

Structural Characterization and Mechanical Properties of As-plated and Heat Treated Electroless Ni-B-P Alloy Coatings

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Abstract— The Ni-B-P alloy coatings were made autocatalytically (electroless) using an alkaline plating bath with nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) as the source of nickel ions, sodium borohydride (NaBH_4) and sodium hypophosphite (NaH_2PO_2) as reducing agents and source of boron and phosphorous ions, respectively. The effects of bath concentrations on the plating rate, composition of coating, surface morphology, structural features and microhardness have been studied by varying NaBH_4 concentration in the plating bath from 0.2 to 0.8 g/l while keeping NaH_2PO_2 concentration constant (12 g/l). The plating rate and boron content of the electroless Ni-B-P ternary alloy coatings increased with increasing NaBH_4 concentration in the plating bath. The scanning electron microscopic images revealed that the morphology of the coating changed from corn cob structure to coarse cauliflower structure with increasing borohydride concentration in the plating bath. Broadening of X-ray diffraction peak is observed, as the borohydride concentration is increased in the plating bath, which is attributed to the large reduction in the crystallite size of the Ni-B-P alloy coatings. The microhardness values of the coating increased with increasing borohydride concentration in the plating bath. The as-plated Ni-B-P alloy coating containing higher boron content (3.2 wt%) shows higher hardness of 700 HV compared to other Ni-B-P alloy coatings. The XRD patterns of heat treated Ni-B-P alloy coatings (500 °C) show Ni_3B intermetallic peaks along with Ni peaks. The presence of Ni_3B intermetallic compound significantly increases the microhardness values of the heat treated Ni-B-P alloy coatings.

Keyword- Electroless plating, Ni-B-P alloy coatings, Plating rate, Surface morphology, Microhardness

I. INTRODUCTION

Electroless plating technique provides unique physicochemical and mechanical properties to the electroless coatings such as uniformity in the coating, excellent corrosion resistance, solderability, high reflectivity, high hardness, high wear and abrasion resistance [1]. Among the various types of electroless plating, the electroless nickel has gained immense popularity due to its ability to provide a hard, wear and corrosion resistant surface [1]–[3]. Electroless nickel plating processes are grouped as Ni–P, Ni–B and pure Ni based on the reducing agents used, i.e., hypophosphite, borohydride or dimethylamine borane and hydrazine, respectively in the plating bath. The autocatalytic deposition of pure nickel using hydrazine as reducing agent is known for many years and has got some industrial applications also. Hypophosphite reduced electroless nickel plating has received commercial success because of its low cost, ease of control, and ability to offer good corrosion and wear resistance surface. Though, the hypophosphite-reduced electroless nickel plating has received widespread acceptance, the attention has now shifted towards borohydride reduced electroless nickel plating in recent years owing to their better mechanical and tribological properties.

Boron-containing reducing agents such as sodium borohydride or dimethylamine borane are commonly used to prepare electroless Ni-B alloy coatings. The reduction efficiency of sodium borohydride is much higher than that of dimethylamine borane and sodium hypophosphite. It can provide up to eight electrons for reduction of some metals as opposed to two electrons that can be provided by sodium hypophosphite, for the same reaction [4]. Besides the high reduction efficiency, borohydride reduced baths are preferred to dimethylamine borane based baths in terms of cost-effectiveness of operation [5]. However, borohydride ions hydrolyze readily in acid or neutral solutions and will spontaneously yield nickel boride in presence of nickel ions in the bath [4], [5].

Hence, the control of pH of the plating bath is important to avoid the spontaneous decomposition of the bath solution and to decrease the cost of operation. The properties of sodium borohydride reduced electroless nickel coatings are often superior to those coatings reduced with other boron compounds or with sodium hypophosphite. The principal advantages of borohydride-reduced electroless nickel coatings are its hardness and superior wear resistance in the as-plated condition. Electroless Ni-B coatings are more wear resistant than tool steel and hard chromium coatings [4]. Though, numerous works have been carried out by different researchers on electroless binary Ni-B and Ni-P alloy coatings, very limited works were carried out on preparation of electroless Ni-B-P ternary alloy coatings [6], [7]. By considering the advantages of both Ni-B and Ni-P alloy coatings, the present work aims to synthesize and evaluate the characteristic properties of ternary electroless Ni-B-P alloy coatings.

