EFFECT OF PARTICLES CONCENTRATION AND CURRENT DENSITY ON THE COBALT/HEXAGONAL BORON NITRIDE NANO-COMPOSITE COATINGS PROPERTIES

Z. Shahri and S.R. Allahkaram*
* *akaram@ut.ac.ir*
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Department of Metallurgy and Materials Engineering, Faculty of Engineering, University of Tehran, Tehran, Iran.

Abstract: *Metal matrix composite coatings reinforced with nano-particles have attracted scientific and technological interest due to the enhanced properties exhibited by these coatings. Cobalt/hexagonal boron nitride nano-composite coatings were prepared by means of the pulse current electroplating from a chloride electrolyte on copper substrates and a comparison was made with the pure cobalt in terms of structure and tribological properties. Effects of particles concentration (5-20 gL^{-1}) and current density (50-200 $mA\ cm^{-2}$) on the characterization of electroplated coatings were investigated via X-ray diffraction analysis, energy dispersive spectroscopy and Vickers micro-hardness. Moreover, the tribological behavior was studied using pin-on-disc method. The results showed that cobalt/hexagonal boron nitride nano-composite coatings have higher hardness, wear resistance and lower friction coefficient than pure cobalt and the plating parameters strongly affect the coating's properties.*

Keywords: *Composite, Cobalt, Hexagonal, Electroplating, Tribological.*

1. INTRODUCTION

Pulse electroplating is an electrochemical processing for producing dense, uniform, and adherent coatings, usually by co-depositing of fine particles (micro or nano) in to the metal or alloys matrix using the act of pulsed electric current [1-3]. The incorporation of inert particles (such as SiC, TiC, ZrO_2, MoS_2, PTFE, graphite) during metal electroplating has been carried out in order to improve micro-hardness, wear and corrosion resistance, friction coefficient and the other properties [4-7]. These properties depend on many process parameters including bath composition, temperature, current density, duty cycle, frequency and many variations [5-6]. It has been reported that controlling the electroplating parameters is necessary for obtaining composite coatings with high quality [7]. For example, the effect of solid lubricant concentration such as MoS_2 and graphite on the tribological properties of Ni and Cu matrix composite coatings has been studied [1-2]. The results show that the properties such as micro-hardness and wear resistance are influenced by the amount of incorporated particles. And it has been concluded that there is a solid lubricant concentration regime where co-deposition of particles into matrix enhances the frictional properties of the coating with a consistently lower friction coefficient.

Boron nitride particle with hexagonal close packed structure is a solid lubricant that compares favorably with the performance of other solid lubricants such as graphite and molybdenum disulfide [8]. In the hexagonal boron nitride structure, the bonding among the molecules within each layer is covalent and the bonding between layers is determined by weak van der Waals forces that can easily slide against each other, leading to a low friction coefficient [9, 10]. This solid lubricant has also found many applications for its high thermal conductivity and chemical stability [8-10]. However, it is only a few papers related to the incorporation of hexagonal boron nitride particles into metal matrices [8, 11]. Therefore, the use of hexagonal boron nitride particles appears attractive for cobalt matrix reinforcements.

Accordingly, in the present work, cobalt/hexagonal boron nitride nano-composites and pure Co were produced by using the electroplating technique. The effect of average current density and particles concentration in the solution on the coatings' properties as well as its comparison with pure C_o was considered.

