

Electroless Ni–B coatings: preparation and evaluation of hardness and wear resistance

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Abstract

The present work aims 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 structure, microhardness and wear resistance of electroless Ni–B coatings, both in as-plated and heat-treated conditions, were evaluated using X-ray diffraction (XRD), Leitz microhardness tester and a pin-on-disc wear test apparatus. XRD patterns reveal that electroless Ni–B coatings are amorphous in as-plated condition and undergo phase transformation to crystalline nickel and nickel borides upon heat-treatment. 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.

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1. Introduction

Electroless deposition process has undergone numerous modifications to meet the challenging needs of a variety of industrial applications since Brenner and Riddell invented the process in 1946. Among the various types of electroless plating, electroless nickel has gained immense popularity due to its ability to provide a hard, wear and corrosion resistant surface [1–3]. Hypophosphite-reduced electroless nickel plating has received widespread acceptance and attention has shifted towards borohydride reduced electroless nickel deposits in recent years. As boron is one of the most important amorphous elements, various boron-containing alloys have been prepared in a search for superior characteristics. The formation of an amorphous solid is extremely difficult by liquid quenching method whereas electroless deposition offers a viable alternative. For elec-

troless plating of Ni–B alloy deposits, boron-containing reducing agents such as sodium borohydride or dimethylamine borane are commonly used. 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 plating bath [4–6]. Hence, control of pH 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 of deposits reduced with other boron compounds or with sodium hypophosphite [7,8]. The principal advantages of borohydride-reduced electroless nickel deposits are its hardness and superior wear resistance in the as-deposited condition [4,6–8].

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Electroless Ni–B coatings are more wear resistant than tool steel and hard chromium coatings and it can replace gold in electronic industries [4]. The columnar structure of Ni–B coatings is useful in retaining lubricants under conditions of adhesive wear [1,7]. The rapid changing needs of engineering industries warrant the development of coatings that possess high hardness and good wear and abrasion resistance and in this respect one such coating which seems promising is the borohydride-reduced electroless nickel deposit. Much remain to be explored about borohydride-reduced electroless nickel coatings so that they can be effectively manipulated to suit the needs. The formation of borohydride-reduced electroless nickel coating and evaluation of its structural characteristics, phase transformation behaviour, magnetic properties and corrosion resistance was reported in our earlier paper [9]. The present work aims to study the hardness and wear resistance of electroless Ni–B coatings.

2. Experimental details

Mild steel (30 mm diameter and 5 mm thick), copper (electrolytic grade; 40×20×2 mm) and stainless steel (AISI 304 grade) were used as substrate materials for the deposition of electroless Ni–B coatings. Copper substrate was employed to assess the plating rate of electroless Ni–B deposits. Stainless steel substrate was used to prepare foils for structural characterization by X-ray diffraction. Mild steel was used as the substrate material for evaluating microhardness of electroless Ni–B coatings. Mild steel substrates were surface ground, 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. An alkaline bath having nickel chloride as the source of nickel and sodium borohydride as the reducing agent was used to prepare the electroless Ni–B deposits. Besides nickel salt and borohydride, the plating bath also contained suitable quantities of ethylenediamine as a complexing agent. Thallium acetate was used as the stabilizer. The temperature of the bath was maintained at 95±1 °C. During plating the bath solution was agitated using a magnetic stirrer at 600 rev./min. The chemical composition of the plating bath employed and its operating conditions are given in Table 1. The boron and thallium content of the deposit was analyzed inductively coupled plasma atomic emission spectrometry (ICP-AES) whereas the nickel content was determined gravimetrically after precipitating nickel as Ni-DMG complex.