II. MATERIALS AND METHODS

In general, electroless plating bath contains source of metal ions, reducing agents to supply electrons to reduce the metal ions, complexing agents to prevent excess of free metal ions concentration, stabilizer to prevent the decomposition of bath and pH regulators to maintain the pH. In the present work, nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) was used as source of nickel and sodium borohydride (NaBH_4) and sodium hypophosphite monohydrate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) were used as reducing agents to prepare electroless Ni-B-P alloy coatings. Initially, the substrates were degreased with acetone, electrolytically cleaned in an alkaline solution and washed thoroughly with de-ionized water. A nickel strike using Watt's nickel bath was given to substrates prior to their immersion in electroless plating bath to enable the catalytic action. The formation of Ni-B-P coatings requires an alkaline plating bath with a pH preferably higher than 12, since NaBH_4 readily hydrolyzes in acidic or neutral condition [4], [5]. Hence, the pH of the plating bath was maintained at 14 in the present study. This warrants the addition of higher concentration of alkali (i.e. NaOH), which in turn necessitates the presence of an effective complexing agent in the bath. Ethylenediamine is the most preferred complexing agent for electroless nickel plating bath. The selection of stabilizer for electroless plating bath containing borohydride is very critical since this bath is highly susceptible for decomposition in the absence of a suitable stabilizer. Thallium acetate was used as the stabilizer, which not only stabilizes the plating bath but also increases the reduction efficiency of borohydride [8-10]. Table I shows the composition of the electroless Ni-B-P plating bath. The temperature of the bath gives the energy to the autocatalytic reaction; hence, the bath temperature was maintained at 95 ± 1 °C in the present study. During the plating process, the bath solution was continuously stirred using a magnetic stirrer at 600 rpm and plating was carried out for one hour. Table II shows the operating conditions used in the present electroless Ni-B-P alloy coating process.

TABLE I
Chemical Composition of the Electroless Ni-B-P Plating Bath

Material	Concentration
Nickel Chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	30 g/l
Sodium Hypophosphite, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	12 g/l
Sodium Borohydride, NaBH_4	0.2, 0.4, 0.6, 0.8 g/l
Sodium Hydroxide, NaOH	90 g/l
Ethylenediamine, $\text{C}_2\text{H}_2(\text{NH}_2)_2$	90 g/l
Thallium Acetate, $\text{C}_2\text{H}_3\text{O}_2\text{Tl}$	14 mg/l

TABLE II
Electroless Plating Process Operating Conditions

Operating Parameters	
pH	14.0
Temperature	95 ± 1 °C
Plating duration	1 hour
Stirring speed	600 rpm

Electroless Ni-B-P alloy coatings were synthesized by varying the NaBH_4 concentration (0.2 – 0.8 g/l) keeping a fixed concentration of NaH_2PO_2 (12 g/l) in the plating bath. The influence of variation in the NaBH_4 concentration on the boron and phosphorous content of the resultant Ni-B-P alloy coatings were studied. The boron content of the electroless Ni-B-P alloy coatings was determined by inductively coupled plasma-atomic emission spectrometer (ICP-AES). The nickel content of the electroless Ni-B-P alloy coatings was determined gravimetrically after precipitating nickel as Ni-dimethyl glyoxime (DMG) complex. The plating rate was determined based on the gain in weight of the resultant coatings as a function of deposition time. The surface morphology of Ni-B-P alloy coatings was studied using scanning electron microscope (SEM). The Ni-B-P alloy coatings were characterized by X-ray diffraction (XRD) using $\text{Fe K}\alpha$ radiation to identify the phases present in the resultant coatings. The microhardness values of the electroless Ni-B-P alloy coatings were measured using

Matsuzawa microhardness tester (model MMT-X3) with a Vickers diamond indenter under a 100 g load and dwell time of 15 s. The Ni-B-P alloy coatings were subjected to annealing heat treatment at different temperatures from 200 to 600 °C. The effect of heat treatment temperature on microhardness and structural features of the electroless Ni-B-P alloy coatings were studied using Vickers microhardness tester and X-ray diffraction technique, respectively.

