

# Effect of Al<sub>2</sub>O<sub>3</sub> and WO<sub>3</sub> Ceramic Additives on the Surface Morphology and Mechanical Properties of Electroless Nickel-Boron Composite Coatings Fabricated on AZ31 Magnesium Alloy

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## Abstract

In the present study, synthesis and a comparison of properties (structural and mechanical) of Ni-B and Ni-B-Al<sub>2</sub>O<sub>3</sub> and Ni-B-WO<sub>3</sub> composite coatings have been presented to elucidate the beneficial role of Al<sub>2</sub>O<sub>3</sub> or WO<sub>3</sub> addition in binary Ni-B coatings. The Ni-B-Al<sub>2</sub>O<sub>3</sub> and Ni-B-WO<sub>3</sub> coatings were synthesized by adding Al<sub>2</sub>O<sub>3</sub> or NaWO<sub>3</sub> powdered particles into the above mentioned Ni-B coating solution. A significant improvement in mechanical properties has been observed by the addition of Al<sub>2</sub>O<sub>3</sub> or WO<sub>3</sub> additions. This novel composite coating composition will be useful for wear and corrosion applications.

DOI: 10.7176/CMR/11-8-05

Publication date: October 31<sup>st</sup> 2019

## 1. Introduction

Magnesium and its alloys are more and more applied in different sectors, including aircraft, motor vehicle as well as metallurgical, chemical and electrical industries. As a light metal having a density of 1.74 g/cm<sup>3</sup>, it is 35% lighter than aluminum (2.7 g/cm<sup>3</sup>) and over four times lighter than steel (7.86 g/cm<sup>3</sup>). Today's interest in magnesium alloys for automotive applications is based on a combination of high strength properties and low density. Magnesium alloys are very attractive as structural materials mostly in applications where weight saving is of great concern. Mg-Al alloy is the most common category of magnesium alloys. Aluminum has a strong passivation tendency in presence of oxygen and results in the precipitation of  $\beta$  phase, which is highly cathodic with respect to the matrix [1,2].

Ni-B coatings have gained a great deal of attraction due to their promising mechanical properties. Owing to tempting properties, Ni-B coatings have succeeded to find their applications in automotive, aerospace, petrochemical, plastic, optics, nuclear, electronics, computer, textile, paper, food and printing industries [3-9].

In the study of Shakoor, et al [10], novel Ni-B-Al<sub>2</sub>O<sub>3</sub> composite coatings have been synthesized through electrodeposition process by reinforcing Ni-B matrix with Al<sub>2</sub>O<sub>3</sub> particles. A comparison of properties of Ni-B and Ni-B-Al<sub>2</sub>O<sub>3</sub> coatings in their as deposited states was presented to elucidate the beneficial role of Al<sub>2</sub>O<sub>3</sub> addition. The nanoindentation results demonstrates that the addition of Al<sub>2</sub>O<sub>3</sub> into Ni-B matrix results in significant improvement in mechanical properties (hardness and modulus of elasticity) which may be attributed to dispersion hardening of Ni-B matrix by hard Al<sub>2</sub>O<sub>3</sub> particles.

Lakeavat, et al. [11] investigated the Effect of surfactant and the effect of Nano-additives Al<sub>2</sub>O<sub>3</sub>, ZnO, and SiO with different quantities on the performance of Ni/P coating on AZ91 Mg alloy. 0.5 g/l Nano Al<sub>2</sub>O<sub>3</sub> additive enhanced the deposition of Ni-P on AZ91 magnesium composite and the same results have been observed in case of SiO addition. Influence of ZnO was also observed. So is very clear that Ni-P coating is very effective to reduce the corrosion and increase the wear behaviour if it is used along with Nano additive and the surfactants.

The work of Subramanian and Palaniradja [12] aimed to study the hardness and wear resistance of electroless Ni-B coatings. An alkaline bath having nickel chloride as the source of nickel and borohydride as the reducing agent was used to prepare the electroless Ni-B coatings. The microhardness of the electroless Ni-B coatings increases with increase in heat-treatment temperature and exhibit two maxima in the hardness vs. heat treatment temperature curve. The specific wear rate increases with increase in applied load from 20 to 40 N and at all applied loads, the specific wear rate and coefficient of friction are less for heat-treated electroless Ni-B deposits compared to that obtained for as-plated ones. The wear process of electroless Ni-B coatings is governed by an adhesive wear mechanism.

Ozcelik, et al [13] proposed a new electroless Ni-B coating in which nano size diamond particles (UDD-Ultra dispersive diamond) are added to after doing Ni-B coating to improve hardness and wear resistance properties of the coating. Microhardness of the coating greatly increased because of the presence of the nanoparticles. The hardest electroless composite coating (1250 HV100) is 30 times more resistant to wear than steel material, 14 times than electroless Ni-B coatings.

Taşçı, et al [14] applied electroless Ni-P-W, Ni-P-W / Al<sub>2</sub>O<sub>3</sub> composite coatings on the hot-rolled, strip casted AZ91(9 Al, 1 Zn) magnesium plates and investigated the effect of applied coating on the corrosion resistance.

