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Effect of TiB_2 Additives on Wear Behavior of NiCrBSi-Based Plasma-Sprayed Coatings

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The influence of titanium diboride additives on microstructure and wear resistance of NiCrBSi thermally sprayed coatings deposited on a steel substrate has been studied. NiCrBSi-based composite powders with 10, 20, 40 wt.% TiB_2 particles content were produced. The structure of NiCrSiB-TiB_2 coatings consists of TiB_2 and CrB grains distributed in Ni-based matrix. The wear resistance of NiCrSiB-TiB_2 plasma sprayed coatings in dry sliding conditions against the same coating using pin-on-disk tester. It was determined that the amount of titanium diboride particles in NiCrBSi-based coatings influences essentially on the wear resistance and wear mechanism. The NiCrBSi-based plasma sprayed coatings containing 20 wt.% of TiB_2 possess the high wear resistance due to the realization of mechanical-oxidation wear mechanism.

Keywords: self-fluxing alloy, titanium diboride, plasma-sprayed coating, wear resistance.

1. INTRODUCTION

In recent the tendency to considerable increase of temperatures, speeds and loads of technical equipment operation is observed. Therefore, modern high-performance machinery and mechanisms require surface protection against wear. As consequence, different types of protective coatings have been widely used to improve surface properties and extend the service life of machine parts.

In the field of surface engineering the thermal spray techniques, such as high velocity oxy fuel (HVOF), plasma and detonation spray, are the most popular and effective to deposit refractory carbides, borides, hard oxides, metals and their composites [1].

Among the variety of materials, the nickel-based self-fluxing alloys have been used traditionally as protective coatings in many fields of engineering application because of their high level of wear and corrosion resistance. Up to now many research studies have been done about the spraying technology, microstructure and properties of Ni-based self-fluxing alloys [1–6].

Ni-based self-fluxing alloys contain chromium, boron, silicon, carbon and iron in different proportions [1, 4, 5]. As it is known, the structure of NiCrBSi spray coatings consist of the Ni-based matrix and carbo-borides (Ni,Fe)(B,C), nickel borides, chromium carbides ($M_{23}C_7$, Cr_7C_3) and borides (CrB, CrB_2) and nickel silicides dispersed in it [4]. During operation the grains of hard borides and carbides take a load and increase a wear resistance, the plastic Ni-based matrix distributes the stresses and prevents the brittle failure of coatings. However, in many applications, the NiCrBSi spray coatings do not have sufficient wear resistance. The comparative study of thermally-sprayed coatings under different wear conditions was performed by S. Houdkova et al [6]. It was found that at high stress and speed in sliding wear condition and in abrasive wear condition plasma and HVOF-sprayed NiCrBSi coatings have shown the lowest wear resistance compared with WC – 17 % Co, WC – 10 % Co 4% Cr, Cr_3C_2 – 25 % NiCr, WC – 10 % Co 4 % Cr, (Ti,Mo)(C,N) – 18.5 % Ni 18.5 % Co. On the one hand, the sizes and amount of hard borides and carbides in the coating structure is too small to put up effectively the resistance as for the action of abrasive particles. On the other hand, at high stress and speed in metal-to-metal sliding wear condition the NiCrBSi coating surface deformation occurs that results in adhesion fracture. High wear of thermal sprayed NiCrBSi coatings at extreme wear condition is also mentioned in [7–9].

The wear resistance of nickel-based self-fluxing coatings can be substantially improved by reinforcement with refractory materials. As a rule, the tungsten and chromium carbides have been more often added to metal coatings to improve their tribological performance [7–10]. The catastrophic oxidation of tungsten carbide at high temperature (700 °C) and shortage of tungsten restrict a wide application of WC as reinforcement additives. The metal-matrix coatings with Cr_3C additives have worse wear resistance then that with WC and TiB_2 reinforcements. It has been determined that Ni(Cr)-TiB_2 coating deposited by HVOF technique is more wear resistant than HVOF-sprayed Ni(Cr)-Cr_3C coating [10].

Titanium diboride is expected to be one of the best reinforcements for Ni-based self-fluxing coatings because of its high hardness ($33 \pm 2 \cdot 10^6$ Pa), low density (4.52 g/m^3) and high melting point (2900 °C) [11, 12].

