International Journal of ISSI, Vol. 13 (2016), No. 2, pp. 19-25

Tribological Properties of B_4C-Ni Cermet Coating Produced by HVOF Process on the Surface of 4130 Steel

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Abstract

In this research, B_4C-Ni cermet coating was sprayed on the surface of 4130 steel from B4C and Ni feed-stock powders using high velocity oxy-fuel (HVOF) method. In order to characterize the tribological behavior of the coating, ball on disk wear tests were done at the ambient temperature and under the loads of 1, 3 and 5 N. Phase analysis of the coating after spraying was studied by X-ray diffractometery (XRD). Microstructure of the coating and wear track was evaluated by scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS). The microhardness test was done to measure the hardness of the produced coating. It was found that a good coating with suitable interface and no significant pores and cracks in the microstructure of coatings was formed. The main wear mechanism of the coating was delamination with some oxide layers due to the frictional heat during wear test.

Keywords: B_4C-Ni coating; Microstructure; Wear test; Delamination.

1. Introduction

Several investigations have been done recently on ceramic and cermet composites, for developing wear-resistant parts and high-temperature structural components [1, 2]. Metal-matrix composites reinforced by hard ceramic particles (cermets) also indicate improved mechanical properties as compared with the conventional composites [3, 4]. In addition, bulk cermet and ceramic composites are candidates for commercial applications. There is also a trend to use these composites as coating, especially for decreasing wear and corrosion [5].

It is reported that, In order to enhance the wear behavior of cermet coatings, high toughness and hardness is needed [6-8]. The cermet coatings containing hard ceramic particles such as B_4C, TiB_2, TiC and other particles deliver unique mechanical and corrosion properties like low density, high hardness, the relatively enough ductility and wettability with metal binders [9,10].

Non-oxide ceramic materials, such as B_4C, TiC, and TiB2, have high potential to be used as resisting wear and corrosion components at ambient or high temperatures. B_4C compound has an exceptional hardness, which is the second hard material after diamond and boron nitride. This property is accompanied by other excellent properties such as high melting point, low density and excellent resistance to chemical agents as well as a high neutron absorption cross section [11]. Because of these extraordinary properties, B_4C has been used for lightweight ceramic materials, wear-resistant parts such as blasting nozzles and grinding wheels, and coating materials in the nuclear fusion reactors [12].

However B_4C is very difficult to sinter as a monolithic component even at high temperatures and pressures. As a result, the application of monolithic B_4C ceramic has been limited, and B_4C based composites (cermets) were developed. In recent years, different additives including Al, Mo, C,

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h-BN and TiB_2, have been used into B_4C matrix. By the pinning effect of the secondary phase particles, the grain growth of B_4C is limited during sintering process and the consolidation of the composite is enhanced [13,14].

Several methodshave been used for creating cermet coatings containing hard ceramic particles and metal binders. Among these methods, the thermal spray has been used in several recent investigations. If metals such as Cu, Ni and Al are mixed with B_4C hard particles, heat transfer improves during thermal spraying techniques. Moreover, the high thermal conductivity and excellent ductility of metal can improve tribological properties of the coating. Systems consisting of carbide particles with metallic binders of Ni have been paid much attention due to their excellent combination of wear resistance and high temperature mechanical properties [15].

Lyu et al. [16] studied the wear resistance of Fe-B_4C composite coatings processed by plasma cladding. They reported that wear resistance was largely increased with the deposition of Fe-based coatings. With the existence of B_4C particles, wear resistance increased further. Rejil et al. [17] investigated the sliding wear behavior of AA6360/ (TiC+B_4C) hybrid surface composite layer synthesized by friction stir processing on aluminum substrate. Their study showed that The wear resistance of the coating was superior to that of matrix alloy. 50% TiC+ 50% B_4C hybrid composite exhibited the lowest wear rate due to the formation of tribofilm. The wear properties of Al7075-B_4C composite layer produced by friction stir processing (FSP) on the surface of Al7075 was studied by Rana et al. [18]. It was found that wear resistance improved compared to parent metal. This increase in wear attributed to B_4C particles dispersed in Al matrix and grain strengthening mechanism. Narimani et al. [19] focused on wear behavior of AA6063-B_4C/TiB_2 mono and hybrid composite layers produced by FSP. They studied the effect of different ratios of TiB_2 and B4C reinforcing particles on the microstructure and wear resistance of surface layers. It was found that the 100 % TiB_2 surface composite layer exhibited the highest hardness and best wear behavior in comparison to other fractions. Tribological studies of vacuum plasma sprayed B_4C-Ni composite coatings showed that the dominant wear mechanisms of this coating were a mixture of oxidation and tribofilm wear. In addition, it has been reported that B_4C-Ni coating displays better wear resistance in comparison to B_4C coating due to the higher thermal conductivity of Ni binder [12].

