



Investigation of mechanical and tribological characteristics of Ni-B coatings deposited on steel

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ABSTRACT

In this study, mechanical properties and wear behaviors of Ni-B coatings were investigated. The mechanical and wear properties of the coating change depending on the nickel boride (Ni_2B and Ni_3B) phases formed after heat treatment at 400°C for 2 hours. Nodular structure formed in the surface morphology and columnar growth in the cross-sectional images of the coating as-deposited and annealed was examined by scanning electron microscopy (SEM). The amorphous structure at as-deposited and the nickel boride phases formed in the structure after annealing were analyzed by X-ray diffraction (XRD). Using the Debye-Scherrer formula, the effect of the phases formed in the structure on the crystalline grain size after annealing was calculated. The hardness values of the coating as-deposited and annealed were calculated by nano-indentation hardness measurement method. Wear tests of the coatings, which were subjected to heat treatment at 400°C for 2 h, were carried out in dry conditions without the use of lubricants, at different loads (1N-3N-5N), at a sliding speed of 25 mm/s and at 25°C. After the wear tests, the wear surfaces of the samples were imaged by SEM and their chemical compositions were analyzed by energy dispersive spectroscopy (EDS). The wear rate and coefficients of friction the samples tested under different loads had compared each other.

1. Introduction

Studies on coating technology to improve the surface properties of materials have been increasing. Although hard chrome is the most used in surface coating processes in the industry, alternative studies are carried out due to the lack of mechanical properties of this coating and the low service life. Mild carbon steels are used more commonly than alloy and mild steels due to their low cost, and they are subjected to different surface treatments since their strength and wear resistance are low [1].

To increase the strength and wear resistance of the material in the industrial area, surface treatments are made on mild carbon steels by electrodeposition coating method. Pure nickel coating produced by electrodeposition method cannot show high resistance in wear environments due to its low hardness. As is known, the strength of the material improves with the

alloying [2]. The most concentrated studies as an alternative to hard chrome plating are Ni alloy coatings. Ni alloy coatings are becoming widespread in industrial areas such as aviation, automobile, and defense due to their low deposition cost, easy of use industry, high hardness values, very good friction, and wear properties. Especially Ni-B alloy coatings are the most preferred research area due to their superior mechanical and tribological properties. Ni-B coatings produced by electrodeposition coating technique are formed in amorphous structure. The mechanical and tribological properties of the Ni-B coatings are affected by the applied heat treatment. Boron element added to improve the mechanical properties of its alloy dissolves in the matrix and crystal nickel boride phases are formed after the coating is subjected to heat treatment [3]. In annealed coatings, there is a significant increase in the hardness of the coating with the grain refining effect resulting from the crystallization of nickel and the

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formation of Ni₃B and Ni₂B phases. Thus, increasing coating hardness also improves the wear properties of the coating [4]. Although it has been reported in the previous studies that the formation of Ni₃B and Ni₂B crystal phases increases the hardness and wear resistance of the coating, it has not been fully explained that these phases also improve the strength and wear behavior of the coating [5,6].

In this study, the microstructure, hardness and tribology properties of Ni-B coatings produced by the pulse current electrodeposition method were investigated. Particularly, attention was paid to the effect of heat treatment on the strength increase of the coating. The results obtained showed that Ni-B coating produced without using any lubricating reinforcement element is resistant to the applied wear medium.

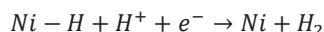
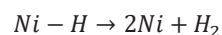
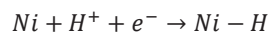
2. Methods

Mild carbon steel of 5 mm thickness, 40 mm x 30 mm size was used for the cathode in Ni-B electrodeposition coating. The substrate surface was polished using alumina after mechanically sanded using 200-400-600-800-1000-1200 grit SiC polishing paper to remove the roughness of the sample surfaces, increase adhesion and ensure homogeneity of the coating. Then, samples that cleaned with ethanol in ultrasonic bath were rinsed with deionized water and dried. Finally, before starting the coating procedure, the samples were immersed in HCl:H₂O (1:3) solution to clean the oxide layer that may form on the substrate surface, then cleaned with deionized water and placed in the coating solution. After the coating process, the samples were heat treated under an argon atmosphere at 400°C for 2 hours.