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This investigation has been carried out to understand the wear behavior of the NiCrBSi-based plasma spray coatings with TiB_2 additives in dry sliding conditions against the same coating. The main goal of this study is to determine the influence of TiB_2 additives content on the wear rate and wear mechanism of the coatings above.

2. EXPERIMENTAL DETAILS

In the present study three grades of NiCrSiB-TiB_2 composite powder with 10 wt.% (NTB10), 20 wt.% (NTB20) and 40 wt.% (NTB40) of TiB_2 particles content were produced for plasma spraying. Commercially available titanium diboride (98.7 %, 2 – 3 μm) and NiCrBSi (Ni – a base, Cr – 16 %, Si – 3.2 %, C – 0.72 %, B – 2.7 %, Fe < 5 %, 30 – 32 μm) powders were used as initial materials to prepare NTB composite powders.

The NiCrBSi and TiB_2 powders weighted in desired proportion were mixed in alcohol medium. The mixed powders were pressed in a bulk, sintered then in vacuum for 30 min. The sintering temperature depends on the TiB_2 content in a mixture and is equal to 900 °C for NTB10, 1100 °C for NTB20 and 1400 °C for NTB40 composite.

The sintered bulk composite materials have heterogeneous structure consisting of the matrix, the latter being reinforced with the borides inclusions. It has been found that during sintering process chromium interacts with boron that leads to formation of CrB grains of 10 – 20 μm in size (Fig. 1 a, Point 1). Their microhardness is equal to 20 – 26 GPa. The grains of titanium diboride of 2 – 3 μm in size (Fig. 1 a, Point 2) are also uniformly distributed in Ni-based matrix (6 – 7 GPa) alloyed with titanium, silicon, chromium and iron (Fig. 1 a, Point 3).

The sintered NTB composite materials were crushed and classified as for a powder of size range (60 – 100) μm for plasma spraying. The particles of NTB powders are conglomerates containing both Ni-based matrix and grains of hard borides (Fig. 1 b).

The NiCrBSi and NTB composite coatings were deposited on the steel surfaces using UPU-3D-M plasma installation. The spraying parameters were the such ones: spray distance 150 – 160 mm, spray current 450 – 500 A, plasma gas flow rate 2.6 – 3.2 m^3/h. Prior to spraying the steel surfaces were cleaned and subjected to grit blasting. The interfacial layer of nickel-aluminium material was deposited to increase an adhesion of coatings to steel surface. The average thickness of obtained plasma coatings is 500 μm.

The sliding pin-on-disk friction and wear tests were performed using CETR UMT Multi-Specimen Test System. A stationary pin was fixed on the upper holder to slide against the flat disk.

All cylindrical pins of 15 mm long were fabricated from 5 mm diameter steel wire. The size of counterpart steel disc was 40 mm in outside diameter and 10 mm in thickness. The friction surfaces of pin and disk were plasma sprayed with NTB composite coatings. In the experiment the dry sliding wear behavior of the NTB10-NTB10, NTB20-NTB20 and NTB40-NTB40 friction pairs were studied. For comparison, the wear resistance and friction coefficient for NiCrBSi plasma-sprayed coatings were determined under the same conditions.

The samples were polished to a surface roughness of Ra 0.5 μm. Before the friction-wear test the specimens were ultrasonically cleaned for 2 min in acetone to remove any possible surface contaminants.

