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Structure and Tribological Characteristics of HVOF Coatings Sprayed from Powder Blends of Cr_3C_2-25NiCr and NiCrBSi Alloy

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HVOF spraying was used to prepare coatings from mechanical blends of Cr_3C_2-25NiCr and NiCrBSi powders. The aim of this study is to study the tribological behavior of coatings prepared from such powder blends. The coatings were studied under dry sliding conditions particularly at high temperatures. Tribological properties of the coatings were characterized using a specific hot-button tribological tester at the temperature of 300 °C in air, and a pin-on-disk test at room temperature. Addition of NiCrBSi resulted in coatings, which showed low coefficient of friction in high temperatures, and in high levels of contact pressure and sliding speed.

Keywords Cr_3C_2-25NiCr coating, HVOF spraying, low friction, sliding wear, tribological properties

1. Introduction

Thermally sprayed hardmetal (Cr_3C_2-NiCr, WC-Co, WC-Ni, etc.) and ceramic coatings (Al_2O_3, Cr_2O_3, etc.) are widely used as antiwear coatings (Ref 1-4). The HVOF process is particularly suitable for deposition of carbide-metal matrix hardmetals (Ref 1, 2, 5). It gives the molten particles high kinetic energy, and thus creates a very consistent microstructure to the coating. Because a Cr_3C_2-25%NiCr coating has good thermal stability and oxidation resistance, it is used in high temperature atmospheres (Ref 4). However, in some tribological applications the friction of the Cr_3C_2-NiCr coating is high even if the coating has good abrasive wear resistance. In such conditions, the coatings are easily worn, particularly under very high contact loads.

One method to lower friction and maintain good abrasive wear resistance is to add some low friction compounds to the hardmetal coating (Ref 6-10). The low friction compound can be a solid lubricant (MoS_2, CaF_2, BaF_2, etc.) or a metal alloy (Ag, Cu, CuNi, etc.). The solid lubricant content has to be high enough to provide lubrication. However, at the same time the solid lubricant lowers the abrasive wear resistance. Owing to this, there is an optimum content of the solid lubricant to provide the best combination of low friction and good abrasive wear resistance (Ref 9).

If the conditions of tribological contact are suitable, the low friction phase can form during sliding in a tribocontact (Ref 11-13). Owing to high local temperatures and pressures the surfaces can react with each other or with the environment and produce solid lubricants at the contact surfaces. Furthermore, some lubricant additives need an activation temperature to adhere to surfaces and to work properly.

In this study, a $Cr_3C_2 + 25NiCr$ hardmetal powder was mixed with a NiCrBSi alloy and HVOF sprayed to form a multicomponent coating. The tribological behavior of the coatings was studied in room and high temperature (300 °C) friction tests. The formation of tribolayers was studied by changing the test time, contact pressure, and sliding speed. Worn surfaces were analyzed with SEM and EDS analyses. In our study, the motivation of using such powder blends was that plain $Cr_3C_2 + 25NiCr$ coatings may wear significantly under high contact loads at high temperatures. The NiCrBSi powder was selected for this research based on experience gathered in a larger research work, in which several carbide powders (WC-CoCr, WC-Cr_3C_2-Ni, Cr_3C_2-NiCr) and several metallic alloys (NiCrBSi, Ultimet alloy, quasicrystalline alloy, Stellite 6, etc.) were studied.

2. Materials and Methods

2.1 Powders and Coatings

Two different powders were used in this study to produce the blend coatings, Table 1. The Cr_3C_2-25NiCr

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Table 1 Powders used to produce the blend coatings

Powder designation	Composition, wt.%
Amperit 584.1 (H.C.Starck)	Cr_3C_2-25NiCr
Diamalloy 2001 (Sulzer Metco)	Ni-17Cr-3.4B-4Si-4Fe-1C

Table 2 Spraying parameters for blend powders

Parameter	Value
Fuel flow, slpm	73
Oxygen flow, slpm	320
Air flow, slpm	360
Spray distance, mm	230
Powder feed, g/min	80

powder was the base powder. It was mixed with a NiCrBSi metal alloy powder, which was used to lower friction in dry sliding. The amount of metal powder in the blend was 15 and 30 vol.%. The blended powders were prepared by weighing correct amounts of the Cr_3C_2-25NiCr and NiCrBSi powders, and by blending these at least for 1 h in a Turbula-type shaker-mixer.