III. RESULTS AND DISCUSSION

A. Plating Rate and Composition

Fig. 1 shows that the plating rates increase with increase in NaBH_4 concentration in the plating bath, since borohydride is a very good reducing agent, which enhances the rate of the reaction. Fig. 2 shows the boron and phosphorous content in the Ni-B-P alloy coatings as a function of NaBH_4 concentration in the plating bath. It was found that boron content increases from 0.98 to 3.26 wt% and phosphorous content decreases from 0.912 to 0.66 wt%. The chemical composition analysis (Fig. 2) revealed that the boron content of the coating increased with increasing NaBH_4 concentration in the plating bath, whereas phosphorous content slightly decreases. When NaBH_4 concentration is increased in the plating bath keeping NaH_2PO_2 concentration constant, the contribution of borohydride to reduction process is very high, limiting the contribution of hypophosphite to the reduction process. This is because of the higher reduction efficiency of NaBH_4 compared to that of NaH_2PO_2 .

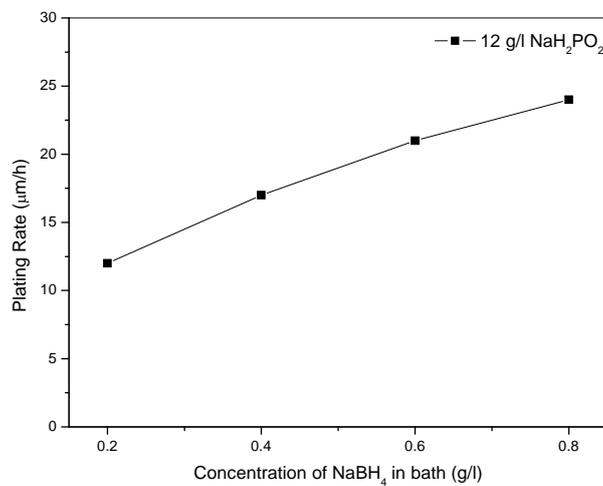


Fig. 1. Plating rate of the electroless Ni-B-P alloy coating as function of NaBH_4 concentration in the plating bath

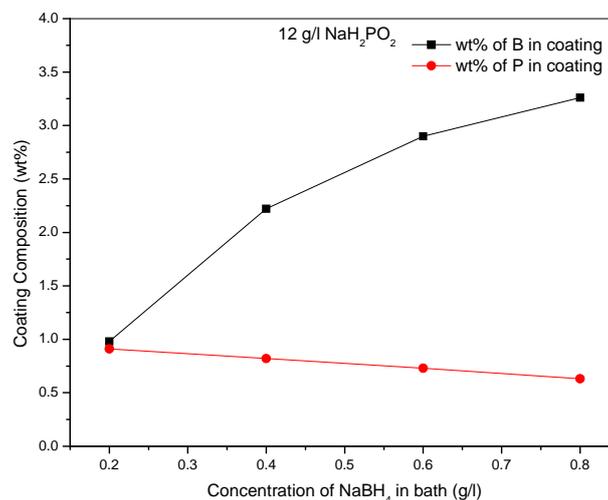


Fig. 2. Composition of the electroless Ni-B-P alloy coating as function of NaBH_4 concentration in the plating bath

B. Surface Morphology

Scanning electron microscopic images reveal the surface morphology of the as-plated Ni-B-P alloy coatings (Fig. 3). The low boron content Ni-B-P alloy coating (i.e. coating obtained from bath containing 0.2g/l NaBH_4) shows a surface morphology with smooth and near spherical nodules, which resembles corn cob structure (Fig. 3a). This morphology was due to lower NaBH_4 concentration and presence NaH_2PO_2 in the plating bath. The micrograph of Ni-B-P alloy coating obtained from bath containing 0.4 g/l NaBH_4 (Fig. 3b) manifests formation

of small bumps over the smooth nodules, which indicates a slight shift to cauliflower structure. Still higher concentration of NaBH_4 in the plating bath (0.6 and 0.8 g/l) results in increase in the number and size of the cauliflower nodules (Fig. 3c and 3d). This cauliflower morphology of the electroless Ni-B-P alloy coatings is similar to the characteristic cauliflower morphology of electroless binary Ni-B coatings [3], [8], [11].