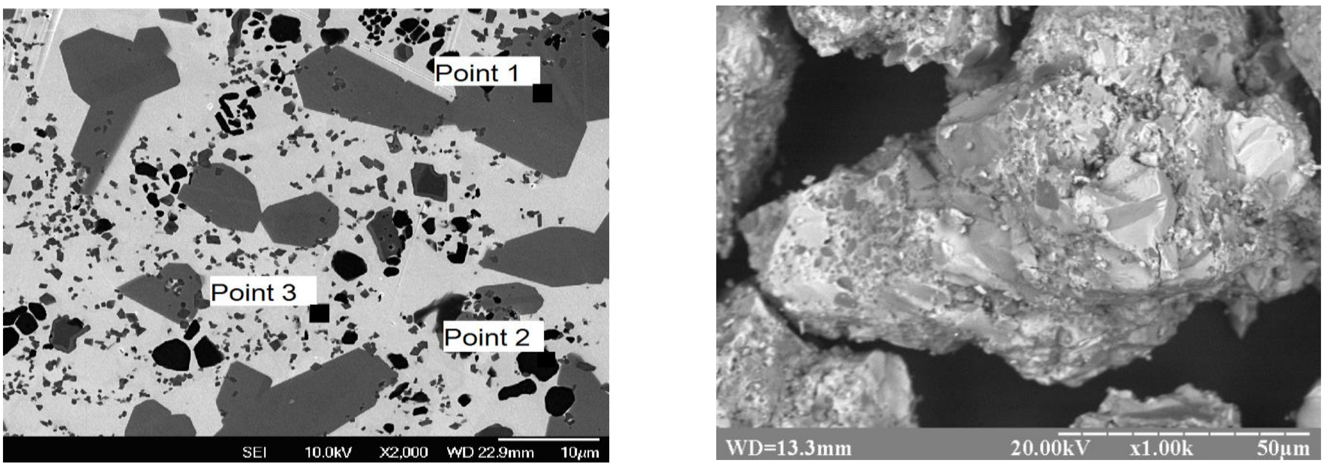
Before each test the working surfaces of the pins were preliminary run-in just against SiC abrasive sheets which were fixed on the flat disk surface. This treatment was performed using 400/800 and 2400 grit paper. Running-in against each grit type of abrasive paper had two minutes duration, normal load was 0.2 N and rotation speed was 60 rpm.

The wear tests were performed at ambient temperature without lubrication. The constant normal load applied to the pin was 0.8 N, while the sliding distance was 678 m with the velocity of 0.5 m/s.

Finally, the wear tracks were investigated using electron scanning microscopy (SEM) in order to investigate the wear mechanisms.

3. RESULTS AND DISCUSSION

The NTB plasma-sprayed coatings have heterogeneous structure which is very similar to that of NTB bulk composite materials (Fig. 2).



a b

Fig. 1. a – structure of NTB20 composite material; b – morphology of NTB20 powder