Ni-P-W coatings with different tungsten content were obtained by adding the various amounts of NaWO<sub>4</sub> to the coating bath. Composite coatings were also obtained by adding 2 gr/lit of Al<sub>2</sub>O<sub>3</sub> to selected NaWO<sub>4</sub> containing baths. Tungsten is highly corrosion resistant material. Co-deposition of W up to a certain amount (Wt. %5) does not have a negative effect on amorphous characteristic of electroless coatings. Above this level corrosion resistance is starting to decrease due to crystalline structure and possible galvanic interaction on newly emerged grain boundaries.

Despite the promising properties of Ni-B coatings, further improvement in their mechanical properties is essential so that more applications can be successfully addressed. The present paper investigates the Effect of Al<sub>2</sub>O<sub>3</sub> and WO<sub>3</sub> Ceramic Additives on the Mechanical Properties of Electroless Nickel Composite Coatings

## 2. Experimental

The experimental work was preceded as follows:

- The surface of the substrates was successively ground using SiC emery paper up to 1200 mesh grit. Samples were rinsed in distilled water, supersonic degreasing in acetone and finally dried in air.
- Substrates were immersed in alkaline media (a mixture of 50 g/l NaOH and 10 g/l Na<sub>3</sub>PO<sub>4</sub>) for 10 min so that dust, grease etc. were removed from the surface of magnesium.
- Samples were pre activated by immersion in 50% H<sub>3</sub>PO<sub>4</sub> for 1 min followed by immersion in 40% HF for 15 min to remove residual oxides and applying a thin layer of MgF<sub>2</sub>.
- The substrates were mounted in this deposition bath and kept at fixed temperature for reasonable time. The bath composition and operation conditions are shown in Table (1).

**Table (1): Bath Composition and Deposition Conditions**

Bath composition	Concentration , g/l
Sodium borohydride (NaBH <sub>4</sub> )	6
Nickel chloride (NiCl <sub>2</sub> )	10
Ethylenediamine	90
Sodium hydroxide	90
Stannous Chloride	0.0145
Conditions: Temperature= 85 °C; Deposition time = 2 h	

Different contents of Al<sub>2</sub>O<sub>3</sub> (0.25, 0.5, 1 & 2g/L) and Na<sub>2</sub>WO<sub>4</sub> (0.125, 0.25, 0.5 & 0.75 g/L) were added to aforementioned plating bath to address the effect of ceramic particles Al<sub>2</sub>O<sub>3</sub> or Na<sub>2</sub>WO<sub>3</sub> on the performance of the Ni-B-composite coatings. Based on the weight gain of the coating and the total area of the AZ31Mg alloy samples, the thickness of the formed coatings were calculated using the following equation:

$$T = W / D * A$$

Where T is the thickness in mm; W is the weight gain in g; D is the density of Ni (8.908 g/cm<sup>3</sup>); A is the area in mm<sup>2</sup>.

The surface morphologies of the coated sample were observed with field emission scanning electron microscopy (FESEM).

Wear tests were performed using the abrasion rate measurements. Tests were carried out using (IKA RW 20 digital) rotator. Samples were rotated in 0.2 M NaCl solution. The rotation speed was kept constant at 400 rpm and the abrasion effect was measured in terms of weight loss expressed in milligrams.

## 3. Results and Discussion

Tables 2&3 show thickness measurements of Ni-B- Na<sub>2</sub>WO<sub>4</sub> and Ni-B-Al<sub>2</sub>O<sub>3</sub> composite coatings formed on AZ31 Mg alloy samples. The highest thickness of Ni-B- Na<sub>2</sub>WO<sub>4</sub> composite coatings was obtained in the presence of 0.125 g Na<sub>2</sub>WO<sub>4</sub> while highest thickness of Ni-B- Al<sub>2</sub>O<sub>3</sub> composite coatings was obtained in the presence of 1.0 g Al<sub>2</sub>O<sub>3</sub>.

**Table (2): Effect of Na<sub>2</sub>WO<sub>4</sub> concentrations on the thickness of formed coating 8 g/L NaBH<sub>4</sub> and 85°C and 2 h**

Na <sub>2</sub> WO <sub>4</sub> /g	Wt gain / g	Area / cm <sup>2</sup>	Thickness /mm
0.125	0.0022	3.70	0.0667
0.25	0.0015	3.42	0.0492
0.50	0.0014	3.80	0.0414
0.75	0.0004	3.23	0.0139

**Table (3): Effect of Al<sub>2</sub>O<sub>3</sub> concentrations on the thickness of formed coating 8 g/L NaBH<sub>4</sub> and 85°C and 1 h**

Al <sub>2</sub> O <sub>3</sub> /g	Wt gain / g	Area / cm <sup>2</sup>	Thickness /mm
0.25	0.0013	3.60	0.0405
0.5	0.0018	3.51	0.0577
1.0	0.0021	3.7	0.0637
2.0	0.0011	3.49	0.0354

Figure 1 shows the SEM images of Ni-B-Na<sub>2</sub>WO<sub>4</sub> composite coating. Fine tungstate particles are shown impeded in the Ni-B matrix.