Table 1. Chemical composition and operating conditions of Ni-B electrodeposition coating.

Chemical composition	
Chemicals	Composition (g/L)
NiSO ₄ .6H ₂ O	240
NiCl ₂ .6H ₂ O	45
H ₃ BO ₃	30
TMAB(Trimethylamineborane)	3
Coating bath conditions	
pH	3
Temperature (°C)	50
Current density (mA/cm ²)	4.5
Stirring rate (rpm)	450
Deposition time (min.)	60
Anode	Ni (%99.9)
Cathode	S-37 steel (mild carbon steel)

Figure 1 shows a schematic of the electrodeposition Ni-B alloy coating bath. The chemical composition and operation conditions of the Ni-B coating bath are given in Table 1. Electrodeposition of nickel in the Ni-B coating and reactions with hydrogen discharge are given below:



Additionally, the TMAB compound used as the boron source in the coating bath is included in the Ni matrix by the following reaction [7]:

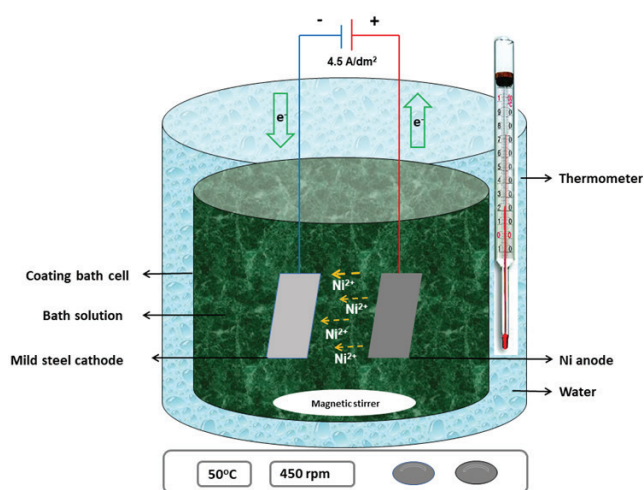
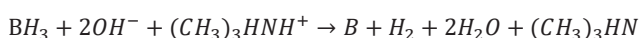


Figure 1. Schematic illustration of electrodeposited Ni-B alloy coating bath.

The surface morphology and cross-sectional view of the coating as-deposited and annealed were examined using the JEOL 6060-LV scanning electron microscope (SEM). The crystal structures of the coatings were characterized by the X-ray diffraction (XRD) technique using the Rigaku D/MAX 2000 X-ray generator and Cu K α radiation diffractometer with a wavelength of 1.54059 Å. Crystalline sizes were calculated by the formula of Debye-Scherrer. The hardness values of the coating after heat treatment were measured using the Nano hardness device (Anton Paar Nanoindentation tester: NHT³) with Berkovich indenter under load of 25 mN. The hardness measurements were made from the cross-sectional area of the coating and hardness values obtained from five different points were averaged for each sample. In addition, the load-depth curves of the samples as-deposited and heat treated were analyzed by nano-indentation test. Tribological behavior of the coatings was performed on the Tribometer (CSM Instruments TRB 18-317) by dry sliding against the Al₂O₃ ball (Ø 6 mm). The wear tests were

carried out at $25^{\circ}\text{C}\pm 2$ room temperature and $45\%\pm 5$ relative humidity media. Wear tests were carried out at different applied loads (1N-3N-5N) at sliding rates of 25 cm/s over 400 m sliding distance, and wear rate and friction coefficient values of each sample were calculated. The image of wear traces on the surface of the coating after the wear tests were obtained by SEM. Elemental analysis of sample surfaces abraded at different loads was performed with EDS. In addition, the coefficient of friction values and wear rates of the samples were analyzed after the friction test.

