TRIBOLOGICAL PROPERTIES AND WEAR MECHANISMS OF WEAR RESISTANT THERMALLY SPRAYED COATINGS

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ABSTRACT

Several different HVOF thermally sprayed coatings were determined to find out their abrasion wear resistance and mechanisms with respect to their mechanical properties and microstructure. Two types of cermets, WC-17%Co, Cr_3C_2-25%NiCr and NiCrBSi and 316L coatings were examined. The aim of this work was to investigate the influence of coating microstructure on abrasive wear behavior and also with regarding their fracture toughness measured by nanoindentation fracture toughness (IFT) method. In case of thermally sprayed coatings evaluation it is necessary to take into account their unique lamellar microstructure and other characteristics such as hardness, Young modulus of elasticity or fracture toughness, porosity, cohesive strength, oxide content etc. The abrasive wear performance of the coatings was assessed using a dry/sand rubber wheel test according to ASTM G-65, wet slurry abrasion test according to ASTM G-75 and pin-on-disc test according to ASTM G-99. In all cases alumina was used as an abrasive medium. Wear mechanisms were assessed by SEM examination of the wear surfaces in the middle of the wear trace and understood in terms of the different coating microstructures.

Keywords: Wear*, wear coefficient, cermets, abrasion, HVOF, thermal spraying, indentation fracture toughness (IFT)*

Introduction

Thermal spraying is an expanding area within the technology of surface engineering. It is a process that involves the deposition of molten or semi-molten droplets of powder onto a substrate to form a coating. In high velocity oxy-fuel (HVOF) thermal spraying, oxygen and fuel gas flow at high pressures and flow rates with internal combustion to produce very high particle velocities with relatively low temperatures compared with other thermal spray process such as air or vacuum plasma spraying [1]. As a result, HVOF has a capability for producing dense coating with low degrees of decomposition which are well bonded to the substrate.

A wide range of material can be thermally sprayed for a variety of applications ranging from gas turbine technology to the electronics industry. Applications include protection from wear, high temperatures and chemical attack. Carbide-based cermets including tungsten carbide (WC) and chromium carbide (Cr_3C_2) are commonly used for wear resistant coatings. Coating performance is strongly dependent on the coating microstructure, which in turn is dependent on the characteristic of the starting powder from which the coating is formed and the spray process parameters employed. It has been reported that an estimated 50% of all wear problems in industry are due to abrasion. Four commercially used materials were examined in this study to find out its ability to resist to abrasive wear in different wear conditions.

Experiment

Materials and methods

Four types of commercially available materials were used in the present study. Table 1 shows a general overview of powder composition, size etc. All coatings were deposited on grit blasted mild steel substrates using HP/HVOF JP-5000® (TAFA) spray equipment in SKODA Research Ltd. Details of the spraying parameters and procedures employed in the spraying of the coatings can be found in [2].

Powder type	Chemical formula	Size (µm)	Trade name	Supplier
Agglomerated and sintered	83%WC-17%Co	15-45	FST K-674.23	Flame Spray Technologies
Agglomerated and sintered	75%Cr_3C_2-25%NiCr	15-45	1375VM	PRAXAIR
Gas atomized	Ni 17Cr 4Fe 4Si 3.5B 1C	20-53	FST M-771.33	Flame Spray Technologies
Gas atomized	Stainless Steel 316L	22-53	FST M-684.33	Flame Spray Technologies

Table 1 Nominal powder characteristic

Abrasive wear testing

The abrasive wear behavior of the coatings was examined using modified dry sand-rubber wheel (ASTM G-65) method described in detail in [3,4], wet slurry abrasion testing was done in slurry of alumina particles in water (ASTM G-75) and pin-on-disc test was done using alumina ball indenter in accordance with (ASTM G-99). The size of the abrasive particles employed for dry test was in the range 212-250 µm. The size used for wet conditions was in the range 40-50 µm. In both cases white alumina as an abrasive was used. The test conditions for all tests are given in Table 2. All tribology wear tests are described in more detail in [9].

Indentation fracture toughness (IFT)

The fracture toughness was assessed on polished cross sections of the coatings using Vickers indenter under the load of 200 N on Scratch tester CSAM equipment. The K_{Ic} values were calculated in accordance with LEM theory reported in [8].