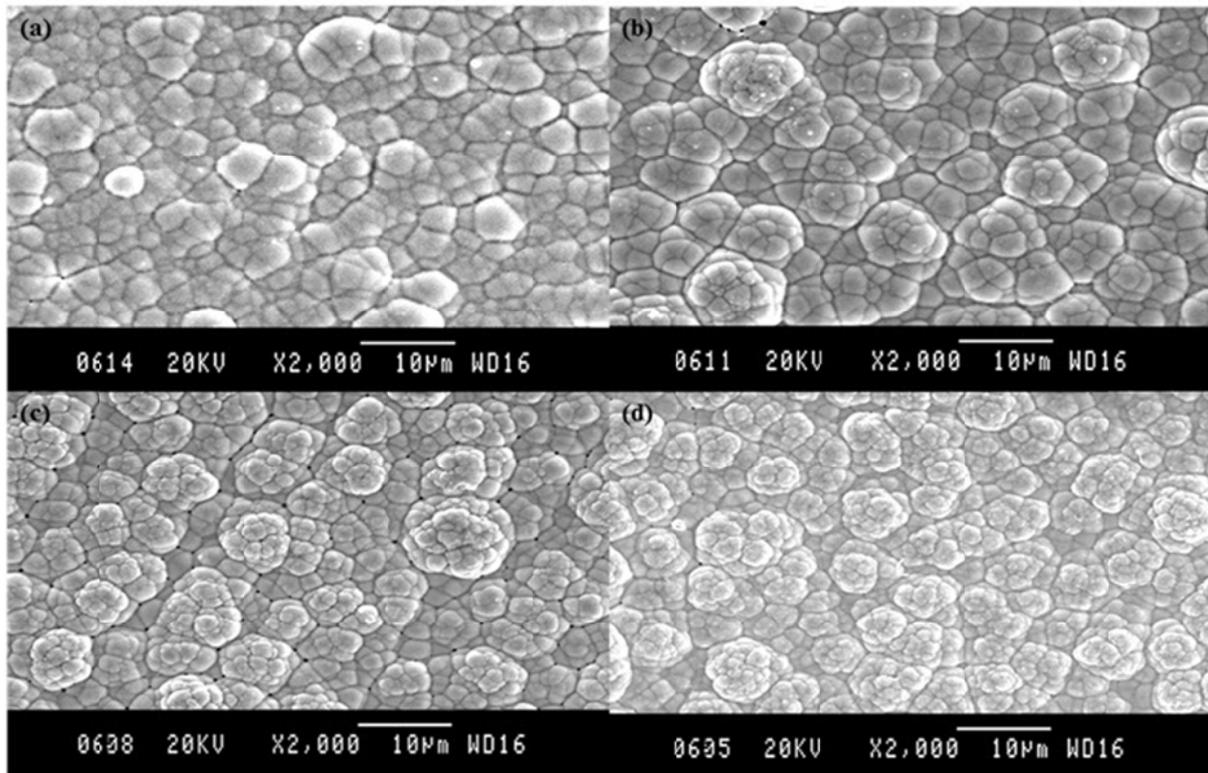


Fig. 3. Scanning electron micrograph of Ni-B-P alloy coating deposited using alkaline bath containing 12 g/l NaH_2PO_2 and NaBH_4 concentration of (a) 0.2 g/l, (b) 0.4 g/l, (c) 0.6 g/l, and (d) 0.8 g/l

C. Structural Analysis

The XRD patterns of Ni-B-P alloy coatings obtained from the electroless plating bath containing varying NaBH_4 concentration (0.2 – 0.8 g/l) were shown in Fig. 4. The XRD patterns of high boron content electroless Ni-B-P coatings show the presence of Ni (111) peak only. But, Ni-B-P alloy coatings with low boron content show sharp Ni (111) reflection along with faint (200) and (220) reflections. The XRD peak becomes broader as the boron content in the Ni-B-P alloy coatings increased (i.e. when the NaBH_4 concentration increased in the plating bath). This may be attributed to the reduction in crystallite size of the Ni-B-P alloy coatings due to formation of nanocrystalline structure. Gaevskaya et al. [12] have observed a similar behaviour, i.e., decrease in intensity of the Ni (111) reflection and an increase in its half-width with increase in boron content of the electrodeposited Ni-B coating. Vitry et al. [13] have observed average grain size of 1 nm for electroless Ni-B coatings obtained from borohydride reduced electroless bath.