The structure of electroless Ni–B deposits, in as-plated and heat-treated (350 and 450 °C for 1 h) conditions was assessed by X-ray diffraction (XRD). The coating hardness was measured on the surface using a Leitz microhardness tester with a Vickers diamond indenter under a 100-g load (0.98 N). The lap time for each indentation was 15 s and the

Table 1

Chemical composition and operating conditions of the borohydride-reduced electroless nickel plating bath

Bath composition	
Nickel chloride	30 g/l
Sodium borohydride	0.8 g/l
Ethylenediamine (98%)	90 g/l
Sodium hydroxide	90 g/l
Thallium acetate	16 mg/l
Operating conditions	
pH	14
Temperature	95±1 °C

values reported represent the average and standard deviation of a minimum of five measurements.

The wear resistance of as-plated and heat-treated (350 and 450 °C for 1 h) electroless Ni–B coatings was evaluated under dry sliding conditions using a pin-on-disc apparatus (DUCOM, India). In this method, the pin and disc are arranged in such a way that the rotating disc served as the counterface material while the stationary pin served as the test specimen. Steel discs (composition conforming to EN 31 specification) of 100 mm diameter and 5 mm thickness were chosen as counterface materials to slide against the test specimens. These discs were fully hardened (R_c 63) and surface ground to a finish (R_a) of 0.02 µm. The applied normal loads were 20, 30 and 40 N. The sliding speed was kept constant at 0.5 m/s for all tests by adjusting the diameter of the wear track and the rotational speed of the disc. Tests were done in air at 25 °C with a relative humidity of approximately 35–45% RH. The frictional force was recorded continuously during the test using a transducer linked to a PC. In this way the coefficient of friction was continuously monitored during the test. After the wear tests, the pins were cleaned in acetone in an ultrasonic bath for approximately 10 min to remove the loose particles and wear debris from the surface. The loss in weight due to wear was calculated by weighing the pins before and after each test on a balance with an accuracy up to 0.1 mg. Two tests were done for each load condition. The specific wear rate was calculated by the expression: $w_s = w/(l \cdot L)$, where w is the wear mass, L is the normal load and ' l ' is the sliding distance. The sliding distance was calculated at the mean radius of the disc. Immediately after the end of each test, the wear track on the pins was examined using a scanning electron microscope.

3. Results and discussion

The plating rate of the electroless Ni–B deposits as a function of plating time is given in Fig. 1. The thickness of Ni–B coating increases with increase in plating time. However, the extent of increase in thickness is not linear throughout the entire duration of plating and it saturates after some time. This is due to the accumulation of oxidation

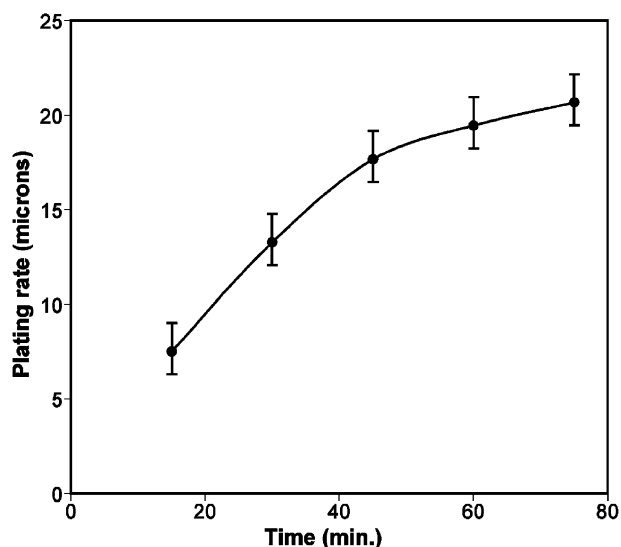


Fig. 1. Plating rate of electroless Ni–B deposit as a function of plating time.

product of borohydride in the plating bath. The Ni–B deposit prepared using the bath composition and operating conditions given in Table 1 contains 93.2 wt.% nickel, 6.5 wt.% boron and 0.3 wt.% thallium. The incorporation of thallium along with nickel and boron is due to the use of thallium acetate as the stabilizer in the plating bath, which is also confirmed by other researchers [4,6–8]. The scanning electron micrograph of electroless Ni–B coating (Fig. 2) exhibits a typical ‘cauliflower’-like structure that makes the deposit naturally lubricious [7,8].