Powders were HVOF sprayed using a Sulzer Metco Diamond Jet Hybrid 2700 HVOF system. The fuel gas used was propane. Standard spraying parameters for hardmetals were used, Table 2. Such a parameter set is appropriate also for the NiCrBSi powder, resulting in adequate melting and deposition. The substrate material was low carbon steel Fe 52. The shape of the specimen was depending on the type of study or test. The substrates were grit blasted with mesh 40 alumina sand before spraying to provide adequate surface roughness.

The microstructure of coatings was analyzed with an optical microscope and a scanning electron microscope (SEM, Philips XL-30 equipped with EDAX DX 4 EDS analyzer). Phase analysis was done with an x-ray diffractometer (XRD, Siemens D-500).

2.2 Tribological Characterization

Tribological properties of the coatings were characterized with two tests, hot-button test and pin-on-disk test. Figure 1 presents the flat contacting faces of the hot-button test samples. In this test, the coatings were tested by a cylinder wear test. The front faces of two cylindrical control bodies (length 25 × diameter 24 mm) were each coated. The coated front faces of the cylinders were pressed against each other by a predetermined normal force N that exerted a predetermined pressure on the surface. One of the test cylinders was then moved back and forth by 45°. The torque that was needed to move the test cylinder was measured, and the friction coefficient calculated on the basis of the torque. The test was carried out at an elevated temperature. In these tests, the temperature was 300 °C, sliding speed 0.01-0.1 m/s and mean contact pressure 10-30 MPa. Plain Cr_3C_2-25NiCr/Cr_3C_2-25NiCr friction pairs were studied only using 10 MPa contact pressures and 0.05 m/s sliding speed, due to the fact that in such conditions and also under more severe conditions the coatings showed too high friction levels and tended to degrade. No lubricant was used in the hot-button tests. The ring sample was coated with blend powder, while the grooved sample was always coated with plain Cr_3C_2-25NiCr with no NiCrBSi addition in the spray powder. Surfaces were polished prior to testing with a diamond polishing additive to an initial surface roughness of Ra 0.45-0.5. Worn surfaces were analyzed by scanning electron microscope (SEM) (Philips XL-30) equipped with an energy dispersive (EDS) analyzer (EDAX DX 4) to reveal the nature of wear particles that were formed during the tribological tests. Additionally, Auger electron spectroscopy was used to study the surface composition (AES surface analysis equipment, University of Turku, Finland).

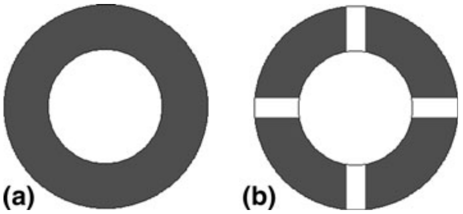

Fig. 1 Sliding contact faces of hot-button test samples. Gray areas are coated and in contact during the hot-button tribological test

In pin-on-disk tests, the disk was coated with a blend coating, but also with the plain Cr_3C_2-25NiCr. The mating surface was AISI 52100-bearing steel ball. Diameter of the ball was 10 mm. No lubricant was used. Normal forces were 12 and 40 N and sliding speeds were 0.5 and 2 m/s. Duration of the test was 300 s. Three different normal force-sliding speed combinations were used: 12 N/0.5 m/s, 40 N/0.5 m/s, and 40 N/2 m/s

A computer measured the friction force during sliding. The wear of the balls was measured with the SEM after tests. Wear of the disks was not quantitatively evaluated in this study; the wear tracks in the coated disks were studied only qualitatively to observe in which coatings the wear was the highest and in which the lowest.