Test parameter	Dry abrasion	Wet abrasion	Pin on disc
Abrasive media	Al_2O_3 flow rate 440 g/min	50 wt. % Al_2O_3 with 50 wt.% water	alumina ball, 6 mm diameter
Test loads	22 N	20 N	10 N
Test distance or cycles	1436 m	9216 m	50 000 cycles
Mass loss measurements	287 m intervals	2304 m intervals	at the end of test
Number of test specimens per coating	3	4	3
Dimension of specimens	76 mm x 25 mm x 5 mm	25 mm x 15 mm x 10mm	25 mm diameter x 5 mm

Table 2 Abrasion wear parameters

Results

Coating microstructure

The as-received coatings were examined using SEM to identify their microstructure and surface morphology before testing (Fig. 1). The surfaces of tested coatings before testing were not grinded with exception of specimens for pin-on-disc test which were polished to surface roughness R_a 0,2.

The surface morphology of WC-Co coating (Fig. 1a) shows a relatively homogeneous structure. The size of WC particles is in the range of 0,5-3,5µm with particles size achieving predominantly the higher values of this range. The carbide phases seem good anchorage in cobalt matrix. The coating produced had no evidence of cracks or another discontinuity. Relatively low degree of porosity can be observed in these coating after spraying. For Cr_3C_2-NiCr coating, there are some changes in surface morphology. Particularly the relative larger size of the carbide particles in the range of 1,1-6,5µm can be observed. The individual splats seem to be good bonded one to another. No cracks on the coating surface can be observed. The XRD patterns obtained from surface of the as-deposited cermets coatings are shown in (Fig. 2). It can be seen that as-sprayed coatings show a very low degree of decomposition of primary WC and Cr_3C_2 phases. The very broad peak at Cr_3C_2-NiCr coating indicates a formation of an amorphous and/or fine grained phase which was observed in WC system as well. However, the amount of these phases is negligible. The similar conclusion for this type systems has been reported by other authors [5,6].

As-sprayed NiCrBSi coating has low size of precipitates that also exist in the powder feedstock. Porosity value is under 1%. In some cases, imperfectly unmelted particles are built-in coating and surrounding melted particle can be observed (Fig 1.c). That has a significant influence on interlaminar bonding strength and mechanical behaviour at wear tests. The CrB, Cr_7C_3 and Ni_3B are ordinary most frequently phases occurring in coating after spraying [7]. The size of these precipitates ranged from around 0,23-1,7 µm. However, its volume fraction in coating is in comparison with volume fraction of carbides in cermets substantially lower. Surface morphology of 316 L coating is shown on (Fig 1.d).