X-Ray diffraction pattern of the electroless Ni–B coating in the as-plated condition exhibits a single broad peak indicative of the amorphous nature of the coating (Fig. 3). Theoretically, a disorder in arrangement of atoms manifests itself as a broad peak in XRD. In electroless deposition process, the extent of segregation of metalloid alloy in the coating determines its crystallinity. Since the required boron segregation (6.5 wt.%) is relatively large, nucleation of nickel phase is prevented and this has resulted in amorphous

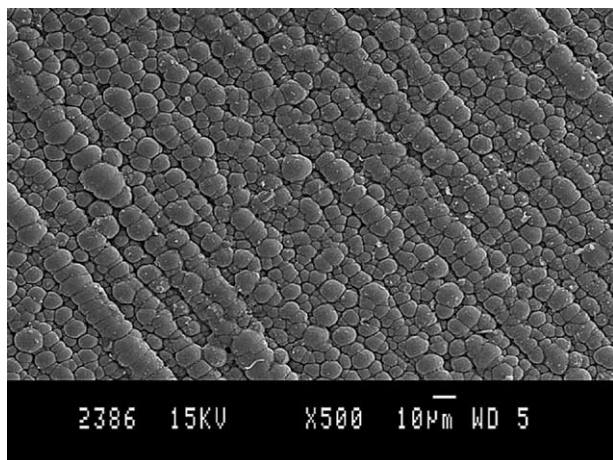


Fig. 2. Scanning electron micrograph of electroless Ni–B deposit.

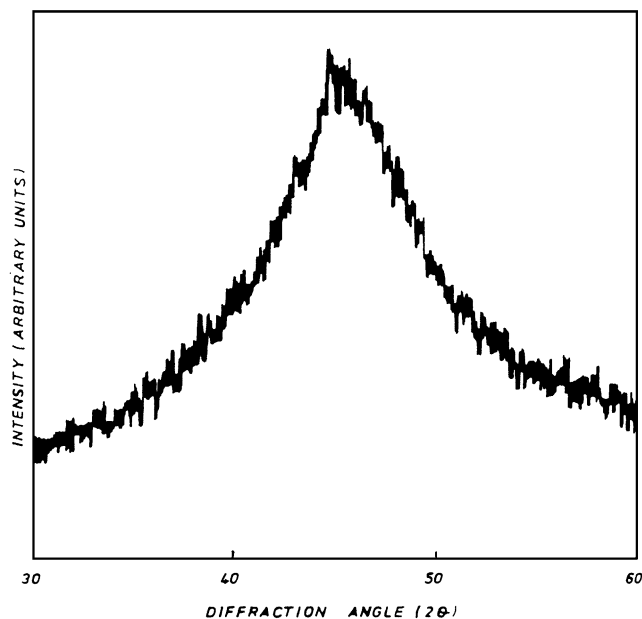


Fig. 3. X-Ray diffraction pattern of electroless Ni–B Deposit in as-plated condition.

structure. Watanabe et al. [10], Srivastava et al. [11] and Evans and Schlesinger [12] also observed the amorphous nature of electroless Ni–B films in the same composition range. Heat-treatment results in the transformation of the amorphous phase to crystalline nickel and nickel boride phases. XRD patterns of electroless Ni–B coatings heat-treated at 350 and 450 °C for 1 h, confirm the formation of crystalline nickel and Ni₃B and Ni₂B phases (Figs. 4 and 5). The formation of these phases upon heat-treatment of electroless Ni–B deposits was also shown by Gorbunova et al. [6], Duncan and Arney [4] and Delaunoy and Lienard [8]. Annealing at temperatures higher than 450 °C results in

