Development and characterization of Ni-B coatings with reinforcement of solid lubricant hBN

Vaibhav Nemane, Avinandan Khaira, Prateek Kumar, Potnuru Niranjan, Satyajit Chatterjee*

Indian Institute of Technology Indore, Indore, India

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ABSTRACT

KEYWORDS

Electroless Coating,
Solid Lubrication,
hBN,
Scratch Test,
Friction Coefficient.

Electroless deposition techniques can be utilized in manufacturing coatings with self-lubricating properties suitable for industrial applications. Electroless Ni-B coatings have emerged as a better alternative to electrodeposited Ni-based coatings and apart from possessing high hardness; these alloy coatings are well-known for their superior resistance to wear and abrasion. Incorporation of hBN as solid lubricating phase in electroless Ni-B alloy matrices can effectively improve its tribological characteristics. This study presents microstructural, mechanical and tribological characterizations of electroless Ni-B and Ni-B/hBN composite coatings developed on steel substrates. Microstructural features and phase compositions of the deposited coatings can be systematically studied involving FESEM and XRD analyses. Studies of deposited coatings with X-ray diffraction reveal a mixed phase amorphous/crystalline characteristic and confirms the existence of hBN in coatings' matrix. Heat treatment of deposited samples (at 450°C, 1hr) is performed to observe changes in structural aspects of coatings. Thorough tribological characterizations on all deposited Ni-B based coatings performed in sliding and scratch modes reveal significant improvements in frictional behaviour with the addition of hBN. Notably, annealing imparts significant changes in electroless Ni-B coatings' structure as new diffraction peaks corresponding to crystalline nickel (Ni) and nickel boride intermetallic phases (Ni_3B, and Ni_2B) are noticed. Formation of these hard intermetallic phases upon heat treatment corroborates to the betterment in mechanical and tribological characteristics of deposited coatings.

1. Introduction

Electroless depositions, with their characteristic high hardness and resistance to wear and corrosion, have found wide range of applications in automobile, aerospace, and chemical sectors. This technique does not require electrical power and is capable of coating irregular shapes with uniform deposit thickness. Here, coatings are deposited through an autocatalytic chemical method involving reduction of metal cations in a liquid bath solution. Electroless techniques can deposit metals (Ni, Co, Au), alloys (Ni-P, Ni-B, Co-B, Ni-P-W) and composite coatings (SiC, Al_2O_3, ZrO_2, Si_3N_4, WC, MoS_2 etc. reinforced in Ni-P/Ni-B alloy matrices). Among various compositions, electroless Ni-B coatings gained recognition due to their mechanical and tribological properties. Friction coefficient of Ni-B based alloy coating is in the range of 0.25-0.55 (Sahoo & Das, 2011) which can be improved by introducing solid lubricants in their matrices. Graphite, MoS_2, WS_2, hBN etc. are few solid lubricants with lamellar structure and weak-in-shear nature popularly used in tribological coatings. Among all, hBN shows favourable lubricating properties in both dry and humid conditions and can remain chemically stable (i.e., oxidation resistant) up to a much higher temperature, close to 700°C in powder form and about 980°C in solid form (Clauss, 1972). This sustainability makes hBN a promising candidate in several applications under extreme tribological conditions. Friction coefficient reported for electroless Ni-P-hBN composite coatings are 0.4, in as-deposited & 0.3, in heat-treated (at 400°C) conditions respectively (Leon et al., 2003). Little

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*Corresponding author E-mail: satyajit@iiti.ac.in

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attempt is made to study the incorporation of hBN as solid lubricant in electroless Ni-B coatings deposited for tribological purposes. This report presents in elaboration the electroless fabrication of Ni-B/hBN composite coatings and a thorough study of hardness along with the wear and scratch responses of the obtained coatings.