3. Results and Discussion

The surface morphology and cross-sectional images of the as-deposited and the annealed coatings are shown in Figure 2. Surface morphologies of Ni-B coatings are in the form of cauliflower structure and it is seen that the nodular structure of the coating is refinement after heat treatment. The void structure seen on the coating surface before heat treatment decreased after the heat treatment. This can be explained by the fact that nickel borides formed after annealed decrease the porous structure of the coating and form a denser layer. In addition, it can be stated that the smoothness of the coating surface increases with the decrease in the nickel crystal's grain size [8]. The columnar growth observed in the coatings was dense and continuous, and there were no defects in the adhesion of the coating to the substrate. When the interface between the coating and the substrate is examined, it is seen that while significant defects are observed in the coating before

heat treatment, it is seen that defects are reduced and adhesion is better after heat treatment. The columnar structure which improves the tribological properties of the coating prevents adhesive wear by reducing the contact area between the coating surface and the opposite surface. Thus, it can be said that heat treatment can positively affect the internal tension of the coating, and the load applied during friction can be distributed evenly and the load on the Ni matrix phase can be reduced [9].

The XRD spectra of Ni-B coatings as-deposited and heat treated are shown in Figure 3. It is seen that the nickel phase structure, which is semi-amorphous before the heat treatment, the Ni crystal phase structures and nickel borides after the heat treatment. This transformation resulted with the formation of (111), (200), (220) planes at 44.36° , 51.80° and 76.28° peaks, respectively. In the phase diagram in the literature, the nickel in the amorphous microstructure crystallizes at different temperatures to form Ni_3B and Ni_2B phases [10]. After the coatings annealed, the amorphous phase of the nickel crystal peaks decreased, while crystal nickel boride (Ni_3B and Ni_2B) phases are formed. Nickel borides formed in the coating prevent nucleation of nickel phases. The formation of narrow and dense peaks of nickel and nickel boride phases after heat treatment shows that the crystallinity of the structure increases [11]. With the Debye-Scherrer formula (Eq.1) given below, the average crystallite size for the nickel crystal was calculated as 41 nm [12]. Nickel borides formed after annealed can reduce the