2. EXPERIMENTAL PROCEDURES

Cobalt/hexagonal boron nitride nano-composite coatings used in this study were deposited on copper substrates from a chloride solution containing hexagonal boron nitride particles with a mean diameter of 70 nm. The detailed bath composition is given in Table 1. Copper and pure cobalt plates (30 mm × 30 mm) were used as the cathode and anode, respectively with distance of 3.5 cm. The copper substrates were ground, degreased in Uniclean 675 solution and chemically cleaned in acetone and distilled water for 4 min. Then they were activated in chloride acid for 30 s. Prior to the electroplating process, the electrolyte was under ultrasonic waves for 30 min, and during the process it was in suspension in an agitating bath solution with the use of a 300 rpm magnetic stirrer placed at the cell bottom. During electroplating, the temperature of plating solutions was maintained at 45°C and the initial pH of the electrolyte was adjusted to a constant value of 3. In pulse deposition experiments the particles concentration and current density of the imposed rectangular pulses were varied in the range of 5-20 g L^{-1} and 50-200 mA cm^{-2}. The deposition time was 2 h. The particles content and crystal size of matrix were evaluated by energy dispersive spectroscope (EDS) and X-ray diffractometer (XRD) technique. The crystal size measurements were obtained from the angular width of main peaks in XRD diffractions at full width half maximum (FWHM) in conjunction with Scherrer's equation (1),

$$D = \frac{0.9\lambda}{B \times Cos\theta} \tag{1}$$

where B is full width half maximum in 2θ degrees, D is the crystallite size in nm and λ is the wavelength of Cu Kα radiation (1.54056 A°) [12]. The micro-hardness was determined using a Vickers indenter on the samples cross section at an applied load of 1 N for 10 s. Pin-on-disc tests (non-conformal contact) with the speed and normal load of 0.1 m s^{-1} and 2 N, respectively, via a 5 mm diameter AISI 52100 ball indenter (60-67 RC) were carried out to determine the wear resistance and friction coefficient of as-plated coatings.

3. RESULTS AND DISCUSSION

3. 1. Effect of Current Density

The effect of pulse current density (from 50 to 200 mA cm^{-2}) on crystal size of composite coatings, which were produced at a constant frequency and duty cycle of 50 Hz and 10% with different current density, is shown in Fig. 1. By increasing the current density from 50 mA cm^{-2} to 100 mA cm^{-2}, the crystallinity size of coatings decreases (from 19 to 15 nm), but further increase in current density up to 200 mA cm^{-2} has an inverse effect on the crystal size (27 nm). In general, it is expected that the crystal sizes of deposits decrease by increasing the current density, because an increase in the current density eventuated in a higher overpotential that alleviates the nucleus process energy and hence increases the nucleation rate [13-15]. However, several authors [7, 16] have reported an increase of deposit's crystal size with increasing the current density. This outcome has been attributed to the co-deposition of hydrogen at the cathode-electrolyte interface and a decrease of the deposition efficiency. In fact, the changes in the surface energy and growth mechanisms in the presence of hydrogen are responsible for the increased crystallite size of deposits by increasing current density.

The particles content (wt%) and micro-hardness of coatings were also investigated, Fig. 2. It is obvious that the incorporation behavior initially shows a rapid increase in co-deposition

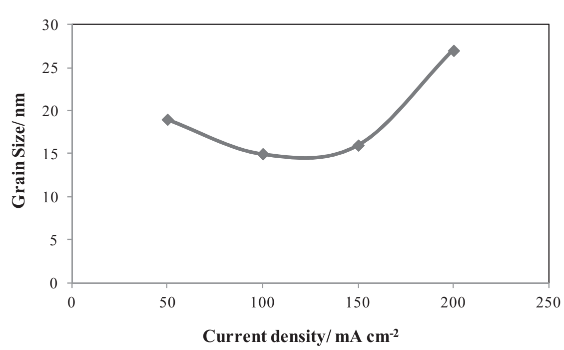

Fig. 1. Effect of current density on the grain size of the coatings.