2. Experimental Details

Here, deposition of both electroless Ni-B alloy and Ni-B/hBN composite coatings are performed on AISI1025 substrates, polished up to $R_a \leq 0.5\mu m$ through standard metallographic sample preparation technique. After proper cleaning, the substrate samples are immersed in a 10wt% of NaOH solution for 15 minutes at a temperature of 50-60°C. The surfaces of the samples are activated by immersing them for 15-20 seconds in a 16vol% of HCl solution. After each subsequent step of the pre-treatment process, the samples are given an intermediate rinse in deionized (DI) water for a few seconds to dissolve the residue chemicals. Electroless plating bath is composed of nickel chloride which provided Ni^{+2} ions for Ni deposition, sodium borohydride ($NaBH_4$) as a reducing agent. Additionally, ethylenediamine ($NH_2–CH_2–CH_2–NH_2$) is used as a complexing agent to make complex with excess Ni^{+2} ions and control the reaction, and lead nitrate ($Pb(NO_3)_2$) as a stabilizer that reduces the number of nucleation sites. The bath temperature is maintained at 90±2°C throughout the deposition process as sudden increment in the solution temperature may lead to bath decomposition or decrement in it may terminate the deposition process. Sodium hydroxide (NaOH) is added to maintain the pH of the bath at a value of nearly 13. Table 1 presents the precise bath composition.

Table 1
Bath composition.

Constituents	Concentration
Nickel Chloride	20 g/l
Sodium Hydroxide	40 g/l
Sodium Borohydride	0.8 g/l
Ethylenediamine	59 ml/l
Lead Nitrate	0.0175 g/l
hBN particles	1 g/l

In order to develop a composite coating containing hBN in the Ni-B alloy matrix, initially, a precoat of Ni-B on the substrate is deposited, and after 20 minutes, submicron sized hBN (average size ≤1µm) are introduced to the bath for obtaining Ni-B/hBN composite coating. The substrate, post deposition, is subsequently immersed into 50°C deionized water, and further cleaned by ultrasonication with acetone. Samples with deposition are heat treated at 450°C (tubular furnace, 5°C/min heating rate). At this temperature, samples are held for one hour and are subsequently furnace cooled up to the room temperature. The structural transformations of phases in coating's matrix are studied with the help of X-ray Diffraction (XRD) analysis. Coated samples are sectioned into smaller pieces for characterization. The hardness of the coatings on the cross-section is measured with Mitutoyo HM-210A microhardness tester. Scratch test is performed on all coatings to evaluate the scratch behaviour. Dry sliding wear tests (reciprocating type) are conducted on the samples using a Si_3N_4 ball as counter body (diameter Φ6mm).

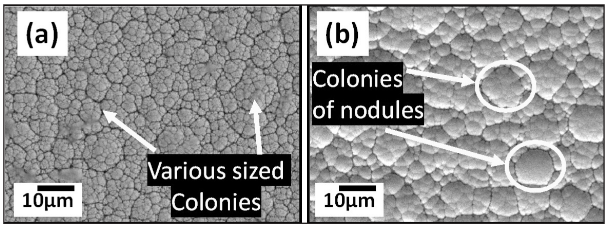

Fig. 1. Top-surface morphologies of (a) Ni-B alloy and (b) Ni-B/hBN composite coatings.

3. Results & Discussions

Careful examination of morphological features of the top surface of both Ni-B, and Ni-B/hBN coatings in scanning electron microscope (SEM) reveals a typical cauliflower-like structure, resulting of nucleation and subsequent grain growth in a columnar form (Figure 1(a-b)). During deposition, the thickness of the diffusion layer around the crystallites developed at several nucleation sites in an electroless bath affect the generation of the columnar structure (Sudagar et al., 2013; Vitry et al., 2022). Moreover, existence of boron retards the crystallization and restricts nucleation of nickel grains during the deposition which subsequently leads to the formation of an amorphous/crystalline (a/c) mixed structure. In the initial stage, Ni atoms get attached to the active sites of the substrate and formation of large nuclei on the surface takes place. Crystallites, with time, grow faster in the vertical direction than that in the lateral direction till a stage is reached where lateral growth gets hindered by the adjacent crystallites due to mutual contact and only vertical growth takes place