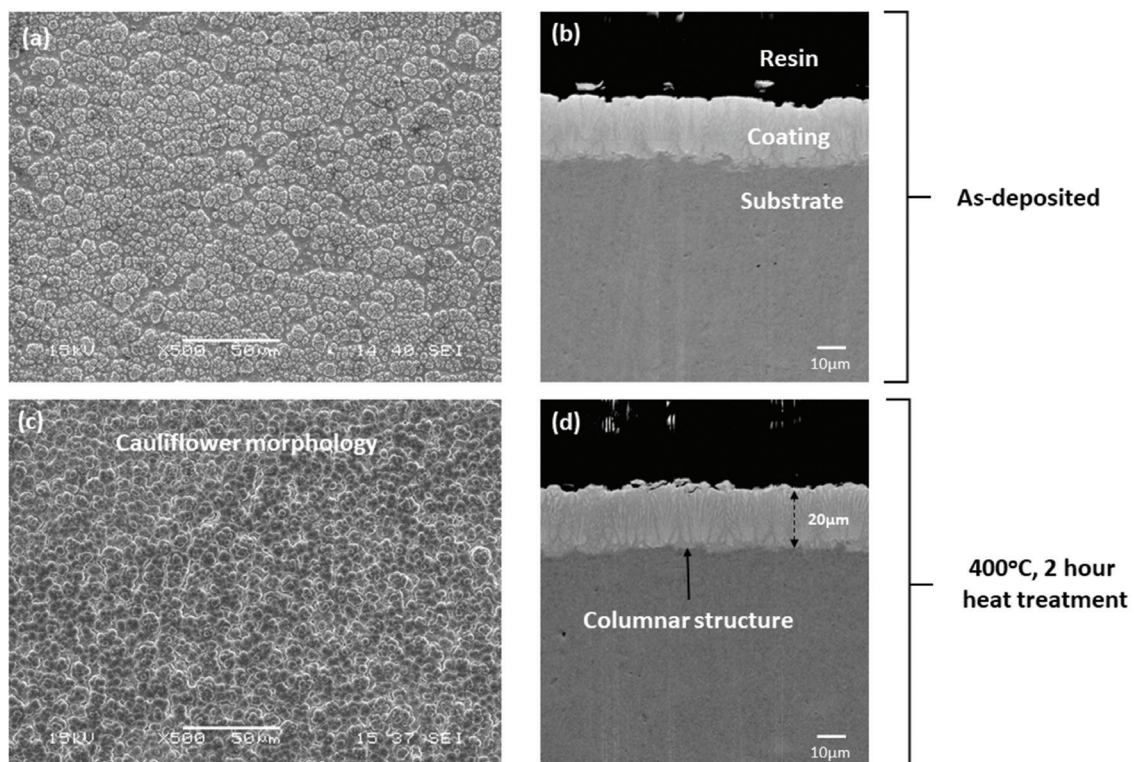


Figure 2. Surface morphology and cross-section images of Ni-B alloy coatings (a, b) as-deposited and (c,d) heat treated, respectively.

crystalline grain boundaries and dislocation areas and make the coating more compact. Thus, increased coating strength can show high wear resistance during friction.

$$d = \frac{0.9\lambda}{B \cos \theta} \tag{1}$$

Where, d is mean crystalline size, λ is X-ray wavelength (0.15418 nm), β is the corrected peak width at half maximum intensity (FWHM) and θ is Bragg diffraction angle. The crystallinity of the coating, which increases because of heat treatment, can be explained by the inhibition of crystal grain growth in the matrix.

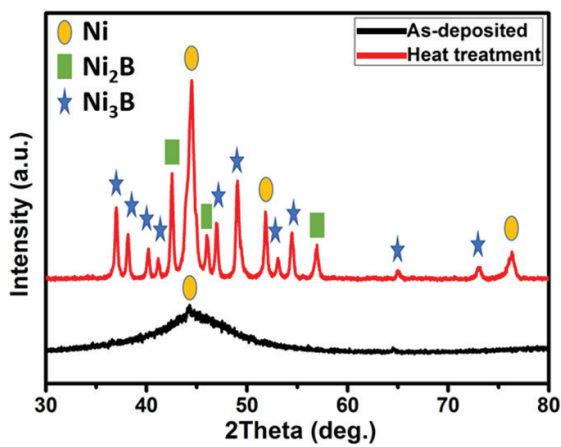


Figure 3. XRD result of Ni-B alloy coating as-deposited and heat treated.

The hardness measurements and load-depth curve performed on the coatings as-deposited and annealed are given in Figure 4, respectively. As can be seen in Figure 4a, the hardness and elastic modulus of the coating after heat treatment was increased significantly. While the hardness of the amorphous coating was 610 HV, it increased to 838 HV with the precipitation of the Ni_3B and Ni_2B crystals. The increase in hardness and elastic modulus can be explained by the precipita-

tion of Ni_3B and Ni_2B phases, which are formed after heat treatment and are compatible with XRD results. Increased hardness after heat treatment increases the wear resistance of the coating surface exposed to wear [13]. Also, the decrease in the grain size of the crystal after heat treatment can be explained by the higher hardness of the coating than the Hall-Petch effect [14]. In addition, the non-porous and dense structure formed on the coating surface improves both the hardness and wear resistance of the coating. The trace images that appear uniformly in the cross section of the coating show the nano-indentation hardness test. Only at the beginning of the loading/unloading plot curve of the test performed under a load of 25 mN for 10 seconds, relatively little curvature is seen. Thus, it can be stated that the samples are not deformed too much. According to the results of the nano-indentation test (Figure 4b), the high indentation depth that occurs when the load applied on the material is removed shows that the material is ductile. It has been observed that the depth decreases with the increase in the hardness of the material after heat treatment. The sample, which showed an elastic structure before heat treatment, became brittle after annealed and increased the coating hardness.