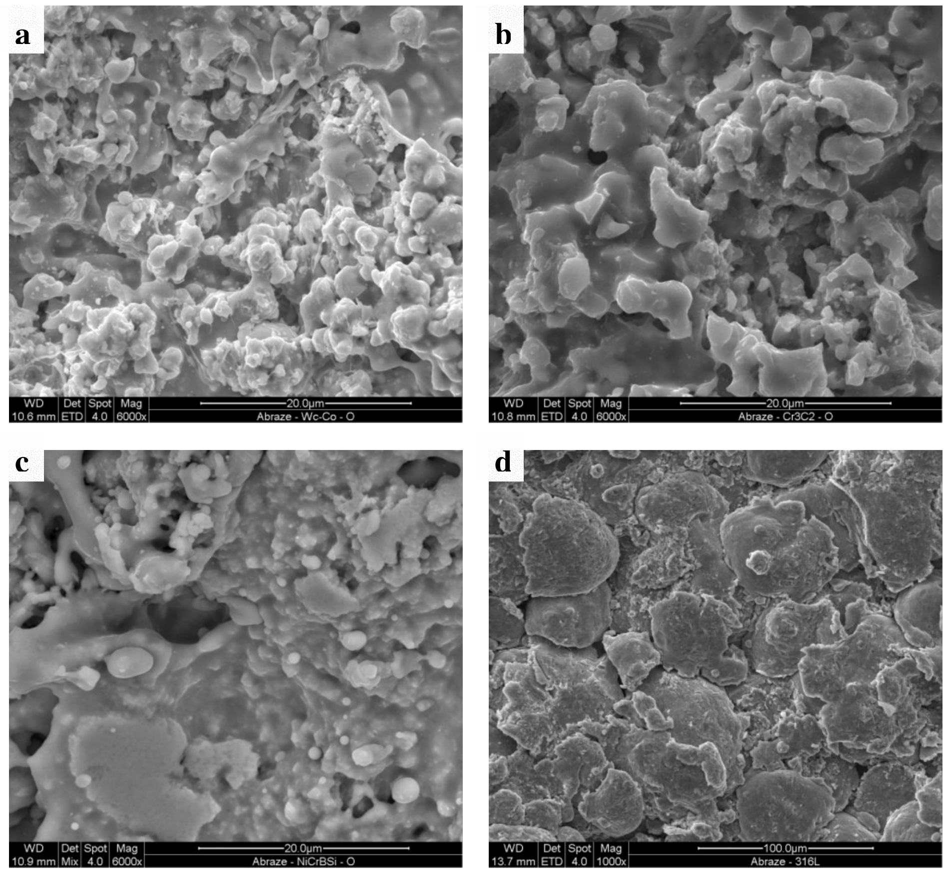

Figure 1 SEM images of the as-sprayed coatings surface morphology a) WC-Co, b) Cr_3C_2-NiCr, c) NiCrBSi and d) 316L steel, before wear testing.

Different shape of individual splat after impact during spraying process can be clearly seen. The temperature during spraying process is relatively low, to reduce the oxidation of sprayed particles. Due to the fact, one can observe relative deflection from the standard shape (Fig.1d). Nevertheless, this shape has a negligible influence on the mechanical properties of the coating. For this type of coating, no evidence of hard phases in microstructure can be seen.

Coating	Porosity	Microhardness HV0,1	Thickness [μm]	Fracture toughness Klc [Mpa. $m^{1/2}$]
WC-Co	<1%	1248±53	442,34±10,85	3,188
Cr_3C_2-NiCr	<1%	984±96	433,42±9,41	1,672
NiCrBSi	<1%	735±65	379,60±12,22	3,13
316L	<1%	329±33	427,32±12,53	0,86

Table 3 Coatings mechanical properties

Microhardness and abrasive wear

Dry and wet abrasion test

The mean microhardness values obtained from the top of the polishing coating surface are given in Table 3. The value of hardness for individual coatings is important for abrasive wear resistance according to Archard´s law described by the equation (1) and will be discussed further. Volume loss measurements for test load 22 N in dry abrasion showed that the WC-Co coating was, in general, most wear resistant and exhibited lower volume loss rates. The same results can be observed for wet slurry conditions as well. It has been reported, that resistance against abrasion wear is strongly influenced by strength of carbide particles themselves, bonding with the binder phase and the content of the carbide. Taking into account above mentioned phenomenon results in different wear mechanism and volume loss (Fig. 4.) in dependence on the material of the coatings. At three - body dry abrasion conditions the indentation of the abrasive tips predominantly takes place. This effect is significant particularly at dry conditions where rolling of the particles takes place. A different wear mechanism at wet conditions occurred. Water or other fluids may affect the wear of a material by a number of mechanisms, primarily as agents of lubrication and/or corrosion.

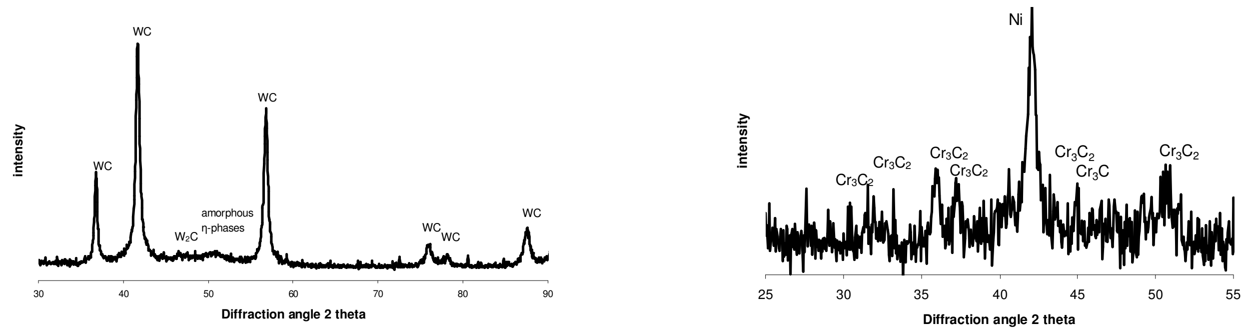

Figure 2 The X-Ray diffraction patterns of WC-Co and Cr_3C_2-NiCr HVOF thermally sprayed coating using JP-5000 gun, with low degree of phase transformation

The role of lubrication and corrosion in abrasion of materials in aqueous environments is reported in [10]. The main effect observed in this study was that the aqueous career was acting as a lubricant and modifying the mechanics of the abrasive particle contact. Morphology of the worn surfaces after dry sand abrasion test is shown in (Fig. 3.). For cermet coatings, the major wear mechanism is the binder removal followed by the pulling-out of carbides (Fig. 3.a) as a result of decreasing the bond strength of the carbides and the metal matrix.