As mentioned before, B_4C is one of the hardest ceramic compounds that can enhance the wear resistance of metallic surfaces, but applying this compound on the metallic surfaces by thermal spraying methods is very difficult due to its high melting point and degradation of this compound at high temperatures. Ni binder can enhance the thermal spray of this compound. Also, lower flame temperature of HVOF method as compared with APS method, leads to lower degradation of B_4C during coating. According to previous studies, it is found that there is no report on the tribological properties of B_4C-Ni cermet coatings produced by HVOF technique. Therefore, in current research the tribological properties of this coating and its main wear mechanism were studied.

2. Materials and Methods

B_4C and Ni powders, with purity of higher than 98 and 99%, respectively, were used as the starting materials. To produce B_4C-20 vol. % Ni cermet powder, the B_4C and Ni powders ball milled for 6 h. The selection of B_4C and Ni percentages was according to the previous studies [12]. The details of MA process and the milling results have been reported elsewhere [20].

Spray drying process was used for increasing the flow rate of powder particles before thermal spraying. This process was done in a home-built spray dryer machine (Malek Ashtar University of Technology, Shahin shahr, Isfahan, Iran). For this purpose, a solution of distilled water and polyvinyl alcohol (PVA) was prepared and then, the composite powders produced by MA process were added to this solution. To create the homogenous slurry, the stirring process was done using a mechanical mixer. Powder to distilled water and PVA to powder weight ratios were 1:10 and 1:100, respectively. The produced slurry was poured in the spray dryer machine. The parameters of spray drying process have been reported elsewhere [20]. 4130 steel is used as mould steel and because of the low wear resistance of it; a coating with hard materials was needed. Coating process was carried out using MET JET III HVOF torch (Metallisation Ltd. at PACO, Isfahan, Iran) on the surface of 4130 steel disk with the diameter and thickness of 50 and 5 mm, respectively. The parameters of the thermal spray process are given in Table 1.

Ball on disk wear tests were carried out using CSM high temperature tribometer. Wear tests were done at the ambient temperature and under the loads of 1, 3

Table 1. The parameters of HVOF process.

Parameter	Value
Nozzle length (mm)	100
Spraying distance (mm)	250
Oxygen flow ($l.min^{-1}$)	750
Carrier gas (nitrogen) ($l.min^{-1}$)	4
Powder feed rate ($g.min^{-1}$)	30
Fuel rate (kerosene) ($ml.min^{-1}$)	240
Spray speed ($m.s^{-1}$)	1000

and 5 N. The selection of these loads was according to the coating thickness and some initial wear tests. The load of 3 N was critical load and two other loads (lower and upper than this critical load) were selected for comparison. The wear radius, sliding speed, and sliding distance were 5.5 mm, 5 $cm.s^{-1}$ and 500 m, respectively. Al_2O_3 with the diameter of 6 mm and the hardness of 2600 HV was used as the ball during wear test. For each sample three wear tests were done for obtaining more valid results. Before wear test, the surface of all samples was cleaned by acetone.

Phase analysis of coating was done by XRD in a Philips X' PERT MPD diffractometer using filtered Cu Kα radiation (α=0.1542 nm) with the degree range of 2θ = 10-100 and the step size of 0.05. The microstructures of the coating and the wear track were characterized by Philips XL30 SEM and EDS and MIRA TESCAN FE-SEM. The porosity of the coating was estimated from the processing of SEM images by ImageJ 1.45 software. 10 measurements were done and the average of these measurements was reported as the porosity number. The microhardness of the coating cross-section was determined by microhardness test using a Vickers indenter at the load of 200 g and the dwell time of 10 s. The average of five measurements for each sample was calculated and reported as the hardness value. The width and depth of the wear track were analyzed using contact surface profilometer (Dektak-6M, Veeco).