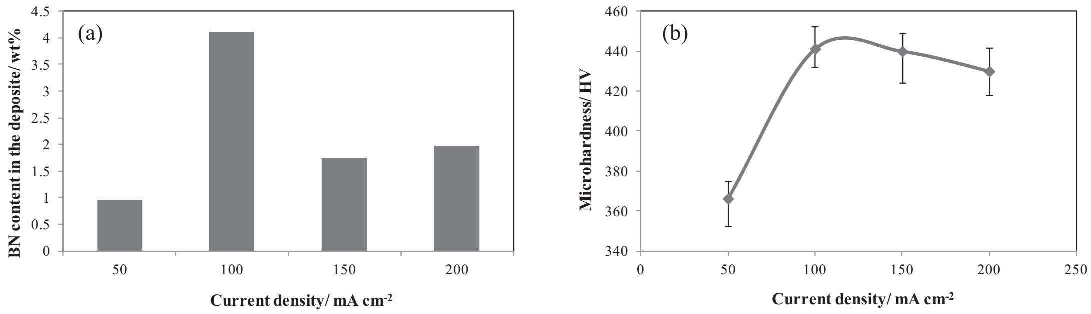

Fig. 2. Effect of current density on (a) the particles content and (b) micro-hardness.

due to the increasing tendency for adsorbed particles to achieve the cathode surface [17]. In fact, at low current densities, there is a weaker electric force amongst the particles and surface, which leads to a lower fraction of the particles in the coatings [18]. Then by increasing pulse current density (from 100 mA cm^{-2} to 150 mA cm^{-2}) and thereby a faster deposition of metal matrix ions, the content of incorporated particles decreases [17]. In addition, the decrease in hexagonal boron nitride particles content at this higher current density can be ascribed to the electrochemical potential, which affects the adsorption of particles on the cathodic surface [19]. Further increase in current density up to 200 mA cm^{-2} results in a marginal increase in the electrodeposited particle content as a consequence of decreased cobalt deposition due to the cobalt's depletion near the surface [14]. It is evident from the Vickers micro-hardness values that at the initial part (in the range of 50-100 mA cm^{-2}), a tendency of increasing hardness are appearing as the particles incorporation increased (from 366.12 to 441.26 HV). However, beyond this current density, the micro-hardness begins to decline. As expected, the micro-hardness of composite coatings decreases due to the lower incorporation of the hexagonal boron nitride particles in the cobalt film. Finally, in this section, it can be deduced that particles incorporation and micro-hardness are favored at a current density of 100 mA cm^{-2}.

Fig. 3 displays changes in friction coefficients and weight loss of as-plated coatings subjected to dry sliding wear test as a function of current density. It can be found that the average friction coefficient drops (from 0.75 to 0.34) with an increased current density up to a 100 mA cm^{-2}, due to the increased particles content. It implies that an increase in the content of hexagonal boron nitride particles in the deposit, as a lubricant, greatly enhance the lubricating properties of the composite coating in accordance with the literature [8, 10].

On the other hand, wear resistance is another significant parameter governing the industrial application of surface coatings [20]. With Regards to the wear resistance (characterized by measuring the weight loss), it can be seen that the weight loss of coatings is dependence on micro-hardness measurements that indicates higher weight loss (3 mg) at lower hardness (366.12 HV) in accordance with Archard equation (2),

$$v = \frac{kWx}{H} \tag{2}$$

Where ν is volume wear, x sliding distance, k non-dimensional wear coefficient, W normal load

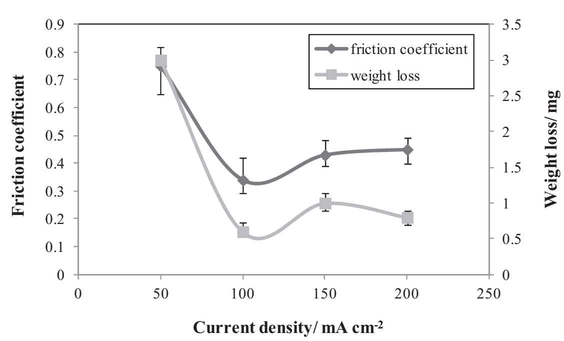

Fig. 3. Effect of current density on the tribological behavior.

and H is the hardness of the surface being worn away [21]. This equation shows an inverse relation between the wear rate and hardness of the coatings.