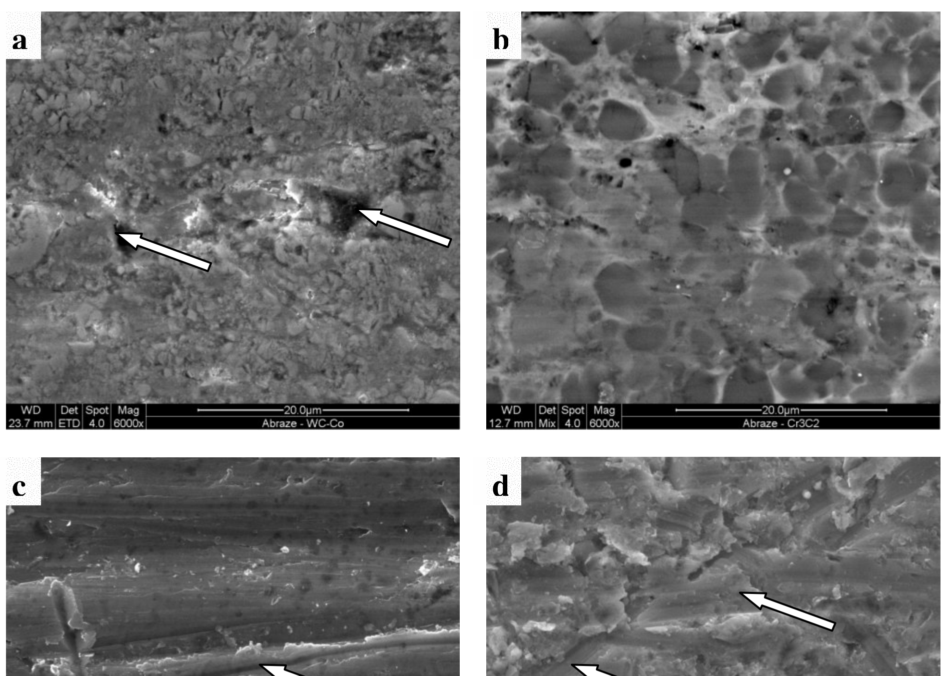

Fig. 3. SEM images of worn surfaces after dry sand abrasion test at a load 22 N using 212 -250 µm alumina particles a) WC-Co, b) Cr_3C_2-NiCr, c) NiCrBSi and d) 316L steel thermally sprayed coatings.

However, brittle cracking of large carbide particles and/or failure caused by the fatigue and grooving with material loss as a result of the fracture can occur as well. The abrasive wear depends on the ratio of hardness of abrasive particles and of the cermets. Results obtained for Cr_3C_2-NiCr are in good agreement with Archard´s law. In compliance with this equation the wear is inversely proportioned to the hardness of material. The measured hardness for coatings is shown in (Table. 3) and correspondence with results of tribological tests in accordance with following equation:

$$V = K\frac{F*l}{H} \quad (1)$$

Where *V* is volume loss, *F* is load, *l* is distance and *H* is hardness of the material of the individual coating. The lowest value of wear resistance was measured for NiCrBSi and 316L steel respectively. Their lower hardness is caused by the absence of the hard phases in material.