3. Results

3.1 Coating Structure

Figure 2 presents an optical micrograph of a blend coating (Cr_3C_2-25%NiCr + 15 vol.% NiCrBSi). The coating is fairly dense and bonding between the coating and the substrate is good. The coating/substrate interface is practically voidless and uniform. There is some porosity found in the coating structure (partly being real porosity, partly due to some artificial pull-outs from metallographic specimen preparation), but it is well within the limits of typical HVOF sprayed coatings. The existence of NiCrBSi is fairly difficult to be detected by visual examination of the micrograph due to similar optical contrasts of the Cr_3C_2-25NiCr and NiCrBSi particles. However, Fig. 2 shows some areas in which the gray scale is very uniform; these areas are due to NiCrBSi in the structure.

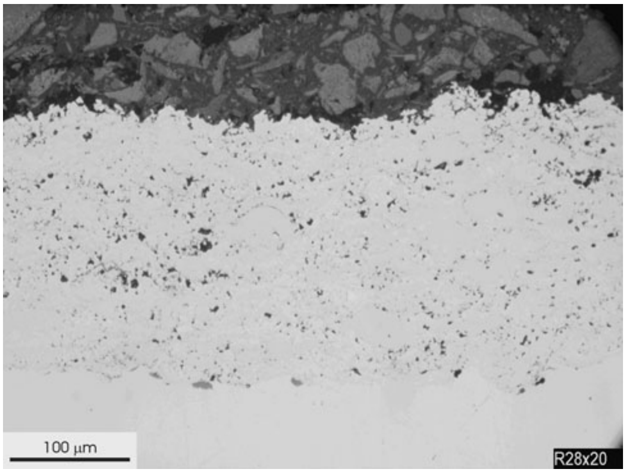

Fig. 2 Optical micrographs of blend coating. NiCrBSi content of the spray powder was 15 vol.%

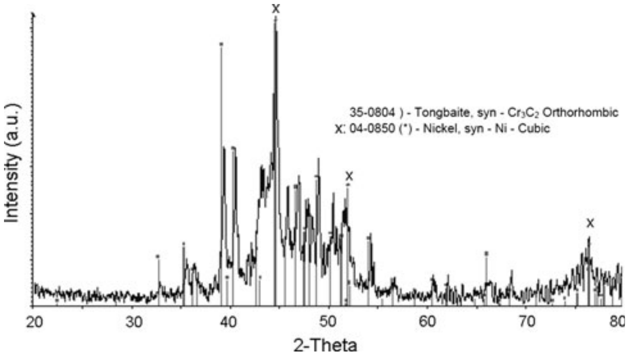

Fig. 3 XRD pattern of Cr_3C_2-25NiCr + NiCrBSi blend coating

The XRD curve in Fig. 3 reveals that the Cr_3C_2-25NiCr powder has maintained its phase structure during spraying. The peaks arising are from the chromium carbide Cr_3C_2, and from the nickel-chromium binder of the cermet powder, and from the main phase of the nickel-based self-fluxing alloy exist in the XRD pattern. It should be mentioned here that peaks from the metallic phases (Ni-Cr and NiCrBSi) seem to overlap each other thus making quantitative analysis of the blended coating practically impossible. Therefore, the approximate compositions of the blended coatings were estimated only by studying the coating cross-sections by optical microscope. These studies confirmed that both powders of the powder blend did build up at reasonably similar deposition efficiencies. Other studies done with WC-CoCr and NiCrBSi powders also confirmed the reliability of such an examination.

3.2 Tribological Properties

Table 3 presents the coefficient of friction (COF) of blend coatings in hot-button tests and surface roughnesses of worn surfaces at different sliding speeds and pressures. The test temperature was 300 °C. It should be mentioned here that in such a specific tribological test, Cr_3C_2-25NiCr coatings without any NiCrBSi addition showed severe scuffing with high friction values. Therefore, no such coatings were further studied and all attention was put on studying the blended coatings. One result in which Cr_3C_2-25NiCr coatings were self-mated is presented in Table 3. This coating showed high friction properties and the surfaces were degraded after the test. This coating pair was not studied in the hot-button tribometer with other more severe conditions.