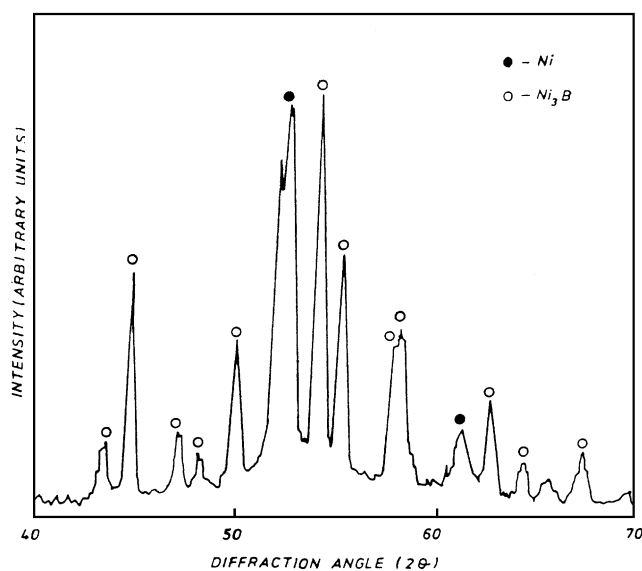


Fig. 4. X-Ray diffraction pattern of electroless Ni–B Deposit heat-treated at 350 °C for 1 h.

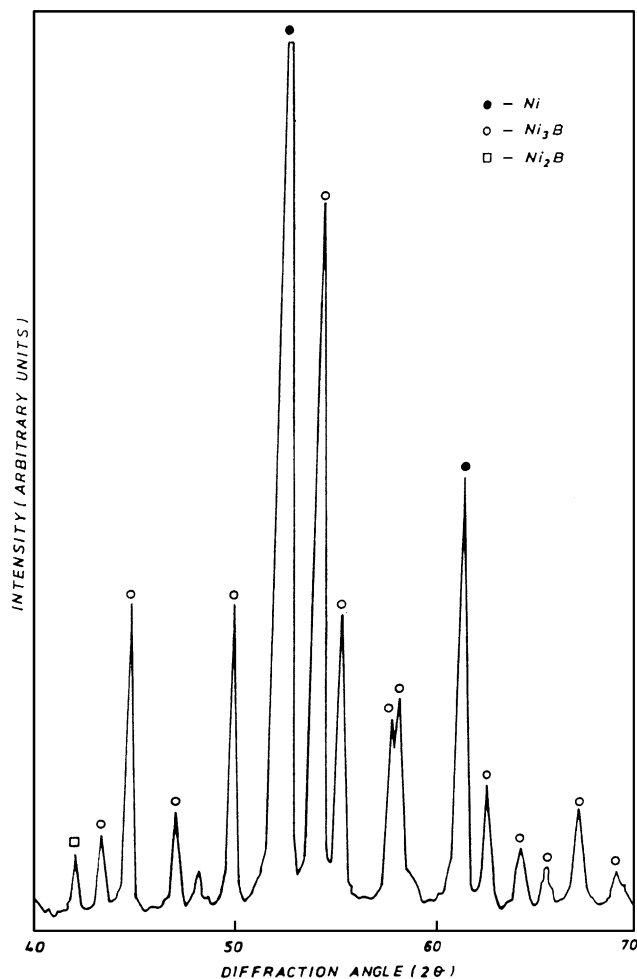


Fig. 5. X-Ray diffraction pattern of electroless Ni–B Deposit heat-treated at 450 °C for 1 h.

growth of crystalline nickel and conversion of Ni_2B phase to the more stable Ni_3B phase. XRD pattern of Ni–B deposits heat treated at 600 °C for 1 h indicate the absence of Ni_2B phase and predominance of nickel and Ni_3B phases in the coating (Fig. 6).