3. Results and Discussions

3. 1. Phase analysis and microstructure of coating

Fig. 1 shows the cross-sectional SEM images of as-sprayed coating and corresponding EDS spectrums. The coatings contained fine and coarse hard ceramic particles (gray and dark areas) and Ni binder (light areas). The coarse microstructure was seen in B_4C-Ni coating. The distribution of B_4C hard particles throughout the coating was nearly homogeneous. No significant pores and cracks were observed in the microstructure of coatings. In addition, the coating indicated relatively low porosity due to the presence of Ni binder which increases the heat transfer during spraying. EDS spectrums from spot A indicated that this black particle is B_4C. Also in spot B, Ni, Fe and traces B and C elements were seen, indicating the formation of Ni borides. The formation of Ni borides was approved by XRD analysis in Fig. 2. The presence of Fe element in coating is due to the entrance of this element into powder mixture from steel cup in previous MA process. Table 2 presents a summary of cermet coating properties. This coating indicated a relatively high microhardness of about 620 HV. Shahoo and Masanta [21] investigated the mechanical properties of TiC-Ni coating with the same weight ratio of Ni and TiC produced by TIG process. They reported that this coating indicated high microhardness of about 1330 HV. The higher microhardness of

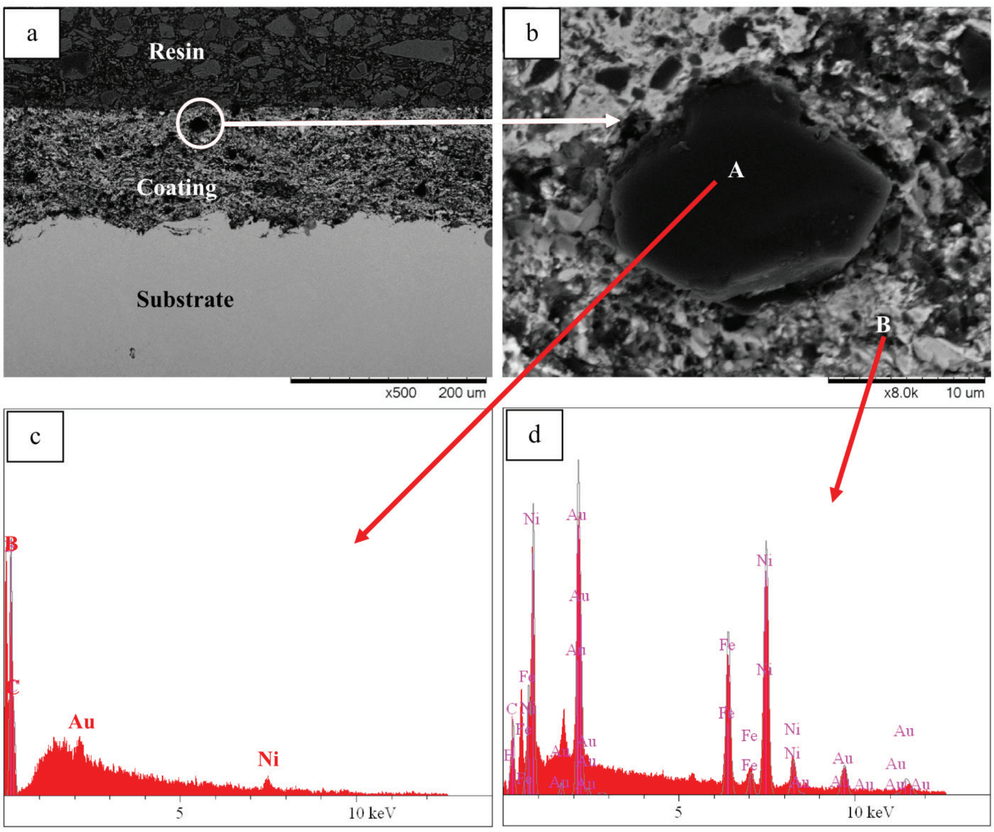

Fig. 1. The microstructure of as-sprayed B_4C-Ni coating (a, b) at different magnifications, (c, d) corresponding EDS spectrums.