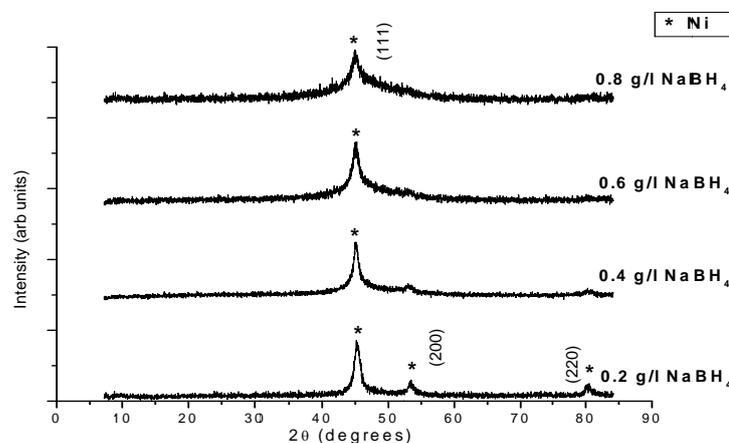


Fig. 4. XRD patterns of as-plated Ni-B-P alloy coatings

Fig. 5 shows the XRD patterns of Ni-B-P alloy coatings heat treated at a temperature of 500 °C. It can be inferred from the figure that broadening of the XRD peak slightly decreased and peaks became little sharper compared to the as-plated Ni-B-P alloy coatings. This structural change may be due to relieving of internal stress and increase in crystallinity of the Ni-B-P alloy coatings during the heat treatment process. The presence of new peaks in the XRD patterns of heat treated coatings (Fig. 5) confirms the formation of secondary phases during the heat treatment process. Phase analysis of the XRD patterns reveals that the new peaks correspond to Ni_3B intermetallic precipitate. The formation of similar secondary precipitates during heat treatment was observed by different researchers [3], [10]. The electroless Ni-B-P alloy coating obtained from bath containing 0.2 g/l NaBH_4 does not show any Ni_3B peaks after heat treatment, because of lower boron content of this coating. The Ni_3B peaks become more prominent in the electroless Ni-B-P coatings obtained from bath containing high borohydride concentration (0.8 g/l) compared to other coatings, because of more boron content in the former electroless Ni-B-P alloy coatings.