The microhardness (HV_{100}) of electroless Ni–B coatings is determined in both as-plated and heat-treated conditions (200, 300, 350, 400, 450 and 600 °C for 1 h). The microhardness of electroless Ni–B coating is of the order of 570 (HV_{100}) (for as-plated coatings) and 908 (HV_{100}) (for coatings heat-treatment at 450 °C for 1 h), which is comparable with the values reported in literature for similar deposits [4,6,8]. Fig. 7 shows the effect of temperature of heat treatment on the hardness of electroless Ni–B coatings. Compared to the hardness of the Ni–B coating in as plated condition, there is not much of a change in hardness at lower temperatures of the order of 200 °C. With further increase in temperatures, however, the hardness increases rapidly, as the structure of the coatings begins to change. The hardness vs. heat treatment temperature curve exhibits two maxima, one at 350 °C and the other one at 450 °C. Beyond 450 °C, the

hardness decreases. The increase in hardness is due to the precipitation of nickel borides, Ni_3B and Ni_2B . The formation of these phases is confirmed by XRD measurement (Figs. 4 and 5). At temperatures above 450 °C, the coating begins to soften as a result of conglomeration of the Ni_3B particles, which thereby reduces the number of hardening sites. Gorbonova et al. [6] have also observed a similar behaviour of change in hardness with heat treatment temperature for borohydride-reduced electroless Ni–B coatings.

The specific wear rate of electroless Ni–B coatings, both in as-plated and heat treated conditions, obtained at different applied loads, are given in Table 2. The specific wear rate increases with increase in applied load from 20 to 40 N and this trend is common for as-plated and heat-treated electroless Ni–B coatings. At all applied loads, the specific wear rate is less for heat-treated electroless Ni–B deposits compared to that obtained for as-plated ones. This is due to the formation of hard nickel boride phases following heat-treatment, which presents a virtually incompatible surface for the counterface material, as there exists very little solubility between iron and these hard phases, leading to a decrease in specific wear rate. Besides, following heat

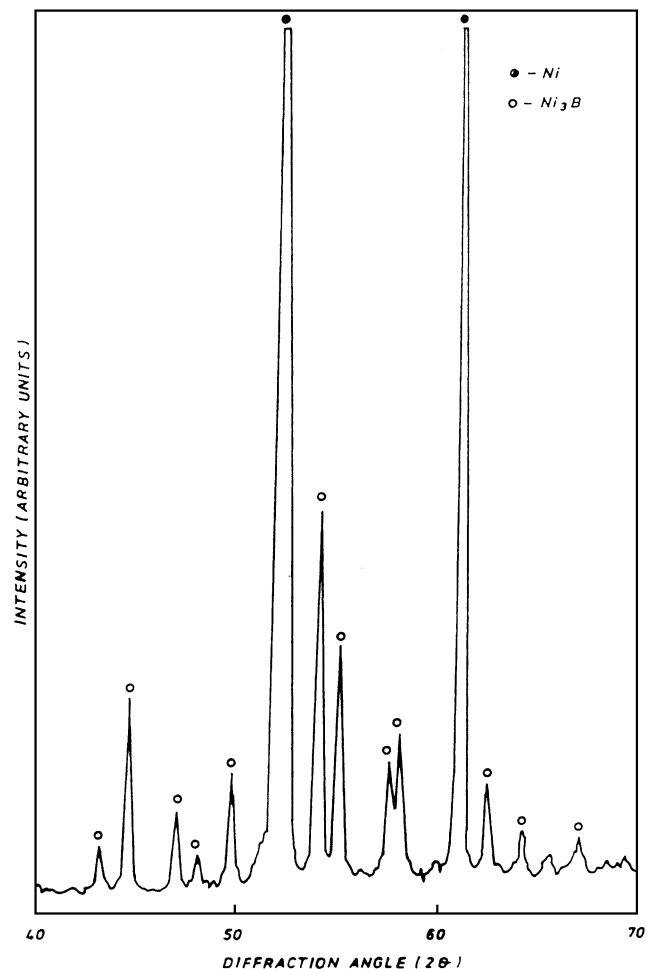


Fig. 6. X-Ray diffraction pattern of electroless Ni–B Deposit heat-treated at 600 °C for 1 h.