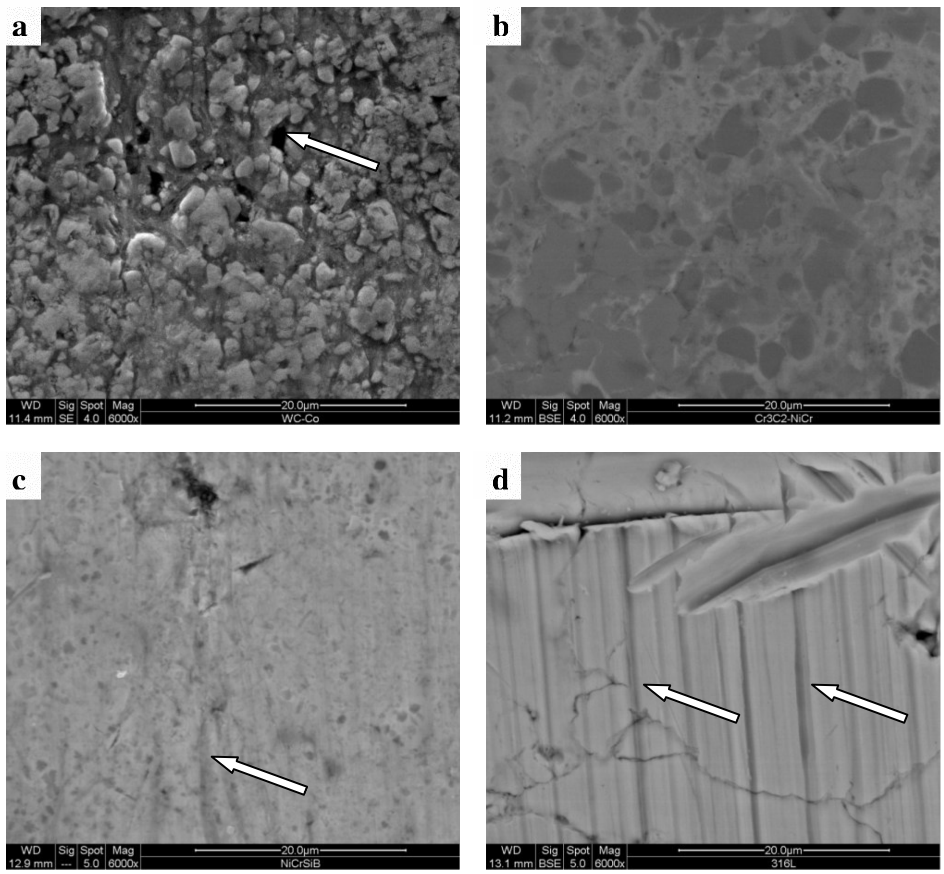

Figure 4 SEM images of worn surfaces after wet slurry abrasion test at load 20N using 40-50µm alumina particles a) WC-Co, b) Cr_3C_2-NiCr, c) NiCrBSi and d) 316L steel thermally sprayed coatings.

Pin-on-Disc test

Wear tracks after pin-on disc test for all test specimens were studied using SEM (Fig. 5). The wear track of the tested WC-Co coating is displayed on (Fig. 5a). The interface between wear trace and the wear edge can be seen. The bottom part of the picture represents the worn surface as a result of the indenter action over the surface. The wear trace is very shallow without plastic deformation on the edge. A preference for the removal of the soft cobalt matrix by an abrasive wear mechanism followed by pulling out of the carbides was observed and also some micro polishing of hard WC particles seems to be a not negligible wear mechanisms factor. It seems that an adhesive mechanism does not play an important role in the wear process because no material transfer from coating to the indenter was found. A similar behavior was determined for Cr_3C_2-NiCr coating. Nevertheless a higher volume loss of the Cr_3C_2-NiCr coating occurred because of more intensive pulling out mechanism during the pin action. The creation of cracks on hard phase and matrix boundaries leads to facilitate these wear phenomena (Fig. 5b). A significant change in wear mechanism and surface morphology of no-cermets coatings is shown in (Fig. 5c-d).

Coating	Dry sand/rubber wheel abrasion test Wear rate [mm^3/m]	Wet slurry abrasion test SAR number	Pin-on-Disc wear test Wear coefficient K [mm^3/Nm]	CoF
WC-Co	1,96E-03	79,84	1,33E-06	0,365
Cr_3C_2-NiCr	7,36E-03	221,79	1,41E-04	0,647
NiCrBSi	3,16E-02	941,86	5,72E-04	0,576
316L	6,13E-02	2555,86	2,97E-03	0,857

Table 4 Results of wear tests

High degree of plastic deformation for these materials by periodic action of ball indenter can take place. This fact leads to the fatigue and adhesive wear mechanism which can result in the delamination in splats boundaries (Fig. 5d). The role of fatigue could have a relevant role in the coating wear because cracks that are observed (Fig. 5.c) may lead to the coating delamination. The main wear processes in the delamination wear are subsurface deformation, crack nucleation and propagation. This wear mechanism leads to the formation of large particle debris. The results of individual wear tests for all tested coating materials are summarized in Table 4.