Low and high magnification SEM images of the wear traces of coatings annealed at 400°C for 2-hours and tested at different loads are shown in Figure 5. The wear trace of the sample, which was abraded by applying 1N load (Figure 5a), is more than the other samples. In addition, it is seen that there are more cracks and spills in the wear trace. When the wear trace images are examined, it was observed that the wear trace width was the lowest in the wear with 3N load (Figure 5c). The contact surface area is increased by increasing the applied load to 5N and thus the wear trace width of the coating is increased (Figure 5e). Also, the residual particles formed by increasing the load to 5N increased the wear trace width and roughness [15]. High magnification SEM images were taken from the regions marked with red to examine the wear traces in detail. As seen in Figure 5b, when a 1N load

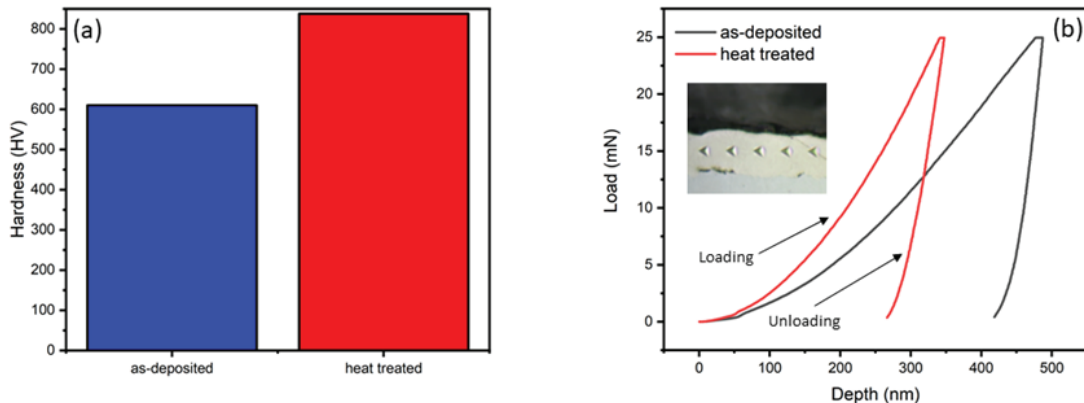


Figure 4. (a) Hardness and (b) load-depth curve for Ni-B alloy coatings as-deposited and heat treated.

is applied to the coating surface, the wear trace observed during the sliding indicates that the coating surface can bear the load. Since nickel is a ductile metal, the boron particles in the matrix are exposed and the load is reduced by the borides in contact with the hard surface. Nickel borides with lubricating properties protect the coating surface against the opposite surface. In addition, nickel crystal and nickel borides facilitate the plastic deformation of the coating. As shown in Figure 5d, when the applied load is increased to 3N, the roughness of the eroded surface has decreased. [16]. Columnar growth increases wear resistance by reducing the actual contact area of the coating. When the applied load is increased to 3N, high contact pressure caused by the increased load leads to an increase in temperature. Thus, the increased oxide layer increases wear resistance.

As seen in Figure 6, EDS analysis in wear traces shows that the Ni and O elements are present in the worn parts. 3N load sample has more O elements on the wear surface than other samples. Severe wear occurs by increasing the applied load to 5N and adhesive wear has occurred in the fragmentation of the wear trace. Since the protective oxide layer starts to break at 5N load and the crystal borides with lubricant properties do not resist sufficiently against the applied load,

the contact area between the coating surface and the opposite surface increases and resulting with high wear. The disruption of the adhesive-induced connection due to chemical interaction between the contact surface causes the formation of local debris particles [17]. As the contact interface temperature increases with increasing the load to 5N, the hardening of the matrix is reduced by the breakdown of the protective oxide layer. Thus, the contact of the load with the soft substrate material causes breaks in the material. Detection of the element Fe, which is the element of the substrate material in EDS analysis (Figure 6), confirms the cracks that occur in wear [18].