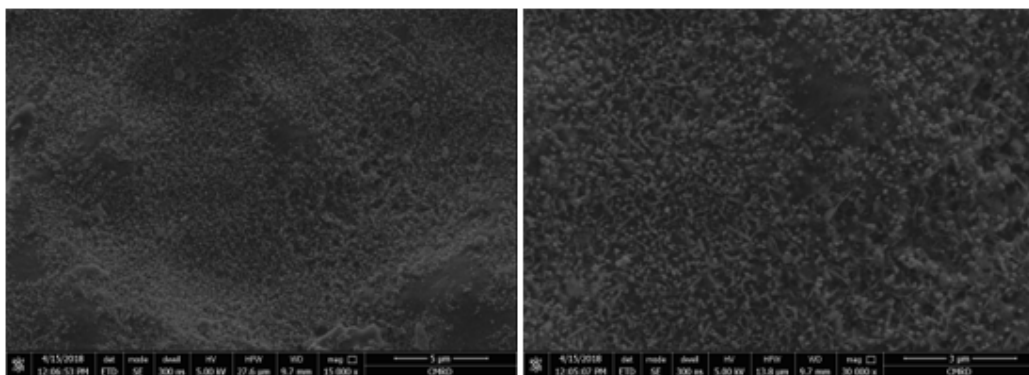


Figure 1: SEM images of Ni-B-W electroless composite coating AZ31 Mg alloy in the presence of 8 g/L NaBH<sub>4</sub> and 0.125 g/L Na<sub>2</sub>WO<sub>4</sub> at 85°C and 1 h

Tables 4&5 show the results of abrasion resistance measurements. The Ni-B- Al<sub>2</sub>O<sub>3</sub> and Ni-B- WO<sub>3</sub> composite coatings show higher abrasion resistance than the Ni-B coating. The incorporation of either alumina or tungstate molecules in the Ni-B coating significantly improves the abrasion resistance of the AZ31 Mg alloy. The highest resistance, i.e. the lowest weight loss, was shown by the composite coatings formed in the presence of either 1 g/l Al<sub>2</sub>O<sub>3</sub> or 0.25 g/L Na<sub>2</sub>WO<sub>3</sub>. It is worthy to note that high concentrations of Na<sub>2</sub>WO<sub>3</sub> deteriorate the wear resistance of the alloy which is not the case of Al<sub>2</sub>O<sub>3</sub> where the wear resistance increases with the increase of Al<sub>2</sub>O<sub>3</sub> content.

Table (4): Effect of Na<sub>2</sub>WO<sub>4</sub> on the abrasion resistance of Ni-B composite coatings

Na <sub>2</sub> WO <sub>3</sub> g/L	Wt Loss g	Area cm <sup>2</sup>	Wt Loss g cm <sup>-2</sup>
0.00	0.0051	3.52	0.0015
0.125	0.0040	2.60	0.0015
0.25	0.0027	2.55	0.0011
0.50	0.0045	3.25	0.0014
0.75	0.0042	2.88	0.0015

Table (5): Effect of Al<sub>2</sub>O<sub>3</sub> on the abrasion resistance of Ni-B composite coatings

Al <sub>2</sub> O <sub>3</sub> g/L	Wt Loss g	Area cm <sup>2</sup>	Wt Loss g cm <sup>-2</sup>
0.00	0.0051	3.52	0.0015
0.25	0.0039	3.04	0.0013
0.50	0.0068	4.80	0.0014
1.0	0.0071	6.48	0.0011
2.0	0.0048	3.91	0.0012

The enhancement in the mechanical properties of composite coatings can be explained by the Orowan

dispersion strengthening mechanism [15]. The presence of hard particles hinders the movement of the dislocations and dislocation pinning effect results in the strengthening effects of the particle dispersion come from the effect. The critical condition for a dislocation to bypass the particles in its moving way is to bend itself to a semi-circle between the particles. The dislocation then moves forward and leaves a dislocation loop behind. Therefore, incorporation of insoluble particles can result in dislocation pinning effect and thus enhancement of strength and hardness. This tremendous improvement in hardness can be regarded as the strong dispersion hardening effect of  $\text{Al}_2\text{O}_3$  or  $\text{Na}_2\text{WO}_4$  particles distributed into the Ni-B matrix.

#### 4. Conclusions

- The Ni-B-  $\text{Al}_2\text{O}_3$  and Ni-B-  $\text{WO}_3$  composite coatings show higher abrasion resistance than the Ni-B coating. The incorporation of either alumina or tungstate molecules in the Ni-B coating significantly improves the abrasion resistance of the AZ31 Mg alloy.
- The improvement in hardness can be regarded as the strong dispersion hardening effect of  $\text{Al}_2\text{O}_3$  or  $\text{Na}_2\text{WO}_4$  particles distributed into the Ni-B matrix.

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