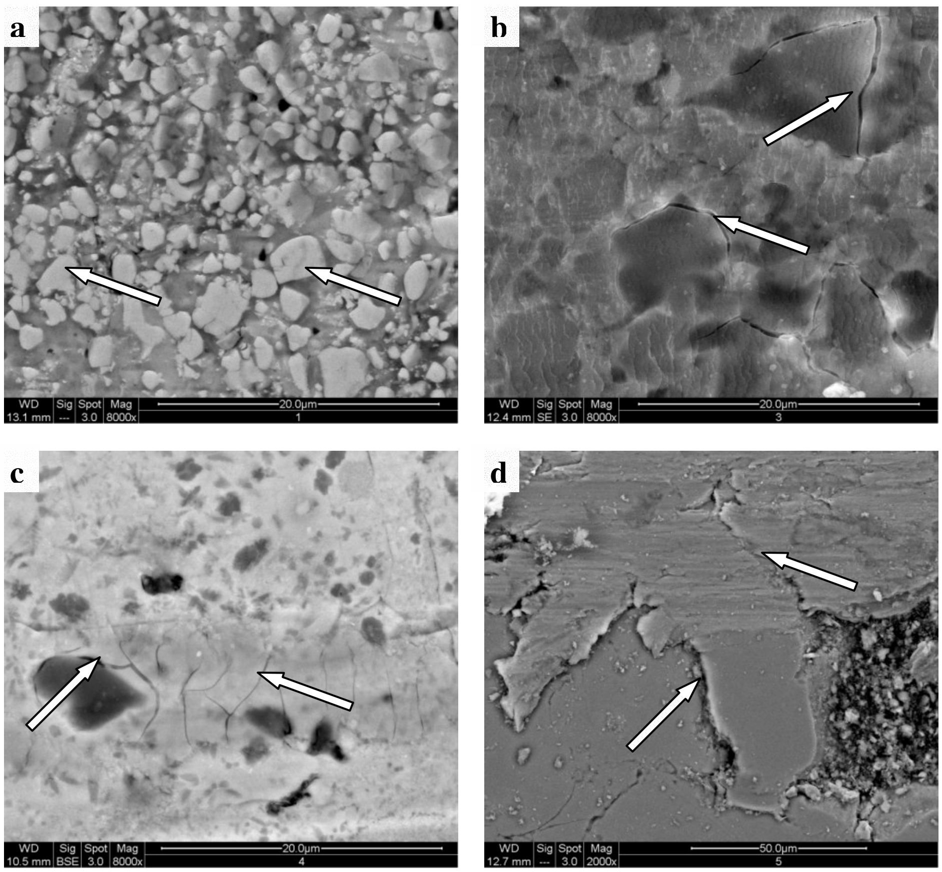

Figure 5 SEM images of worn surfaces after pin-on-disc test at load 10 N using alumina ball indenter, a) WC-Co, b) Cr_3C_2-NiCr, c) NiCrBSi and d) 316L steel thermally sprayed coatings.

Discussion

All HVOF thermally sprayed coatings evaluated in this study show relatively high wear resistance. The best wear resistance was established for cermet coatings WC-Co followed by Cr_3C_2-NiCr. This is due to the fact that Co matrix has excellent carbide wettability and adhesion properties and also the highest hardness value. The wettability of the WC hard phases is also better than that of the other employed carbides. Generally, it is accepted that the effect of carbides on wear resistance depends on their quantity, morphology and distribution.

So, as it can be seen, the important element for the abrasion resistance of cermets is the bond strength of hard particles and matrix. This phenomenon results for WC-Co coating in high resistance in the wear process by inhibition of pulling of the carbides and cracks creation.

