owing to the formation of crystalline nickel boron phases such as Ni_2B and Ni_3B [13], [19].

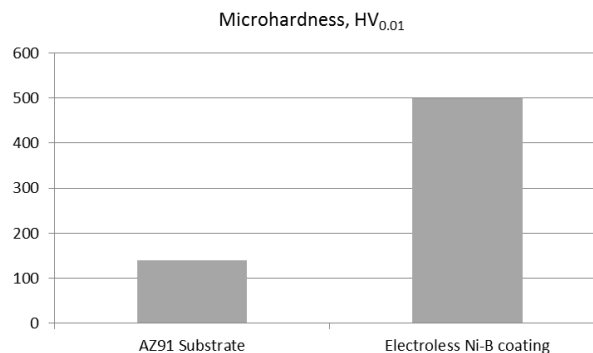


Fig. 7 Variation in microhardness after the electroless Ni-B deposition on the AZ91 magnesium alloy substrate

IV. CONCLUSION

The electroless deposition process of present study on AZ91 magnesium alloy substrate has produced a Ni-B coating, with a thickness of about 6 μm . A high degree of average surface roughness (from 0.8 μm to 1.95 μm) was revealed after electroless Ni-B deposition on the substrate. The amorphous electroless Ni-B coating determined by XRD analysis as found from a broad peak between $2\theta=40$ to 50° diffraction angles possesses a cauliflower-like morphology consisting of globular grains. It is found that crystalline stoichiometric nickel boron compounds do not occur in electroless Ni-B coatings if heat treatment is not applied. A 3.5-fold increase in the hardness can be attributed to the boron, which exhibits a significant strengthening effect in the amorphous Ni-B lattice.

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