(Vitry et al., 2022). This develops the cauliflower-like surface, and a coating will be developed on the substrate. As thickness of the coating increases with further deposition, variation in the contribution from amorphous and crystalline structure can also be observed (Nemane & Chatterjee, 2021). The presence of hBN particles in the electroless bath during the deposition of Ni-B/hBN composite causes generation of a dissimilar top surface morphology, as shown in Figure 1(b) as compared to that of Ni-B coating in Figure 1(a). An increase in the size of colonies of nodules in case of composite Ni-B/hBN coatings can be related to the change in nucleation and growth rate of as-deposited coatings with the addition of hBN particulates in the electroless solution.

Broad peaks at around 45° (2θ) in X-ray diffraction spectra of the as-deposited samples (Figure 2) represent diffraction by short range order of coatings consisting of both microcrystalline and amorphous phases. The peak at 26.8°(2θ) in the XRD spectrum of Ni-B/hBN confirms the presence of hBN. The structure of the coating, on heat treatment, changes from amorphous to micro-crystalline form, and harder crystalline compounds of Ni and B such as Ni_2B and Ni_3B are developed. SEM micrograph obtained at Ni-B alloy coating's cross-section (Figure 3(a)) shows a homogeneous and crack free microstructure. The same observation on Ni-B/hBN composite coating reveals (Figure 3(b)) reinforcement of particles and its uniform distribution which can be noticed in the form of dark spots. Figure 3(b) also clearly depicts the Ni-B alloy precoat applied on the substrate to facilitate better adhesion of the composite coating developed atop it.

Figure 4 shows the improvement achieved in average hardness values of as deposited electroless Ni-B/hBN composite coatings as compared to Ni-B alloy coating. Further improvement in the microhardness values of coating is obtained after heat treatment (450°C, one hour, shown with red colour in Figure 4), which changes microstructures of coatings to a crystalline form containing Ni_2B, Ni_3B etc. These newly formed phases promote precipitation hardening within the crystalline matrix leading to the enhancement in the hardness values of the coatings.

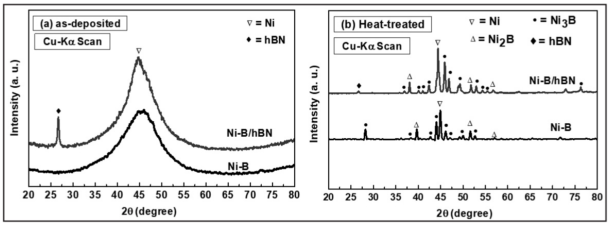

Fig. 2. X-ray diffraction spectra of developed coatings (a) as-deposited (b) heat-treated.

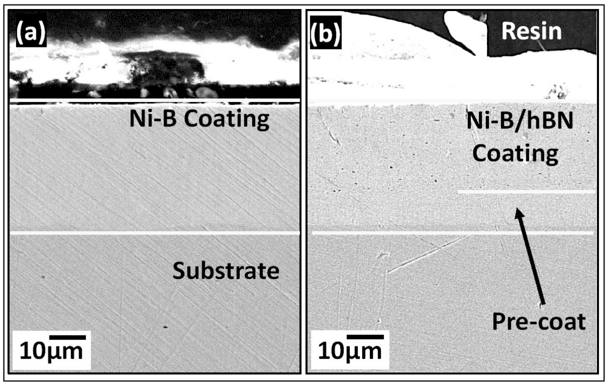

Fig. 3. Cross-sectional morphologies of (a) Ni-B alloy and (b) Ni-B/hBN composite coatings.