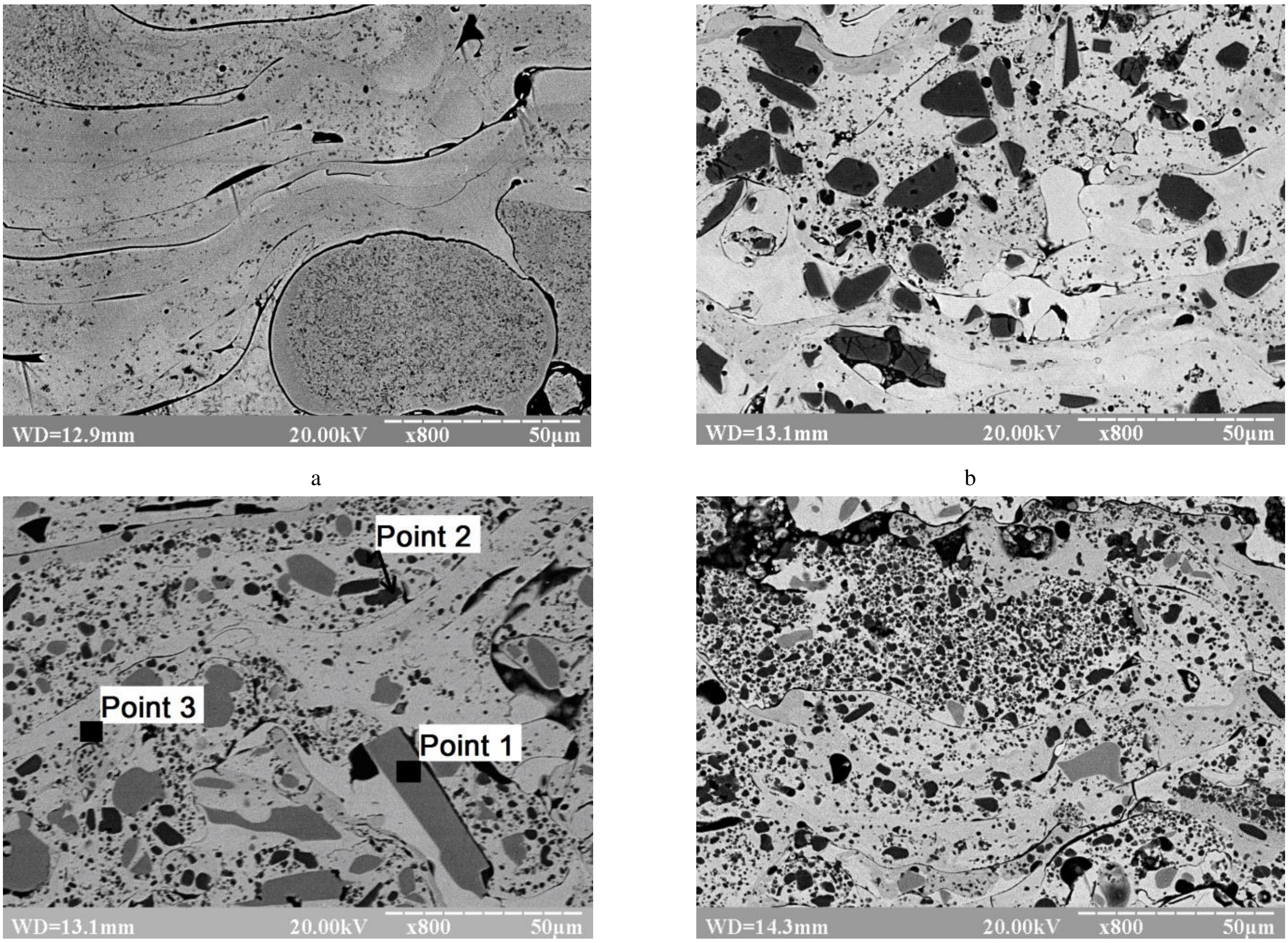


Fig. 2. Microstructure of plasma-sprayed coatings: a – NiCrBSi; b – NTB10; c – NTB20; d – NTB40

The structure of NTB coatings represents itself the metal matrix reinforced with hard boride particles. The grey colour phases reaches up to 20 μm in size and correspond to chromium boride grains (Fig. 2 c, Table 1, Point 1). Their microhardness is equal to 20 – 26 GPa. The black grains of titanium diboride are of 2 – 3 μm in size that corresponds to initial size of TiB_2 powder (Fig. 2 c, Table 1, Point 2). Microhardness of Ni-based matrix alloyed with titanium, silicon and chromium and iron is equal to 6 – 7 GPa (Fig. 2 c, Table 1, Point 3).

Table 1. Chemical composition of NTB20 plasma-sprayed coating according to EDS analysis

Point	B	C	Si	Ti	Cr	Fe	Ni
1	14.5	1.01	0.00	1.1	79.9	1.2	2.3
2	28.0	0.9	0.00	69.6	0.6	0.3	0.6
3	2.2	0.6	2.7	2.4	1.8	3.4	86.9

The wear rates of investigated plasma sprayed coatings calculated for steady stage of sliding are shown in Fig. 3. The NiCrBSi-NiCrBSi friction pair exhibits higher wear rate of 70 μm/km and the lower friction coefficient of 0.58 comparing with NTB coatings. Fig. 4 a shows the worn surface of NTB pin after the wear test. In the wear track the signs of plastic deformation and the scars of sliding surfaces damages in the form of adherings and tears are observed. It means that adhesive wear mechanism is dominant for dry sliding friction of the NiCrBSi-NiCrBSi couple.

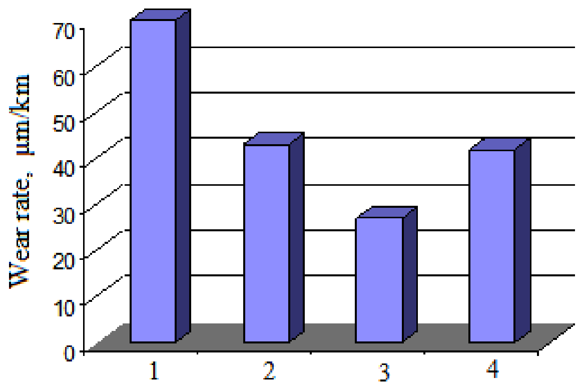


Fig. 3. Wear rate of friction pair: 1 – NiCrSiB-NiCrSiB; 2 – NTB10-NTB10; 3 – NTB20-NTB20; 4 – NTB40-NTB40

The poor adhesive wear resistance of NiCrBSi can be concerned with not high enough strength, high ductility and relatively low temperature of surface softening. During dry sliding friction process the temperature in contact area increases that promotes the NiCrBSi coatings surfaces intense plastic deformation and adhesive seizure.