Table 3 Coefficient of friction (COF) of blend coatings and surface roughnesses of worn surfaces with different sliding speeds and pressures

NiCrBSi content, vol.%	Speed, m/s	Pressure, MPa	COF	Ra, μm
0	0.05	10	0.53	…
15	0.05	10	0.4	0.39
15	0.10	30	0.2	0.75
15	0.03	5	0.6	…
15	0.01	5	0.07-1.2	…
30	0.05	10	0.5	0.51
30	0.05	20	0.4	0.64
30	0.10	20	0.25	0.44
30	0.10	30	0.2	0.81

Temperature in the hot-button tests was 300 °C. Mark "…" refers to high surface roughness due to worn mating surfaces

The test results performed with the blended coatings showed that as the speed and contact pressure increased the COF decreased. However, the content of NiCrBSi did not affect the COF in this study. When sliding speed and contact pressure were at their highest, COF was remarkably low, 0.2, which means that the blend coating exhibited very interesting low friction properties in these conditions. Surface roughness increased slightly as COF decreased, but did not lead to severe failures of the sliding surfaces. This indicates that the surfaces were worn to some degree despite the low COF. Two of the samples, which were tested with 5 MPa normal pressure, had almost seized and their surface roughnesses were not measured.

Figure 4 shows worn surface after 1000 test cycles. The surface was partly covered with large and thin layers. EDS analyses revealed that the layers were oxides of chromium. Otherwise, the surface was ground or polished owing to sliding.

To study the growth of the layers, a test series of increasing sliding cycles was conducted. The blend coating was tested at 10, 20, 50, 100, and 200 cycles. The test parameters were the following: speed 0.1 m/s, contact pressure 30 MPa, and temperature 300 °C. For an unknown reason, the sample that was tested for 10 cycles exhibited a higher COF, 0.4, than other samples. Their COF was 0.2 for the whole test time. Figure 5 shows the surface after 10 and 20 cycles. The surface after 10 cycles was partly covered with metallic layers, which are 50 % Cr and 50 % Ni, and the surface after 20 cycles was pitted. Oxide was not detectable with EDS. Figure 6 reveals that the oxide layers started to form after 50 cycles and were clearly detectable after 100 cycles. Layers grow during the

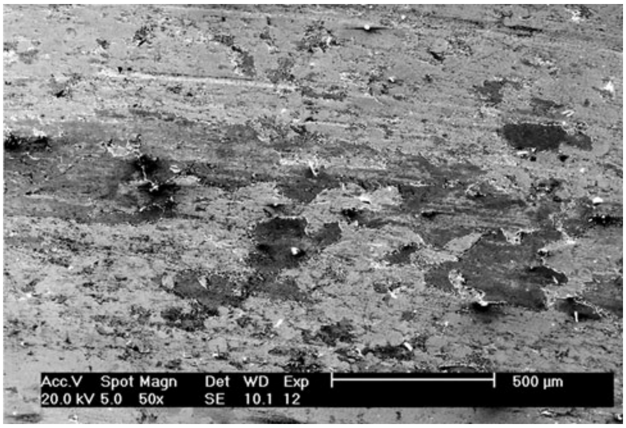

Fig. 4 Surface of blend coating after 1000 test cycles in hot-button test. Surface is covered with large layers of chromium oxide