TiC-Ni coating as compared with B_4C-Ni coating can be attributed to the stable TiC particles that were not decomposed during deposition, while in B_4C-Ni coating, decomposition of unstable B_4C particles during spraying, led to decrease the microhardness of the coating. XRD pattern of as-sprayed coating is presented in Fig. 2 [20]. As can be seen, XRD pattern of as-sprayed B_4C-Ni coating showed Ni and B_4C peaks. Moreover, some Ni borides (Ni_2B, Ni_3B) were seen. Formation of these Ni borides is due to the B_4C decomposition during HVOF process and the reaction of Ni with B. This indicates that, the B_4C compound is unstable at high temperatures. In B_4C-Ni coating due to the high volume percentage of B_4C phase (80 vol. %) and decomposition of this unstable phase at high temperature of HVOF torch, the intense peaks of Ni borides were seen. Zhu et al. [12] studied the tribological properties of vacuum plasma sprayed B_4C-Ni composite coatings. They reported that due to the reaction between Ni and B4C particles during spraying, some Ni borides (NiB, Ni_2B and Ni_4B_3) were formed which improved the wettability of the carbide phase by the Ni and led to the improvement of the carbide-matrix interface strength. Xibao [22] reported the formation of Fe borides and carbides during plasma transferred-arc (PTA) of Fe-B_4C composite powder, as well.

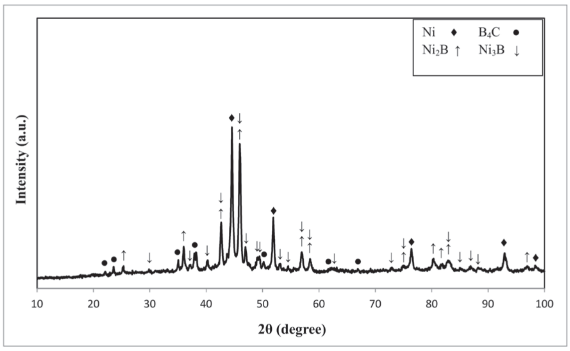

Fig. 2. XRD pattern of as-sprayed B_4C-Ni coating [20].

3. 2. Tribological studies of B_4C-Ni coating

Fig. 3 shows the surface profiles of the wear track and the columnar diagram of wear volume loss versus normal load for B_4C-Ni coating. As shown, with increasing normal load both width and depth of wear track increase, indicating an increase in the wear value with the normal load. In compounds including hard ceramic phases with increasing the normal load, more plastic deformation and tension are occurred under surface, leading to the higher wear value.

Table 2. Characteristics of as-sprayed coating.

Characteristics	Value
Thickness (μm)	115±7.2
Surface roughness, R_a (μm)	12±2.5
Porosity (%)	1.7±0.4
Microhardness (HV)	620±35

Fig. 4 presents SEM, FESEM and the EDS spectrums of wear track and wear particles after the wear test of B_4C-Ni coating under 3 N load. No evidence of abrasive and adhesive wear mechanisms was seen. The presence of network cracks that cause formation of flake-shape wear particles and also the micro-voids on the wear track demonstrate the delamination wear mechanism. Moreover, according to Fig. 4 (f), no evidence of adhesive particles was seen on the wear track counterface (Al_2O_3 ball), showing the adhesive wear has not occurred on the surface of the coating. Zhu et al. [12] reported that the main wear mechanisms in B_4C-Ni cermet coating produced by vacuum plasma spray were oxidation and tribofilm formation. Considering current study it can be concluded that the method of spraying has a great effect on the main wear mechanism of the coating and can change the wear behavior of the material. In addition, jafari et al. [23] investigated the trobological behavior of WC-12Co and WC-17Co cermet coatings produced by HVOF method and reported that the main wear mechanism of these coatings against Al_2O_3 ball was delamination. Weng et al. [24] studied the trobological properties of laser clad Ni-WC composite coating. They reported that by increasing the percentage of WC, abrasive wear raised and adhesive wear decreased, which can be explained that WC particles can reduce adhesive wear. This coating did not show delamination wear mechanism due to the presence of high percentage of Ni phase (over 40 wt.%) that has a great effect on wear behavior of the coating, while cermet coatings including high percentage of ceramic particles (like the present study) shows delamination wear behavior.