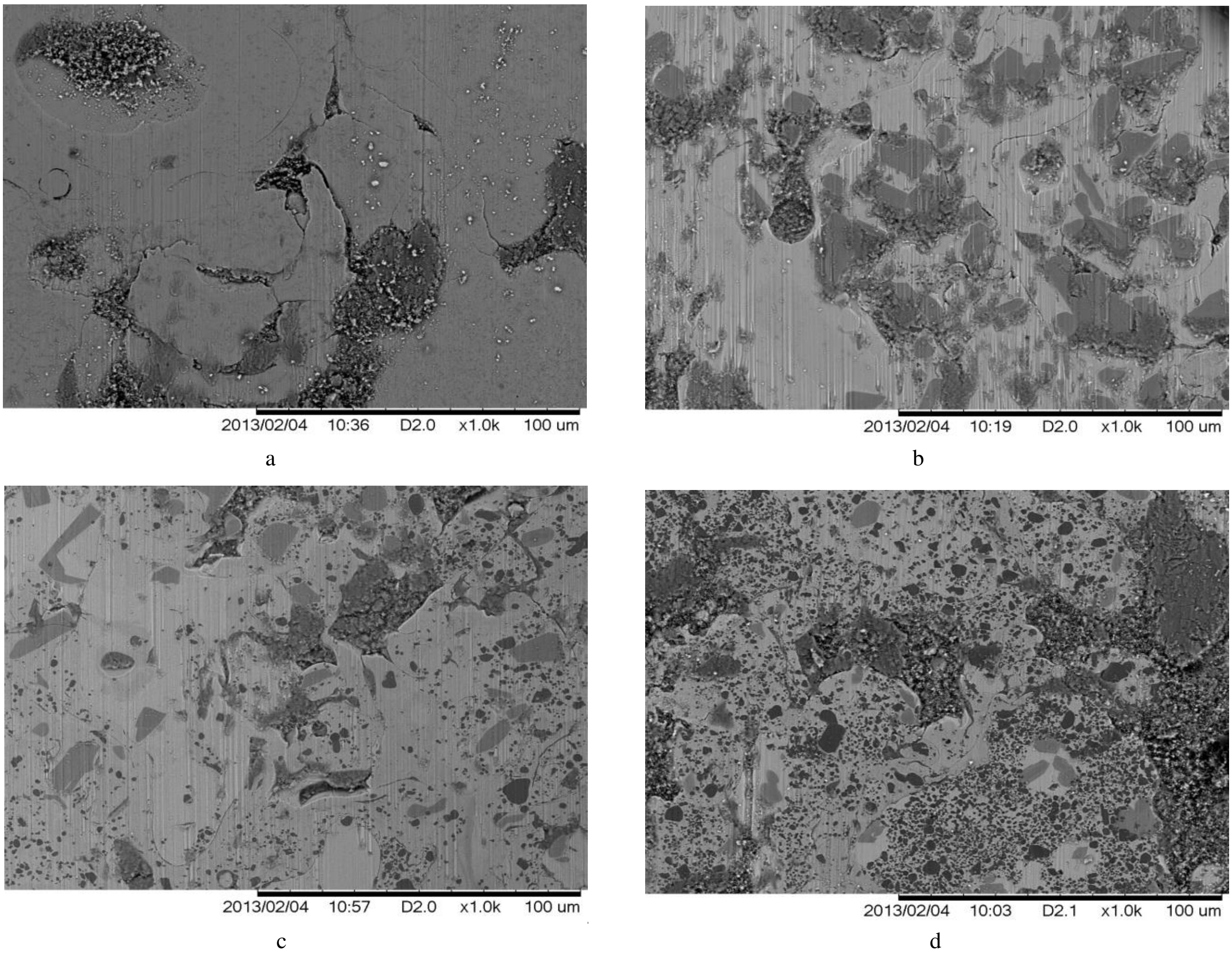


Fig. 4. SEM images of the worn surface of plasma sprayed coatings after pin-on-disk test: a – NiCrSiB; b – NTB10; c – NTB20; d – NTB40

As it has been mentioned earlier, the size and content of hard phases in NiCrBSi coatings are too small to protect friction surfaces against adhesion interaction.