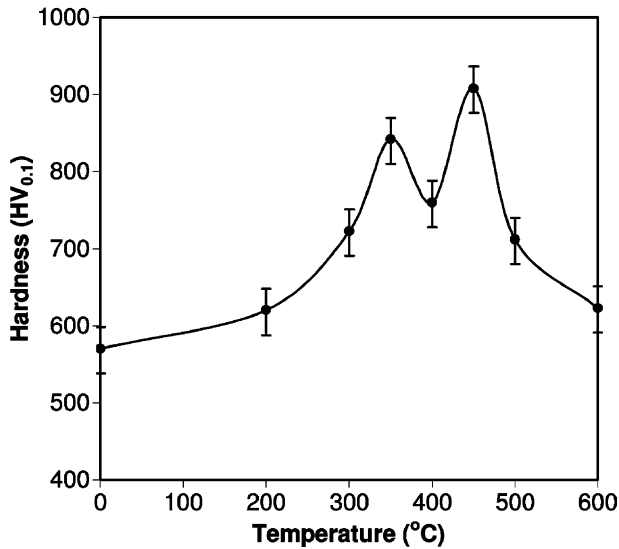


Fig. 7. Change in hardness of electroless Ni–B deposit as a function of heat-treatment temperature.

treatment, there is a considerable increase in the hardness of the coatings. Hence, when the counterface material comes in contact with the matrix, because of the high hardness, the electroless Ni–B matrix experiences lesser wear.

The coefficient of friction recorded simultaneously during the wear test clearly reveals the characteristics of the wear process. The average friction coefficient, μ_{av} of electroless Ni–B coatings in as-plated and heat-treated conditions, is given in Table 3. The coefficient of friction is less for heat-treated electroless Ni–B deposits compared to that obtained for as-plated ones. As already mentioned, this is due to the ability of the heat-treated Ni–B deposits to present a virtually incompatible surface for the hard counterface material. The relationship between the coefficient of friction and the sliding distance of electroless Ni–B coating, heat treated at 450 °C for 1 h, is shown in Fig. 8. The coefficient of friction though exhibit an initial abrupt increase, stabilize after some distance, which signifies the removal of coating and the onset of a friction process between the counter disc and the coated mild steel pins, perhaps with some coating particles entrapped in the contact.

The mechanism of wear of electroless Ni–B coating depends on the attractive force that operates between the

Table 2
Specific wear rate of electroless Ni–B coatings in their as-plated and heat-treated conditions obtained at different applied loads after a sliding distance of 2700 m

Applied load (N)	Specific wear rate* ($\text{kg N}^{-1} \text{m}^{-1} \times 10^{-10}$)		
	As-plated	Heat treated at 350 °C/1 h	Heat treated at 450 °C/1 h
20	0.52	0.39	0.30
30	1.36	0.68	0.59
40	2.46	1.72	1.04

* Average of two determinations.

Table 3

Coefficient of friction of electroless Ni–B coatings in their as-plated and heat-treated conditions obtained at different applied loads after a sliding distance of 2700 m

Applied load (N)	Average coefficient of friction* (μ_{av})		
	As-plated	Heat treated at 350 °C/1 h	Heat treated at 450 °C/1 h
20	0.742	0.710	0.682
30	0.770	0.732	0.703
40	0.784	0.749	0.714

* Average of two determinations.

atoms of nickel from the coating and iron from the counter disk (hardened steel of EN 31 specification). Scanning electron micrographs of electroless Ni–B coatings subjected to pin-on-disc wear test clearly indicate the presence of torn patches and, in some places even detachment of the coating, in their as-plated condition (Fig. 9a). This type of morphological feature, commonly called as ‘prows’ is reported for adhesive wear failure of electroless Ni–P coatings, by several researchers [13–17]. The transferred patches from the electroless Ni–B coatings and the wear debris are also observed on the surface of the counter disc, which clearly indicates an adhesion between the electroless Ni–B coated mild steel pins and the counter disc had occurred. The possibility of occurrence of adhesive wear under the experimental conditions used is also supported by the high mutual solubility of nickel and iron. Hence adhesive wear appears to be the most likely mechanism during the wear process of electroless Ni–B coatings in their as-plated condition. In contrast to the as-deposited coatings, heat-treated coatings, after wear exhibit a bright and smooth finish with fine grooves along the sliding direction (Fig. 9b,c). In a substantial portion of the wear tracks, no gross adhesion