In fact, the shear plastic deformation, crack nucleation and its propagation near the surface of coating lead to the activation of delamination wear. At the initial stages of wear test, the surface asperities are plastically deformed and the wear track becomes smooth. With increasing the sliding distance during wear test, dislocations density increases under the surface. The presence of B_4C ceramic particles as the reinforcement in this coating assists in increasing dislocation density. Also as seen in Fig. 1 (b), B_4C particles had irregular shape with sharp angles. This morphology leads to stress concentration around these sharp angles and therefore crack nucleation. Moreover the cracks can nucleate in the B_4C-Ni interface because of the different mechanical properties of these two phases and formation of brittle Ni borides at this area. With plastic deformation of Ni binder around the B_4C particles, the voids are formed. Besides, by joining the cavities, the cracks form parallel to surface. Increasing the crack length over the critical limit leads to the formation of flake-like wear particles.

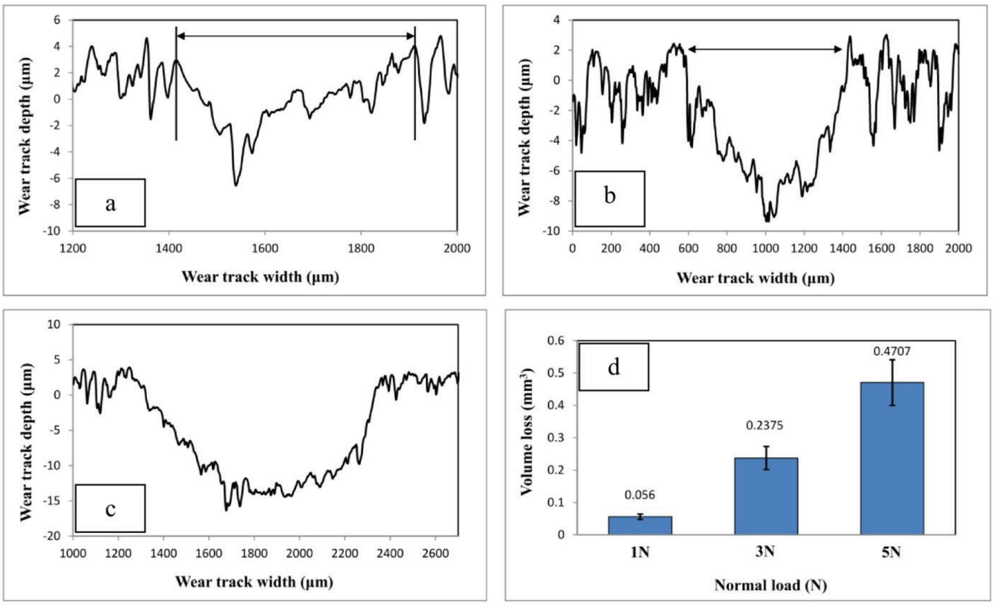

Fig. 3. Surface profiles of the coating wear track under (a) 1, (b) 3 and (c) 5 N loads, and (d) columnar diagrams of wear volume loss versus normal load.