The insertion of 10 wt.% titanium boride into the NiCrBSi alloy results in the increase of plasma sprayed coating wear resistance and friction coefficient. The specific wear rate of NTB coatings is equal to 42 μm/km. The value of friction coefficient rose gradually during test, and the average value of μ is 0.68. The wear track of NTB coatings on the pin after test can be seen in Fig. 4 b. Worn surface of NTB10 coating contains signs of adhesive interaction and brittle failures.

The subsequent increase of TiB_2 content in nickel-based self-fluxing alloy up to 20 wt.% promotes a decrease of friction coefficient value down, approximately to 0.63. In contrast with the data of other NTB plasma sprayed coatings, the NTB20-NTB20 friction pair has lower wear rate of 24 μm/km. It can be seen from the Fig. 4 c, that the NTB20 pin worn surface proved to be smooth, without sings of adhesive seizure.

The sliding of NTB40 coatings against the same NTB40 coatings was characterized by value of friction coefficient of 0.58. However, the specific wear rate of NTB40 plasma sprayed coating of 40 μm/km is higher in comparison with NTB20 coating. The worn surface of NTB40 pin comprises a lot of cracks and wear debris particles.

The developed NTB plasma sprayed coatings have the heterogeneous structure consisting of nickel-based matrix, the latter being reinforced with the borides inclusions (Fig. 2). Because of difference in the hardness and wear resistance, the hard grains of TiB_2 and CrB protrude slightly from the matrix after grinding. On the one hand, the hard TiB_2 and chromium boride grains take the load during the sliding, preventing coatings surfaces intensive plastic deformation and adhesion interaction. On the other hand, the titanium diboride and chromium boride grains are responsible for the complex oxide phases formation on the NTB coatings surface which further behaves like a protective and lubricative film eliminating the chances of severe material loss [13]. The formation of oxide films in contact region promotes the friction coefficient value decrease and prevents from coatings surfaces adhesive seizure. In the case of NTB10 friction pair the hard boride phases content is not enough to protect contact surfaces effectively against an adhesive wear. At first the major wear mechanism of the plasma sprayed NTB10 coatings was connected with the adhesive interaction of metal matrixes resulting in ruptures occurrence and hard phases pull-out from the coatings surfaces. The wear debris contains the nickel-based alloy particles as well as TiB_2 and chromium boride grains. Getting to contact region they serve as abrasive medium relative to coatings surface that leads to abrasive wear. Therefore the wear mechanism of

NTB10 plasma sprayed coatings changes from adhesion to abrasive. In this case the oxide films does not play a significant role in the coatings wear behavior.

As it has been mentioned above, the NTB20 friction pair has the low wear rate, and there are not significant failures of coatings surfaces after test. The wear behaviour of NTB20 coatings can be explained in the following way. The plasma sprayed coating NTB20 is characterized by the uniform distribution of hard boride and carbide grains in a metal matrix. So, the oxide films are also formed uniformly on the coatings surface and protect them effectively from the adhesive interaction. The relatively high hardness of TiB_2 and chromium boride grains, strongly fastened in a metal matrix, as well as tribo-oxidation prevent from wear of these coatings. Therefore, the mechanical-oxidation wear proved to be the main wear mechanism of NTB20 composite coatings.

The worn surface of plasma sprayed coatings NTB 40 contains a great amount of hard boride phases taken parts in the tribo-oxidation. The more intensive formation of oxide compounds on the NTB40 friction surface results in a decrease of friction coefficient value in comparison with NTB20 coatings. However, the wear rate of NTB40 coatings is higher than that for NTB20 coatings. The wear process of NTB40 friction pair is accompanied by brittle cracking of coatings material and hard phase grains pull-out from the coatings surface that leads to the abrasive medium occurrence in a contact region (Fig. 4 d). The wear resistance of coatings is also determined by properties of wear debris. In the case of NTB40 coatings the abrasive particles have the same or higher hardness then the coatings material. Therefore they cause the severe damage of coatings surfaces and promote the increase of coatings brittle failure and wear rate. Hereby, the tribooxidation and abrasive wear proved to be a dominant wear mechanism for the NTB40 tribo-couple.