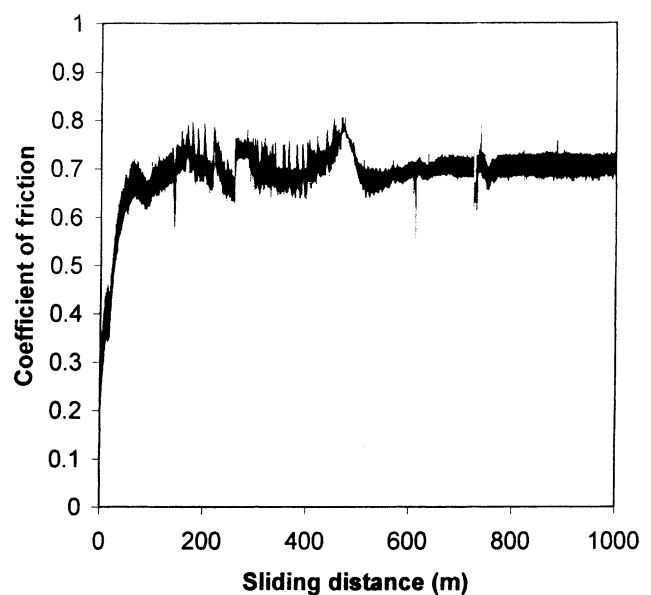


Fig. 8. Coefficient of friction of electroless Ni–B coating heat-treated at 450 °C for 1 h as a function of sliding distance.

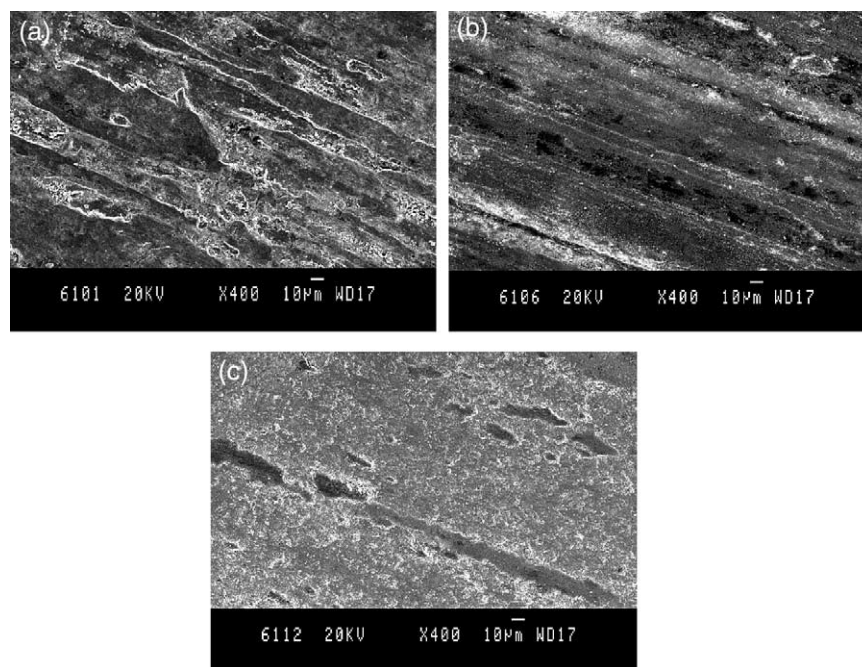


Fig. 9. Scanning electron micrograph of the wear track pattern of electroless Ni–B coatings (a) as-plated; (b) heat-treated at 350 °C for 1 h; and (c) heat-treated at 450 °C for 1 h (Applied load: 40 N; Sliding distance: 2700 m).

between the coated pins and the counter disc is observed. The increase in coating hardness following heat-treatment increases the plastic resistance of the coating and decreases the true area of contact between the mating surfaces, supporting the observed decrease in friction coefficient in the case of these deposits. The loose debris generated during the wear process gets displaced to the sides leading to the formation of grooves along the wear track.