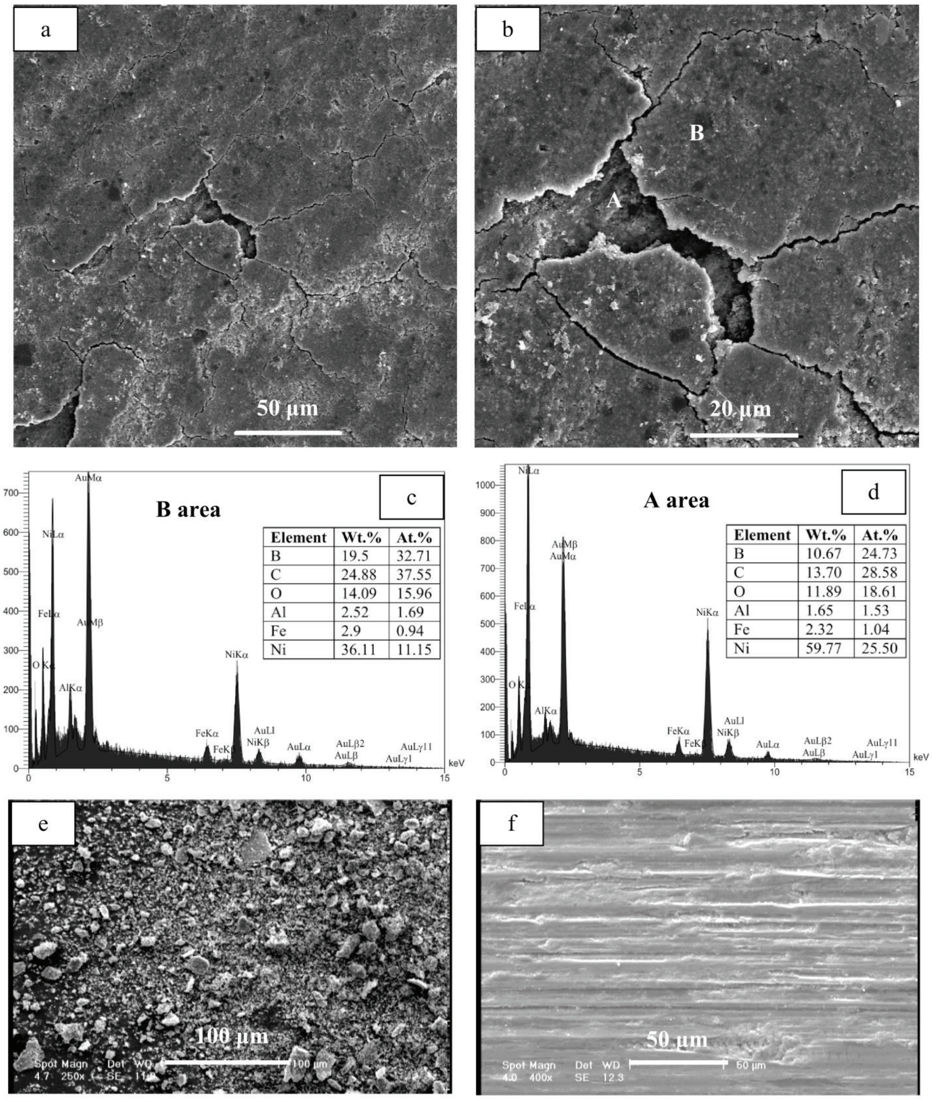

Fig. 4. (a, b) FESEM images of the coating wear track, (c, d) EDS spectrums of the wear track, (e) SEM image of the wear debris and (f) SEM image of Al_2O_3 counterface wear track.

EDS spectrums of wear track in A and B areas indicate the presence of O, B, C, Al, Fe and Ni elements that show surface layers of wear track consist of cermet coating and particles removed from Al_2O_3 ball. This brittle surface layer assists in delamination wear. The amount of elements is different in areas A and B, area B has more oxygen content than area A. The formation of brittle oxide phases at this area helps the occurring of the delamination wear. By removing this layer from the surface, a new surface (point A) includes lower oxygen content forms. These stages have occurred several times, leading to delamination of the surface. Furthermore, the presence of Fe in EDS spectrum stems from the entrance of Fe contamination from previous MA process. The presence of oxygen in the surface layer is due to the frictional heat that can oxidize the surface layer and helps the occurrence of the delamination wear. The formation of fine wear particles occurred during wear test according to Fig. 4 (e). The produced brittle flake-like particles during wear test, stuck between two surfaces and crashedto very fine irregular particles. Zhu et al. [12] studied the tribological properties of B_4C-Ni cermet coatings produced by vacuum plasma spray (VPS). They reported that the main wear mechanisms of this coating against WC-Co ball were oxidation and tribochemical, while in present research the main wear mechanism was delamination. Therefore it can be concluded that the ball material and spray technique have a significant effect on wear behavior.