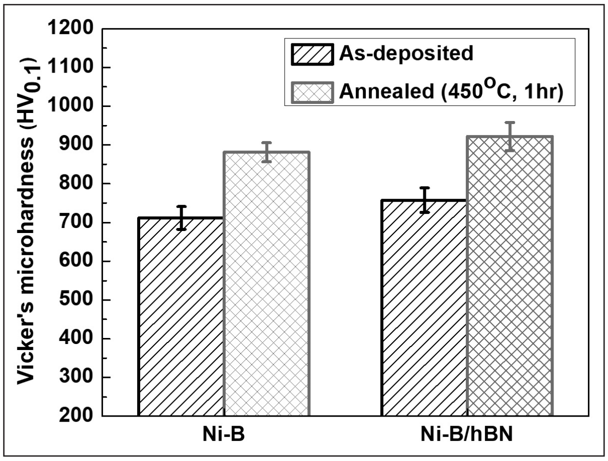

Fig. 4. Bar chart displaying the variation of microhardness values of coatings before and after annealing treatment.

Scratch tests are also performed at the top surface of coatings to evaluate the scratch responses of the deposits in their both as deposited and heat-treated conditions. Figure 5 represents calculated average values of scratch hardness which clearly indicates electroless Ni-B/hBN composite, in its both as deposited and heat-treated forms possess higher resistance to scratch deformation as compared to electroless Ni-B alloy coatings of all forms. Higher scratch hardness achieved with heat treatment can also be attributed to precipitation hardening obtained with the formation of crystalline phases, such as Ni_2B, and Ni_3B.

Values of scratch hardness of as deposited and heat-treated samples (Figure 5) are observed to follow a similar trend as that of Vickers microhardness. The heat treated hBN reinforced coating shows much higher scratch hardness as

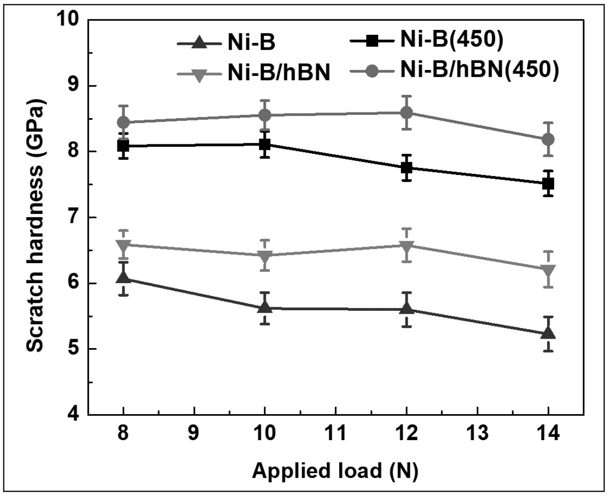

Fig. 5. Scratch hardness variation at various values of load for both as-deposited and heat-treated Ni-B alloy and Ni-B/hBN composite coating.

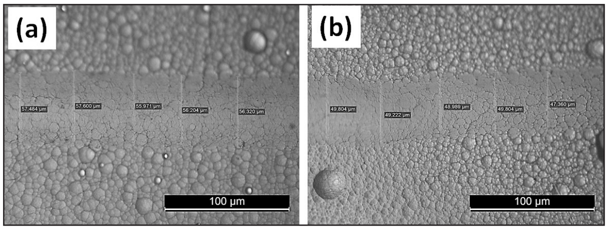

Fig. 6. Scratch tracks at 8N load of Ni-B/hBN composite coatings (a) as-deposited and (b) heat treated at 450°C under optical microscope.

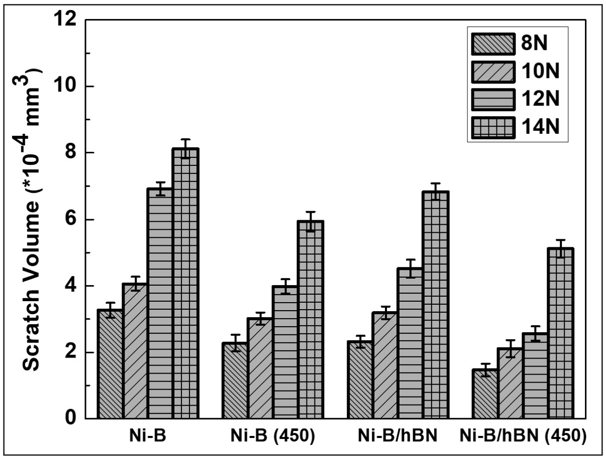

Fig. 7. Evaluation of scratch volume of coatings before and after annealing.

compared to other Ni-B alloy coatings. Optical micrographs of scratch tracks formed in both as-deposited and heat-treated Ni-B/hBN coatings are presented as Figure 6.