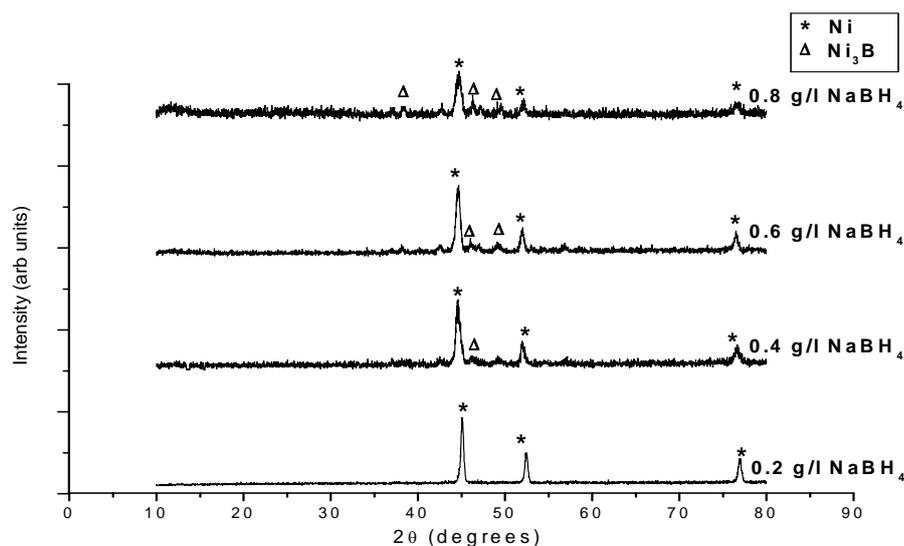


Fig. 5. XRD patterns of Ni-B-P alloy coatings heat treated at 500 °C

D. Microhardness

Vickers microhardness values of the as-plated and heat treated Ni-B-P alloy coatings were shown in Fig. 6. The effect of plating bath composition and heat treatment temperature on hardness of the prepared electroless Ni-B-P alloy coatings are presented here. In as-plated condition, the microhardness values of the Ni-B-P alloy coatings increases with increasing borohydride concentration in the plating bath due to the corresponding increase in the boron content of the final electroless Ni-B-P alloy coatings. The boron forms interstitial solid solution with Ni, thereby increases the strength and hardness of the coatings markedly. The heat treated Ni-B-P alloy coatings show higher hardness values compared to as-plated coatings. This is because of the formation secondary intermetallic precipitate (Ni_3B) in the Ni-B-P alloy coatings during heat treatment. It is evident from the figure (Fig. 6) that the heat treatment temperature has profound effect on the hardness values of the electroless Ni-B-P alloy coatings. The hardness values of heat treated Ni-B-P alloy coatings initially increases with increasing heat treatment temperature and later (after 500 °C) start to decrease. Similar trend was observed by Abdeli et al. [14] for heat treated electroless Ni-B-Tl alloy coatings. The higher temperature reduces the activation energy needed for the formation of Ni_3B precipitates thereby promotes formation of more amount of Ni_3B intermetallic precipitate in the coating. Significant enhancement in the hardness of the Ni-B-P alloy coatings is due to formation of secondary Ni_3B intermetallic precipitate by precipitation hardening. The decrease in the hardness values of Ni-B-P alloy coatings heat treated at 600 °C may be due the coarsening of Ni_3B intermetallic precipitate.

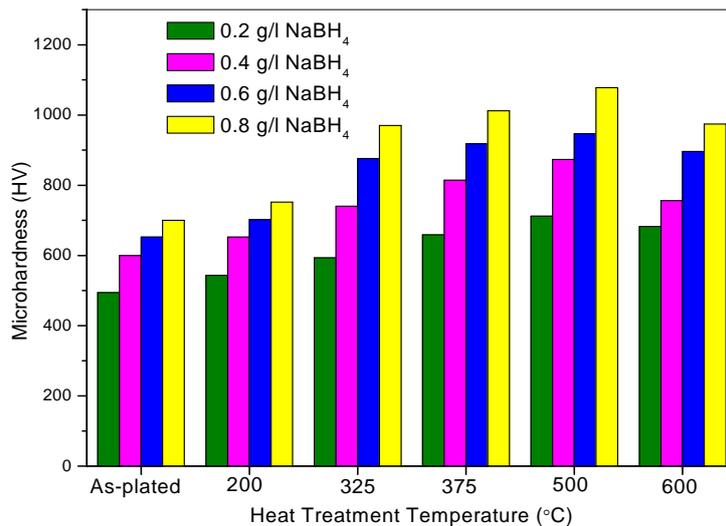


Fig. 6. Microhardness values of Ni-B-P alloy coatings as a function of heat treatment temperature

IV. CONCLUSION

The electroless Ni-B-P alloy coatings were successfully prepared using sodium borohydride and sodium hypophosphite as reducing agents. In the present study, the plating rate increases with increasing borohydride concentration in the plating bath because of higher reduction efficiency of NaBH₄. The composition of the resultant Ni-B-P alloy coating is directly influenced by the plating bath concentrations; the boron content of the coating increases with increasing NaBH₄ concentration in the plating bath, subsequently it slightly decreases the phosphorous content in the Ni-B-P alloy coating. The surface morphology of ternary Ni-B-P alloy coatings show typical cauliflower structure, which is beneficial for retaining lubricants under lubricated wear conditions. The XRD peak broadening of the electroless Ni-B-P alloy coatings obtained from plating bath containing higher borohydride concentration indicates a large reduction in the crystallite size of the Ni-B-P alloy coatings. The formation of Ni₃B precipitates have been confirmed by the presence of Ni₃B peaks in the XRD patterns of heat treated electroless Ni-B-P alloy coatings. Microhardness values of the Ni-B-P alloy coatings increased with increasing boron content of the electroless Ni-B-P alloy coatings. It has been found that the annealing heat treatment increased the hardness of the Ni-B-P alloy coatings due to formation of Ni₃B precipitates during the heat treatment process. The decrease in the microhardness values of Ni-B-P alloy coatings heat treated at 600 °C might be attributed to coarsening of Ni₃B precipitate.

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