Fig. 5 indicates the wear track of Al_2O_3 ball after wear test under different loads of 1, 3 and 5 N. As can be seen, by increasing normal load during the wear test, the wear value increased on the surface of Al_2O_3 ball. According to Fig. 5 (d) the predominant wear mechanism on the surface of Al_2O_3 ball was abrasive. The presence of hard B_4C particles in the composite matrix results abrasive wear of Al_2O_3 ball.

The friction coefficients of B_4C-Ni coating at different loads are presented in Fig. 6. As shown, by increasing normal load the friction coefficient slightly decreases. Also, at 1 N load compared with 3 and 5 N loads, lower oscillation was seen in friction coefficient curve. In fact, at 1 N load, the applied normal load on the surface of B_4C-Ni coating is not enough for deformation of asperities, low plastic deformation occurs and a rough surface is created. In other words, at 1 N load, a relatively elastic contact occurs, therefore, high friction coefficient is seen at this load compared with two other loads. By increasing the normal load up to 5 N, plastic deformation of asperities occurred and at longer sliding distance both surfaces will be smooth. Thus, the friction coefficient decreased at higher loads. It has been reported that the friction coefficient for smooth surfaces is lower than rough surfaces at a plastic contact [25]. As before mentioned, with increasing the normal load at this specimen, more wear occurred that creates more wear particles. Therefore, more oscillation is seen on friction coefficient curves. In addition, it has been reported that creating more wear particles at higher loads leads to decreasing the friction coefficient [26].

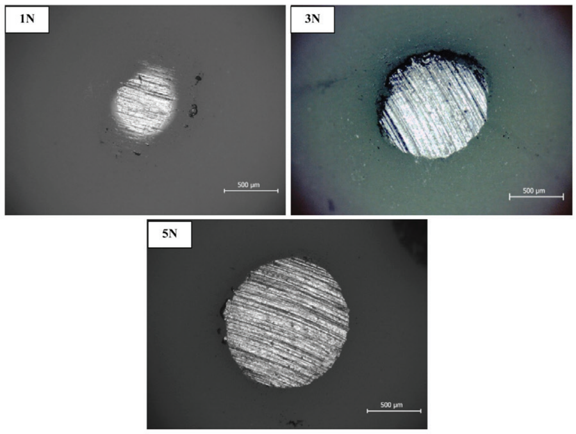

Fig. 5. Optical microscope images of Al_2O_3 wear track at different loads.

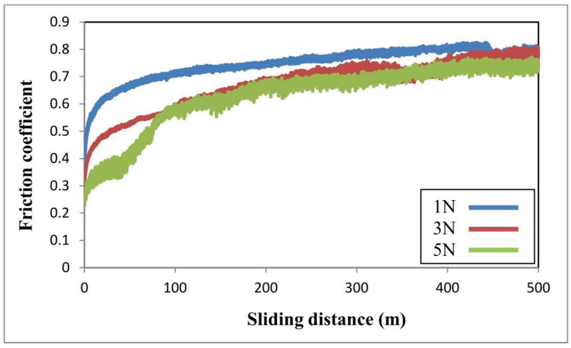

Fig. 6. The curves of friction coefficient versus load for B_4C-Ni cermet coating.

4. Conclusions

In this research the tribological behavior of B_4C-20 vol. % Ni cermet coating produced by HVOF technique was evaluated and the following results were obtained:

- B_4C-Ni cermet coating with no significant pores and cracks, good interface, and relatively low porosity due to the presence of Ni binder that increases the heat transfer during spraying, was successfully formed on the surface of 4130 steel.
- XRD analysis showed that mostly B_4C and Ni, and some Ni borides were formed while coating due to the decomposition of unstable B_4C compound during thermal spraying and the reaction of Ni with B at high temperature of HVOF flame.
- The presence of network cracks that causes formation of flake-shape wear particles, also the micro-voids on the wear track due to the presence of B_4C hard particles, demonstrated the delamination wear mechanism

in the coating with formation of some oxide layers on the wear track caused by the frictional heat.

• By applying the load of 1 N because of lower plastic deformation of asperities and interlocking of asperities, higher friction coefficient was seen. By increasing the normal load up to 5 N, more plastic deformation of asperities due to the higher contact stresses and creating the smooth surface led to the decreasing in friction coefficient of the coating.

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