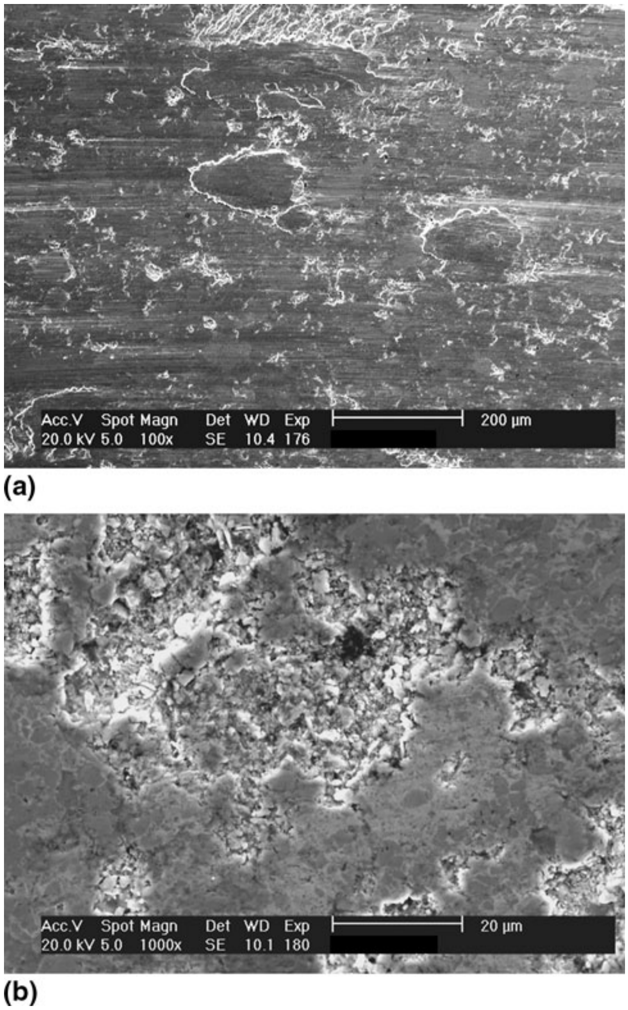

Fig. 5 Surface of blend coating after (a) 10 and (b) 20 cycles of hot-button test. Surfaces are pitted and partly covered with metallic Cr-Ni (50-50%) layers

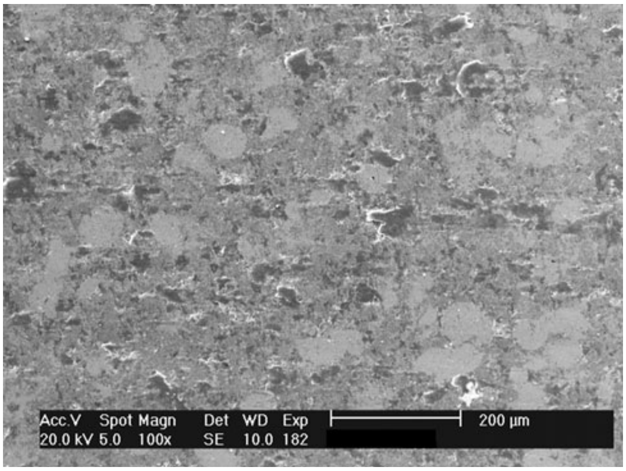

Fig. 6 Surface of blend coating after 50 cycles of hot-button test. Surface is partly covered with chromium oxide layers

Table 4 Chemical compositions of blend coating surfaces after 0, 10, 20, and 50 hot-button test cycles

Cycles	Depth, nm	B	N	O	Si	Ni	Cr	Fe
10	0	7.8	1.6	43.0	1.7	22.7	23.2	0.0
20	0	0.0	20.1	25.0	0.0	28.6	17.9	8.4
20	5	7.1	1.3	13.1	0.6	23.9	38.0	16.0
20	10	6.1	1.4	14.5	0.6	23.8	37.9	15.7
50	0	0.6	15.7	37.8	0.0	7.8	25.0	13.1
50	5	0.6	1.7	27.2	0.0	33.3	34.0	3.2
0	0	10.5	16.8	31.3	0.0	16.0	19.5	6.0

20 and 50 cycle samples were sputtered between analyses to get depth profile of composition

test so that after 200 cycles the surface is largely covered with a chromium oxide layer. At this time layers did not contain a detectable amount of nickel.

Table 4 presents chemical compositions of worn blend coatings. Carbon was found in every sample but the carbon content was left out in the analysis because it is a very common contaminant and the exact amount of carbon is therefore impossible to determine. The most notable constituent is nitrogen content of surfaces. Even the untested surface contains over 15% of nitrogen. Only the surface contains nitrogen since after 15 s of sputtering, which removed about a 5 nm layer of the surface, the nitrogen content decreased to less than 2%. The surface, which exhibited a high COF did not contain nitrogen remarkably. The oxygen content of surfaces was also high, but that was expected since surfaces are bound to oxidize during sliding. Also the iron content was higher than the iron content of powders.