3. 2. Effect of Particles Concentration

Fig. 4 shows the crystal size of pure cobalt and cobalt/hexagonal boron nitride nano-composite coatings at different particles concentration (5-20 gL^{-1}). By comparing the crystal size of pure cobalt and cobalt composite coatings, it is understood that co-deposited hexagonal boron nitride particles apparently increase the deposition overpotential and retard the growth of the cobalt grains [22], which leads to a smaller grain size of approximately 15 nm. However, an increase in particles concentration from 5 to 20 gL^{-1} in the solution does not significantly affect the grain size of the metal matrix.

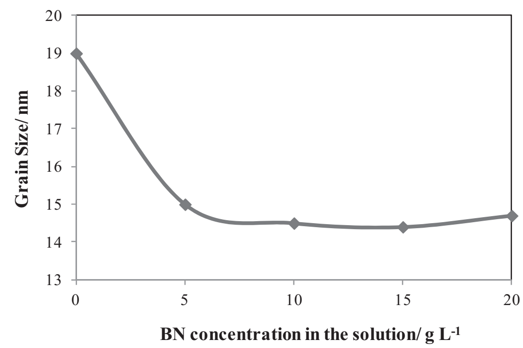

Fig. 4. Effect of particles concentration on the grain size of coatings.

The effect of particles concentration (5-20 gL^{-1}) in the solution on the particles content and micro-hardness of deposits is shown in Fig. 5. These coatings were produced under pulse plating conditions with constant current density, duty cycle and frequency of 100 mA cm^{-2}, 10% and 50 Hz, respectively. Fig. 5 shows that the amount of hexagonal boron nitride particles in the solution has significant effect on the weight percentage of the particles incorporated into the metal deposit. The particles content in the coating increases from 4.12 to approximately 5.17 wt% with the increase in the concentration of hexagonal boron nitride from 5 up to 20 gL^{-1} in the coating bath. Increment in the incorporated particles can be attributed to the increasing of the flux of particles adjacent to the electrode surface. Actually, increasing hexagonal boron nitride particles concentration in the solution creates higher particle density (particles per liter), and produces more opportunities for particles adsorption onto the electrode [23]. On the other hand, it is evident that the particles content in the coating increases with decreasing rate until a saturation state has been reached at high particle bath concentrations. This behavior is attributed to particles adsorption at the electrode surface according to the Langmuir adsorption isotherm [23]. The micro-hardness of the coatings is also shown in Fig. 5. As can be seen the incorporation of hexagonal boron nitride particles into cobalt coating causes increase in micro-hardness. Micro-hardness values of the composite coatings are relatively higher as compared to that of pure cobalt coating. The mean value of Vickers micro-hardness of the pure cobalt coating has been found at about 308 HV, while the hardness for that of composite coatings is in the

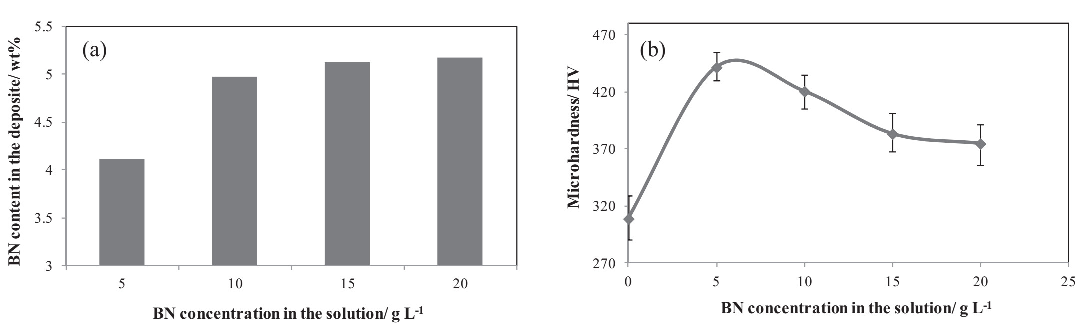

Fig. 5. Effect of BN concentration on (a) the particles content and (b) micro-hardness.