The friction coefficients and wear rates of Ni-B coatings abraded at different loads are given in Figure 7. Friction coefficients increased at the beginning of each coating due to surface roughness. Then progressed steadily throughout the wear test. As seen in the figure, the lowest friction coefficient and the lowest wear rate were observed in the abraded coating with 3N load. High volume nickel crystal and crystal borides increase the wear resistance of the coating. Nickel borides formed after heat treatment increase the hardness of the coating, thereby increasing the plastic resistance of the coating. The contact area between the coating surface and the opposing surface decreases

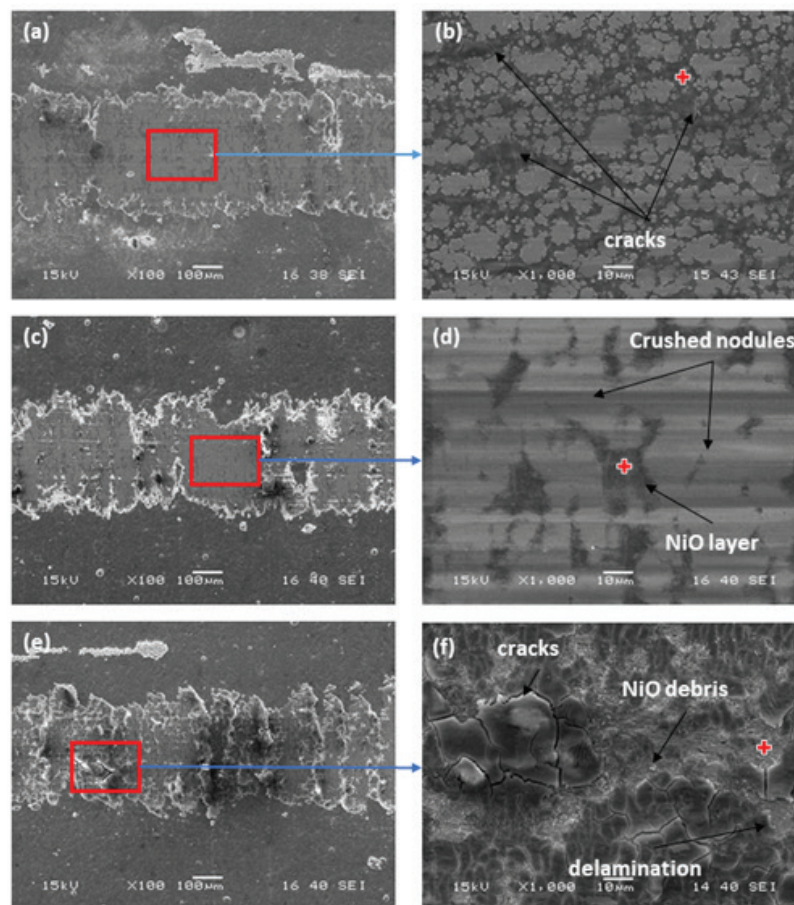


Figure 5. Low (a,c,e) and high (b,d,f) magnification SEM images of wear marks of Ni-B alloy coatings, which are formed as a result of friction tests performed under 1N, 3N and 5N load at room temperature, dry shear conditions, respectively.