In pin-on-disk tests, the blend coating did not exhibit significant low-friction properties, apparently due to a low temperature of the test, Fig. 7. It is expected that no clear friction reducing tribolayers are formed in such low

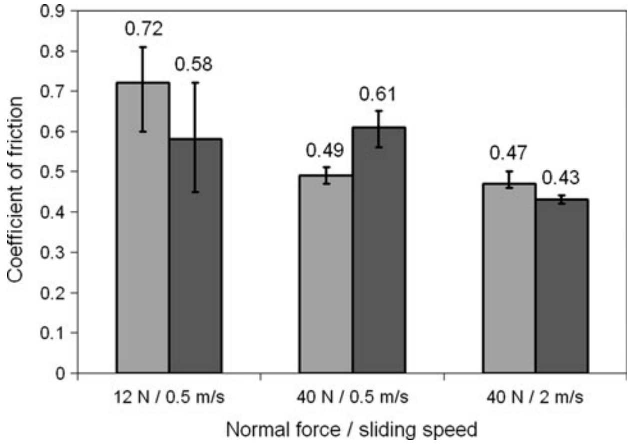

Fig. 7 Coefficients of friction of Cr_3C_2-25NiCr and Cr_3C_2-25NiCr + NiCrBSi coatings in pin-on-disk test. Counter surface was AISI 52100 bearing ball steel. Left column: Cr_3C_2-25NiCr; right column: Cr_3C_2-25NiCr + NiCrBSi

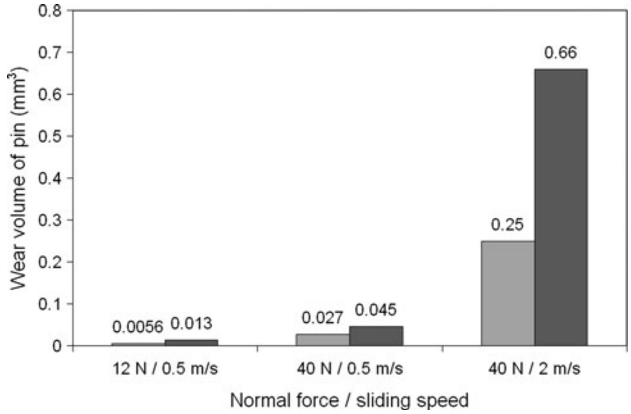

Fig. 8 Wear volume of pin surface in pin-on-disk test. Pin material was AISI 52100 bearing ball steel. Disks were coated with Cr_3C_2-25NiCr and Cr_3C_2-25NiCr + NiCrBSi blend. Left column: Cr_3C_2-25NiCr; right column: Cr_3C_2-25NiCr + NiCrBSi

temperature sliding conditions. The COF of both Cr_3C_2-25NiCr and Cr_3C_2-25NiCr + NiCrBSi decreased when normal force and sliding speed were increased. However, there was no difference between the coatings.

Figure 8 shows wear of the pin in pin-on-disk tests. Although the COF of the coatings were the same, adding NiCrBSi to coatings increased the wear of the pin dramatically. Also the increase of normal force and sliding speed increased pin wear. The wear of the disk was not quantitatively measured, but according to qualitative evaluations of the wear tracks of the disks, the coating that contained NiCrBSi seemed to wear more.

4. Discussion

Adding of NiCrBSi to Cr_3C_2-25NiCr coating was successful in obtaining low friction behavior of such blended coatings, particularly in the specific hot-button test tribometer. Mechanical mixing was enough to prepare the blend powder, which was used to spray the blend coating with HVOF. The coating was fairly dense and bonding between coating and substrate was good. The coating/substrate interface was practically voidless and uniform. Detecting the existence of NiCrBSi in the Cr_3C_2-25NiCr coating was found to be fairly difficult by visual examination of the micrograph due to similar optical contrasts of the Cr_3C_2-25NiCr and NiCrBSi particles. However, optical microscope studies revealed that there are areas of NiCrBSi in the structure, which roughly corresponds to that in the feedstock material.