As displayed in the Figure 7, among all, measured values of scratch volume loss (calculated from the width of the scratch tracks employing the method described in one of the previous publications of the author (Nemane & Chatterjee, 2021)) in heat-treated Ni-B/hBN coating is found to be the lowest. It is also observed that with the increase in the normal load, material loss increases. Further understanding the scratch response, scratch friction coefficient of coatings against the Rockwell diamond indenter is plotted against scratch length. The friction coefficient is observed to be increasing with the increase in scratch load, and the heat-treated samples displayed much lesser friction at all loads as compared to as-deposited samples.

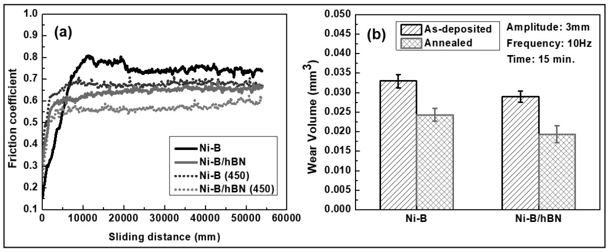

Fig. 8. Variation in (a) friction coefficient and (b) wear volume of coatings.

The interaction between the counter-bodies is governed by the combined effect of their mechanical and elastoplastic behaviour at specific test parameters (e.g., load, sliding speed, and sliding distance) chosen for evaluation. The frictional force in the sliding wear test is dependent on the shear strength of interacting materials and their contact area. A harder coating is less prone deformation and thus reduces the contact area which affects friction and wear. In case of coatings containing hBN as lubricious phase, the friction coefficient decreases when compared with Ni-B alloy coatings deposited without any lubricious phase in it. During wear test, hBN, being weak in shear helps the counter-body to slide over it and contributes to the reduction in friction coefficient. Figure 8(a) represents variations in friction coefficient values of all coatings. Tests performed at 10H$_z$ frequency with a stroke length of 3mm against 10N normal load show decrease in coefficient of friction with the incorporation of hBN in deposits. Further reduction in the friction coefficient is noticed for heat treated coatings and it can be credited to the lower area of contact and reduction in the debris particles due the precipitation hardening of the coatings attained with the harder nickel boride phases. As shown in Figure 8(b), after heat treatment, a slight reduction in specific wear rate of the coatings is observed. This may be due to strengthening of coating matrix and presence of harder Ni-B crystallites which resist the deformation of coating

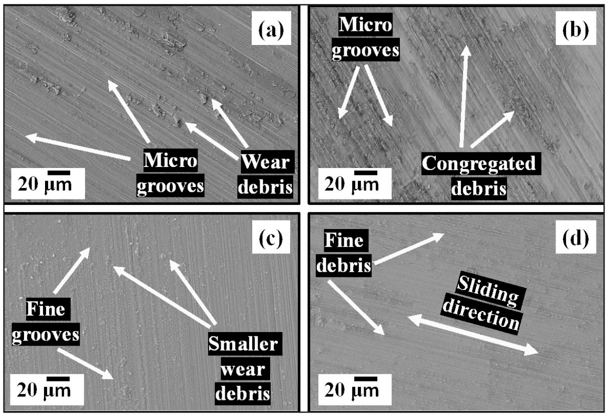

Fig. 9. SEM micrographs of worn surface of coatings (a) Ni-B (b) Ni-B/hBN (c) Ni-B (annealed) (d) Ni-B/hBN (annealed).

due to external load. After dry sliding wear test, the micrographs of worn surfaces are presented in Figure 9(a-d).