4. CONCLUSION

Thus, as a result of study carried out it has been determined that introduction of TiB_2 additives into NiCrBSi alloy contributes to the increase of plasma sprayed coatings wear resistance. The amount of titanium diboride particles in composite coatings influences essentially on the wear mechanism, wear resistance and friction coefficient in self-mating friction pair. Adhesive and abrasive wear mechanisms are found to be responsible ones for the wear down of NiCrBSi-based composite coating reinforced with 10 wt.% of titanium diboride. The NTB plasma sprayed coatings containing 20 wt.% of TiB_2 possess the highest wear resistance without the surface cracks because of the realization of mechanical-oxidation wear mechanism. The increase of TiB_2 particles content in the NiCrSiB-based coating up to 40 wt.% makes it brittle and results in the abrasive wear mechanism occurrence.

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REFERENCES

1. **Das, A.C.** Stereometric Analysis and Relation Between the Porosity of Sprayed and Sintered NiCrSiB Plasma Spray Protective Coating *Journal of Materials Processing Technology* 101 2000: pp. 322 – 331. http://dx.doi.org/10.1016/S0924-0136(99)00475-6
2. **Wu, Y.S., Zeng, D.C., Liu, Z.W., Qiu, W.Q., Zhong, X.C., Yu, X.Y., Li, S.Z.** Microstructure and Sliding Wear Behavior of Nanostructured Ni60-TiB2 Composite Coatings Sprayed by HVOF Technique *Surface and coatings technology* 206 2011: pp. 1102 – 1108. http://dx.doi.org/10.1016/j.surfcoat.2011.07.096
3. **Pawlowski, L.** The Science and Engineering of Thermal Spray Coatings. Wiley, Chichester, 1995.
4. **Lin, M.C., Chang, L.S., Lin, H.C., Yang, C.H., Lin, K.M.** A Study of High-Speed Slurry Erosion of NiCrBSi Thermal-Sprayed Coating *Surface and Coatings Technology* 201 (6, 4) 2006: pp. 3193 – 3198.
5. **Zhao, W., Wang, Y., Dong, L., Wu, K., Xue, J.** Corrosion Mechanism of NiCrBSi Coatings Deposited by HVOF *Surface and Coatings Technology* 190 (2 – 3) 2005: pp. 293 – 298.
6. **Houdkova, S., Zahalka, F., Kasparova, M., Berger, L.** Comparative Study of Thermally Sprayed Coatings Under Different Types of Wear Conditions for Hard Chromium Replacement *Tribological Letters* 43 2011: pp. 139 – 154.
7. **Niranatlumpong, P., Koiprasert, H.** Phase Transformation of NiCrBSi–WC and NiBSi–WC arc sprayed coatings *Surface and Coatings Technology* 206 (2–3) 2001: pp. 440 – 445.
8. **Sari, N. Y., Yilmaz, M.** Improvement of Wear Resistance of Wire Drawing Rolls with Cr–Ni–B–Si + WC Thermal Spraying Powders *Surface and Coatings Technology* 202 (13, 25) 2008: pp. 3136 – 3141.
9. **Chen, H., Xu, C., Qu, J., Hutchings, I.M., Shipway, P.H., Liu, J.** Sliding Wear Behavior of Laser Clad Coatings Based Upon A Nickel-Based Self-Fluxing Alloy Co-Deposited with Conventional and Nanostructured Tungsten Carbide-Cobalt Hardmetals *Wear* 259 (7 – 12) 2005: pp. 801 – 806.
10. **Hazoor, S., Sidhu, B., Sidhu, S., Prakash, S.** Wear Characteristics of Cr_3C_2–NiCr and WC–Co Coatings Deposited by LPG Fuelled HVOF *Tribology International* 43 (5 – 6) 2010: pp. 887 – 890.
11. **Matkovich, V.** Boron and Refractory Borides. Springer-Verlag, New-Yourk, 1977.
12. **Horlock, A.J., McCartney, D.G, Shipway, P.H., Wood, J.V.** Thermally Sprayed Ni(Cr)–TiB2 Coatings using Powder Produced by Self-Propagating High Temperature Synthesis: Microstructure and Abrasive Wear Behavior *Materials Science and Engineering* 336 (1 – 2) 2002: pp. 88 – 98.
13. **Umanskyi, O., Hussainova, I., Storozhenko, M., Terentyev, O., Antonov, M.** Effect of Oxidation on Sliding Wear Behavior of NiCrSiB-TiB_2 Plasma Sprayed Coatings *Key Engineering Materials* 604 2014: pp. 16 – 19. http://dx.doi.org/10.4028/www.scientific.net/KEM.604.16