At high temperature and with high contact pressure and sliding speed NiCrBSi decreased coefficient of friction of the coating. In such a specific tribological test, Cr_3C_2-25NiCr coatings without any NiCrBSi addition showed severe scuffing with high friction values. No such coatings were further studied and all attention was put on studying the blended coatings. The test results performed with the blended coatings with 15 and 30% NiCrBSi showed that as the speed and contact pressure increased the COF decreased. However, the content of NiCrBSi did not affect the COF in this study. When sliding speed and contact pressure were at their highest the COF was remarkably low, 0.2, which means that the blend coating exhibited very interesting low friction properties at these conditions. Surface roughness increased slightly as COF decreased, but did not lead to severe failures of the sliding surfaces. This indicates that the surfaces were worn to some degree despite the low COF. No differences were found between coatings having 15 or 30% NiCrSiB. We believe that it is the formed tribolayer that drastically influences the friction behavior of the mating surfaces, and the content of NiCrSiB does not play such a significant role that the differences could be seen in the hot-button tribological test. The most important result of the study is that adding some NiCrBSi in the Cr_3C_2-25NiCr coating so drastically changes the high-temperature tribological properties of these coatings and allows application of the coatings in conditions where high surface pressure levels are present.

At room temperature and with low contact pressure and sliding speed the COF remained at the same level as with the pure Cr_3C_2-25NiCr coating. This proves that the decrease of COF is a result of a tribochemical reaction that is catalyzed by high temperature, speed, and pressure. The low-friction tribolayer forms at the beginning of the test, since the friction coefficient is low at the beginning and does not change during the test. Although the chromium oxide layers form during the test, it can be assumed that chromium oxide is not causing the low friction at the beginning of the test.

An Auger study revealed that the nitrogen content of surfaces is high even before the test. The amount cannot be explained with contamination. Probably nitrogen is due to pre-treatment of the surface or a reaction with the surface and nitrogen in air. It is not adsorbed during the tribochemical reaction because the surface that was not tested contained nitrogen. However, influence of nitrogen on COF is remarkable. The surface after 10 cycles did not contain nitrogen and the button exhibited higher COF than other buttons. It is hard to tell what the exact composition of the nitrogen-containing compound is. It probably contains also iron since its content is also high on the surface.

The increase of surface roughness in conjunction with a decrease of COF indicates that the reaction, which decreases the friction, wears the surface of the coating. The micrograph of the worn surface after 20 cycles shows that large platelets have worn out and the surface is pitted. The surface is worn selectively. NiCrBSi and NiCr matrix particles detach from the surface and form large platelets between surfaces. After being pulled out, the wear particles form low-friction tribolayers between the mated surfaces. Surface roughness also has an influence on the wear of the counter surface. NiCrBSi increased wear of the AISI 52100 pin in the pin-on-disk test. A coating that contains NiCrBSi is softer than pure Cr_3C_2-25NiCr and therefore it also seemed to wear more during sliding according to qualitative evaluation of the wear tracks of the disks.

5. Conclusions

HVOF spraying was used to prepare coatings from mechanical blends of Cr_3C_2-25NiCr and NiCrBSi powders. The aim of the study was to study the tribological behavior of coatings prepared from such powder blends. The coatings were studied under dry sliding conditions particularly at high temperatures. Tribological properties of the coatings were characterized using a specific hot-button tribological tester at the temperature of 300 °C in air, and a pin-on-disk test at room temperature. Addition of NiCrBSi resulted in coatings that which showed low coefficient of friction in high temperatures, and in high levels of contact pressure and sliding speed.

The friction of a HVOF sprayed Cr_3C_2-25NiCr coating can be decreased by mixing the hardmetal powder with a small amount of soft low-friction powder prior to spraying. The amount of low-friction alloy is not significant assuming the amount is enough to provide a protective tribolayer on the surface of coating surface. The decrease of friction seems to be a result of tribochemical reaction, which takes place in high temperature, high pressure, and high sliding speed. In room temperature, the COF is not clearly affected by NiCrBSi addition. Worn surfaces contain a high amount of nitrogen, which also may play a significant role in forming the low-friction layer between mated surfaces.

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