The morphological appearances of the as deposited and heat-treated coatings are also in agreement with the evaluated results of wear volume. As evident from Figure 9(a-b), worn surfaces of as-deposited coatings exhibit the presence of deeper microgrooves and large amount congregated debris at the wear tracks. The lesser capability of the as-deposited coating matrix in terms resistance to deformation can lead to the higher degree of damages during tribological interaction. Notably, in comparison with the as-deposited composite coatings (Ni-B/hBN), the microgrooves and size of the generated debris is higher in case Ni-B alloy coatings.

Further marked reduction in the extent of damages and magnitude of micro-grooves at the wear tracks is observed in coatings after heat treatment (Figure 9 (c-d)). Much finer grooves and relatively smaller debris particles dispersed at the wear tracks can be ascribed to the superior resistance offered by the heat-treated coatings' matrix to the deformation under the application of load during the wear testing. It should be noted that, abrasive wear is the most common characteristic feature in case of electroless Ni-based metallic coatings (Mukhopadhyay et al., 2017). The observed trend of friction coefficient can also be correlated with the morphological features of wear tracks. Higher friction coefficient values of as-deposited specimens can be observed due to the visibly higher degree of damages causing the large amount of debris generation and their entrapment within the counter bodies. In sliding wear tests, heat-treated Ni-B/hBN coatings are found to be much superior in terms of both the frictional behaviour and wear resistance. It is also noteworthy that the heat-treated composite (Ni-B/hBN) coatings have not lost their lubrication property even after getting a prolonged exposure to 450°C.

4. Conclusions

Electroless Ni-B, Ni-B/hBN composite coatings are successfully deposited on AISI1025 steel substrates with both having a characteristic nodular structure at the top surface. XRD of deposited samples helped in revealing the short-range order present in coatings consisting of both microcrystalline and amorphous phases. After heat treatment at 450°C, conversion to crystalline nature takes place in coating matrices. Also, formation of harder boride phases in coating matrices, such as Ni_3B, Ni_2B impart precipitation hardening, leading to significant improvement in mechanical and tribological characteristics relating to microhardness, and scratch behaviour. A much lower scratch friction coefficient is observed in Ni-B/hBN composite coating after heat treatment. Frictional responses of coatings also improve significantly in a dry sliding wear condition owing to the incorporation of solid lubricious hBN in the Ni-B alloy matrix.

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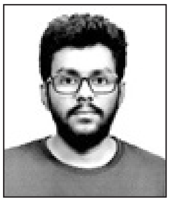
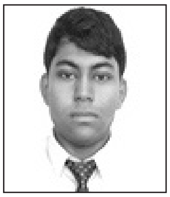
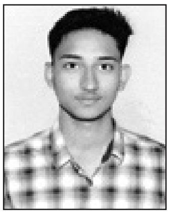


Vaibhav Nemane is a Doctoral Research Scholar in the Department of Mechanical Engineering, IIT Indore and is working on the microstructural and tribological assessment of electroless composite coatings involving solid lubrication properties.
(E-mail: phd1701203005@iiti.ac.in)



Avinandan Khaira was a Doctoral Research Scholar in IIT Indore and has worked on electroless composite coatings.
(E-mail: phd1901203005@iiti.ac.in)



Prateek Kumar has graduated with B.Tech in the Department of Mechanical Engineering from IIT Indore.
(E-mail: prateekjr999@gmail.com)

Potnuru Niranjan has graduated with B.Tech in the Department of Mechanical Engineering from IIT Indore.
(E-mail: npotnuru8@gmail.com)

Dr. Satyajit Chatterjee, Ph.D (Mechanical Engineering), is currently Associate Professor in the Department of Mechanical Engineering, IIT Indore. His research interests include Surface Technology and Solid Lubrication.