4. Conclusions

Electroless Ni–B coatings of the present study are amorphous in the as-plated condition. Heat-treatment (350 and 450 °C for 1 h) results in the transformation of the amorphous phase to crystalline nickel and nickel boride (Ni_3B and Ni_2B) phases. Annealing at temperatures higher than 450 °C results in growth of crystalline nickel and conversion of Ni_2B phase to the more stable Ni_3B phase. XRD pattern of Ni–B deposits heat treated at 600 °C for 1 h indicate the absence of Ni_2B phase and predominance of nickel and Ni_3B phases in the coating. The microhardness of electroless Ni–B coating is of the order of 570 (HV_{100}) (for as-plated coatings) and 908 (HV_{100}) (for coatings heat-treatment at 450 °C for 1 h). The hardness vs. heat treatment temperature curve exhibits two maxima, one at 350 °C and the other one at 450 °C. Beyond 450 °C, coating begins to soften as a result of conglomeration of the Ni_3B particles and the hardness decreases. The specific wear rate increases with increase in applied load from 20 N 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. The presence of torn patches and detachment of the coating, in as-plated condition confirm the adhesive wear mechanism. For heat-treated coatings, the increase in coating hardness increases the plastic resistance of the coating and decreases the true area of contact between the mating surfaces. Hence no gross adhesion between the coated pins and the counter disc is observed and the wear track pattern exhibits a bright and smooth finish with fine grooves along the sliding direction.

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References

- [1] G.G. Gawrilov, Chemical (Electroless) Nickel Plating, Portcullis Press Ltd, Surrey, 1979.
- [2] G.O. Mallory, J.B. Hadju (Eds.), Electroless Plating: Fundamentals and Applications, AESF, Orlando, 1991.

- [3] W. Riedel, *Electroless Plating*, ASM International, Ohio, 1991.
- [4] R.N. Duncan, T.L. Arney, *Plat. Surf. Finish.* 71 (1984) 49.
- [5] Y.L. Lo, B.J. Huang, *Ind. Eng. Chem. Res.* 33 (1994) 56.
- [6] K.M. Gorbunova, M.V. Ivanov, V.P. Moissev, *J. Electrochem. Soc.* 120 (1973) 613.
- [7] D.W. Baurand, in: *Electroless Plating*, ASM Handbook, Surface Engineering 5, ASM, 1994, p. 290.
- [8] F. Delaunois, P. Lienard, *Surf. Coat. Technol.* 160 (2002) 239.
- [9] T.S.N. Sankara Narayanan, S.K. Seshadri, *J. Alloys Compd.*, (in press).
- [10] T. Watanabe, Y. Tanabe, *Trans. Jpn. Inst. Met.* 24 (1983) 396.
- [11] A. Srivastava, S. Mohan, V. Agarwala, R.C. Agarwala, *Z. Metallkd.* 83 (1992) 251.
- [12] W.T. Evans, M. Schlesinger, *J. Electrochem. Soc.* 141 (1994) 78.
- [13] M.H. Statia, E.J. Castillo, E.S. Puchi, D.B. Lewis, H.E. Hintermann, *Surf. Coat. Technol.* 86–87 (1996) 598.
- [14] D.T. Gawne, U. Ma, *Wear* 120 (1987) 125.
- [15] D.T. Gawne, U. Ma, *Mater. Sci. Technol.* 33 (1987) 228.
- [16] N. Kanani, *Trans. Inst. Met. Finish.* 70 (1) (1991) 14.
- [17] J.K. Dennis, K.S. Sagoo, *Met. Finish.* 89 (6) (1991) 111.