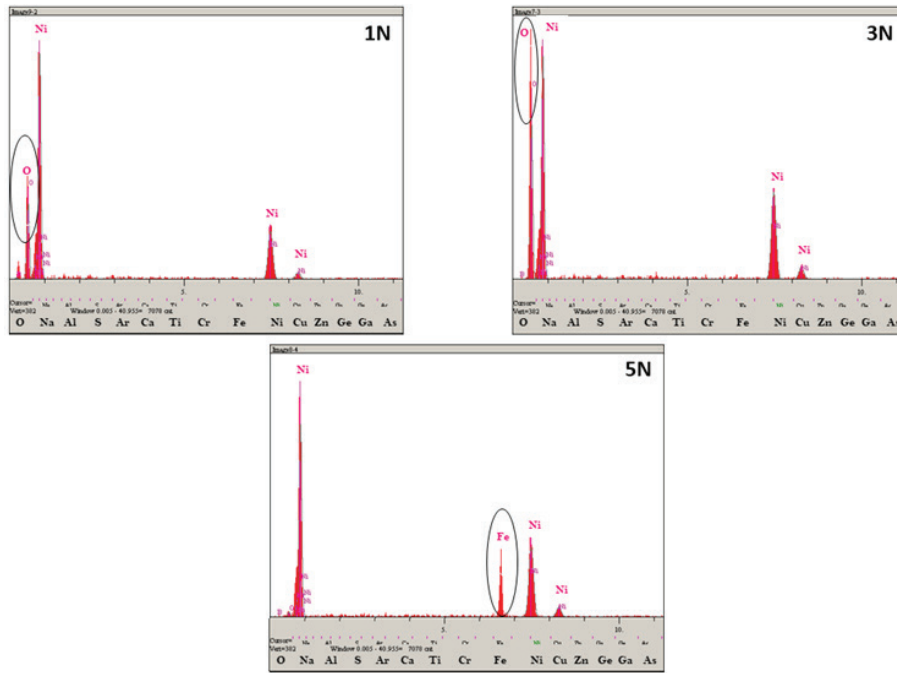


Figure 6. EDS analysis of worn surfaces at different loads, respectively.

and the friction coefficient value of the coating decreases. In addition, as described in Figure 6, the oxide layer formed on the coating surface plays an important role in reducing the contact area. As seen in the figure, when the load applied to Ni-B coatings is increased to 5N, the wear rate and friction coefficient increase due to friction force is more severe. Thus, increasing the load causes the protective tribo-oxide layer to break, cracks to form and increased friction. With the decrease of the plastic deformation in the contact area at 5N load, direct contact occurs between the coating surface and the opposite surface. Also, the volume of the nickel crystal and the presence of nickel boride phases in the adhesive wear mechanism affect the wear of the coating. Increasing the load causes the borides in the matrix to break and an increase in wear rate. Therefore, with increasing the applied load to 5N, because of the high adhesion between the coating surface and the opposite surface, the friction coefficient value of the coating increases [19].

4. Conclusion

Electrodeposited Ni-B coatings were heat treated at 400°C for 1 hour. While nickel crystallized after heat treatment, the deposits in the precipitated state were observed to precipitate the Ni₃B and Ni₂B phases. The mechanical and tribological properties of Ni-B coatings have been improved by the precipitation of Ni₃B and Ni₂B crystals and formation of smaller grain size after heat treatment. The hardness of the coating increased significantly after heat treatment. Increased coating hardness has shown high wear resistance by reducing the contact area between the coating surface and the opposing surface. The increase in coating hardness in heat treated coatings increased the plastic resistance of the coating and reduced the contact area between the coating surface and the opposing surface. When the coating surface is worn with 3N load, the nickel borides and the Ni-O layer formed with the increasing temperature due to the contact pressure during wear increased the wear resistance. By increasing the applied load to 5N, the separations formed by the adhesive wear mechanism on the coating surface and the residual particles increased the wear rate and friction coefficient of the coating. The wear rate and coefficient of friction of coatings that was abraded at room temperature with different loads increased with increasing higher load.

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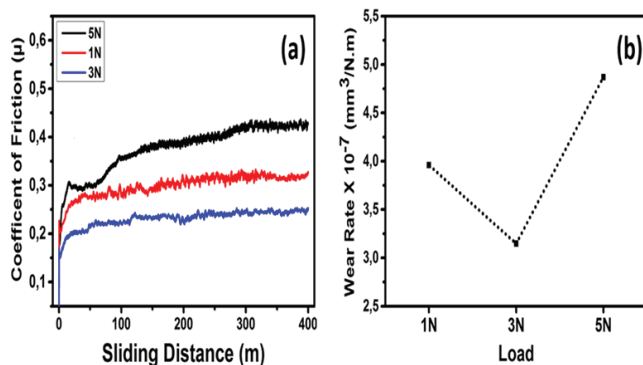


Figure 7. Coefficient of friction and wear rate of coatings abraded in different loads.

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