range of 375-441 HV. Furthermore, it is observed that the micro-hardness of composite coatings decreases with increasing of particles content in the coatings. Higher micro-hardness of composite coatings as compared with pure cobalt can be attributed to the combination of the grain refinement and dispersion strengthening effects of the nano-particles. The nano-particles in the composite coatings block the dislocations motion and the grain boundaries sliding of the matrix. This leads to the dislocation's pile up and consequently to an increase in stress concentration and hardness [22, 24-26]. In addition, as it was previously explained, incorporation of hexagonal boron nitride particles in the cobalt matrix causes a decrease in the crystal size of metal matrix and accordingly increases its micro-hardness. Moreover, it should be noted that the effect of particles content on the micro-hardness of composite coatings depends not only on the amount of the particles, but also on the size and distribution of the particles incorporated in the metal matrix [27]. Hence, the agglomeration of hexagonal boron nitride particles is considered as a possible reason for the reduction in micro-hardness at higher concentrations [28-29].

In Fig. 6, friction coefficient values and wear resistance are reported as a function of particles concentration. It is evident that the friction coefficients of composite coatings (0.34-0.55) are nearly two times lower than pure cobalt (0.89). Due to the hexagonal structure of particles, the slippage can be easily produced among the layers of hexagonal boron nitride. These particles adhere to the wear surfaces and a layer of solid self-lubricating film comes into being on the wear surfaces [26-30]. Finally, the contacts between metal-metal would be changed into the contacts between boron nitride film-metal or boron nitride film -boron nitride film, which indicates that the layered lattice structure of BN (h) provides good lubricating properties, as shown previously in the literature [11]. As this figure shows, incorporation of hexagonal boron nitride particles into the pure cobalt coating leads to an increase in its wear resistance of composite coatings. It is obvious that the weight loss of all composite coatings (0.6-1.09 mg) is always lower than that of the cobalt coating (1.35 mg). The fact that the cobalt/hexagonal boron nitride nano-composite coatings have a higher wear resistance can be attributed to the enhancement of hardness by presence of ceramic particles in the matrix of nano-crystalline cobalt, which in turn hampers plastic deformation at the surface [11, 31]. However, as the weight percentage of particles increases, the wear resistance decreases. This can be ascribed to: 1. the agglomerated particles which are loosely bound to cobalt matrix that could be easily removed from the matrix [32] or/and 2. the hardness measurements that indicate lower micro-hardness for composite coatings with higher particles content [30].

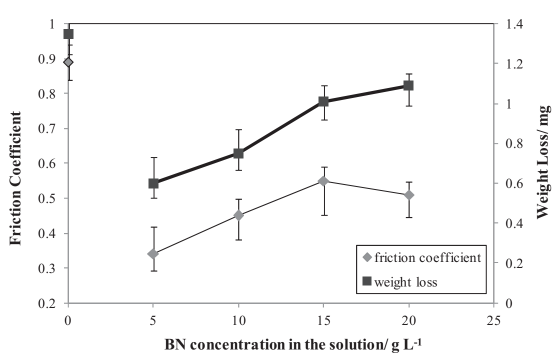

Fig. 6. Effect of particles concentration on the tribological behavior.

4. CONCLUSION

In this study, the application of cobalt/hexagonal boron nitride nano-composite coatings and pure cobalt, as a comparison, was conducted by electrodeposition. The effect of pulse plating conditions such as particles concentration (5-20 gL^{-1}) and current density (50-200 mA cm^{-2}) on properties of composite coatings was investigated. Compared with pure cobalt, the cobalt/hexagonal boron nitride nano-composite coatings have lower friction coefficient and higher micro-hardness and wear resistance in optimum particles concentration (5 gL^{-1}). Moreover, it has been shown that the change in the amount of co-deposited hexagonal boron nitride and current density results in changing properties of the film.

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