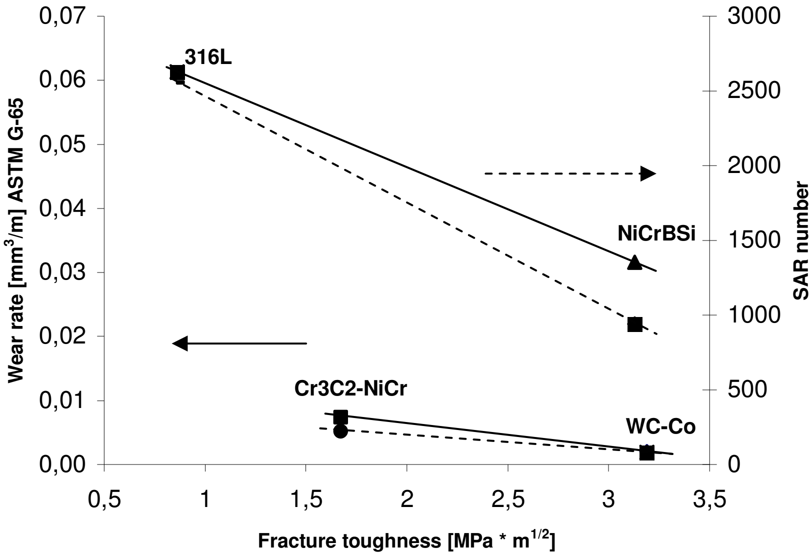

Figure 6 Wear rate W_R, at x = 1436 m and SAR number as a function of fracture toughness, K_{CI}, for HVOF thermally sprayed coatings

This is in a good agreement of the wear test with the measurements performed by indentation fracture toughness method (IFT) given in Tab.3.
A different situation was identified for Cr_3C_2-NiCr coating. While for WC-Co coating there is no evidence of cracks (Fig. 5a), the Cr_3C_2-NiCr shows initiation of microcracks in boundary of Cr_3C_2 carbides and NiCr matrix (Fig. 5b). This phenomenon corresponds with low fracture toughness of Cr_3C_2-NiCr coating mentioned in Tab. 3. The lower bond strength of the individual carbides in the matrix the higher volume loss in wear test was measured. Based on wear test results the hardness effect by the three body abrasion in dry and wet conditions plays a predominant role. On the other hand, the hardness does not play such a significant role during the two body abrasion test (pin-on-disc). This is confirmed by the results of pin-on disc test where WC-Co was 100 times better resistance compared to Cr_3C_2-NiCr. The higher volume loss attended by relatively large material removal is caused by semibrittle behavior of Cr_3C_2-NiCr due to its low fracture toughness value.

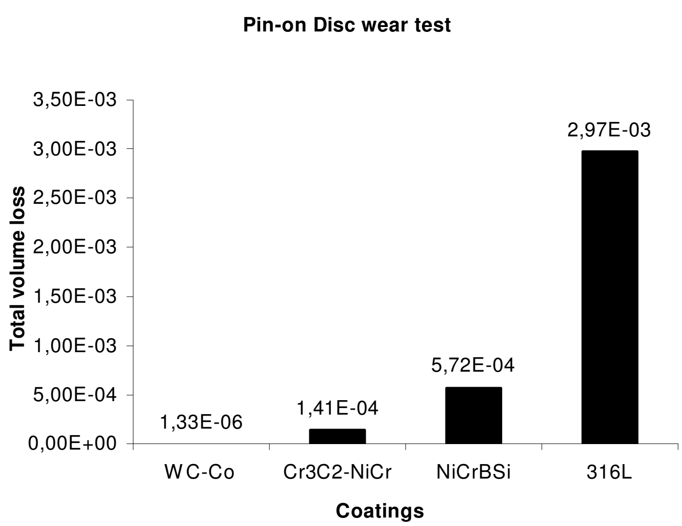

Figure 7 Wear coefficient of tested coatings using Pin-on-Disc wear test according to ASTM G-99 after 50 000 cycles using alumina ball indenter

The coefficient of friction also influences the wear mechanism because of its relationships with shear stress value. The higher friction coefficient of Cr_3C_2-NiCr coating causes the crack initiation and propagation during abrasion test. However the hardness of coating plays a significant role as well. This fact could be taken into account with fracture toughness value of the NiCrBSi coating.

Fig. 6 shows the relationship between wear resistance (wear rate and SAR number) and fracture toughness. For dry abrasion conditions the WC-Co coating was 3,7 times better than Cr_3C_2-NiCr coating though for wet abrasion conditions the ratio was only 2,8. This phenomenon can be explained by higher corrosion resistance of Cr_3C_2-NiCr in corrosion environment during wet abrasion test [11] as well as different wear mechanisms for dry and wet conditions. For wet conditions the scratching is the predominant mechanism and therefore the hardness is the key parameter. For dry conditions the indentation of the abrasive tips is the predominant mechanism and therefore in addition to hardness the coatings fracture toughness is also an important parameter in this case. The fracture toughness of Cr_3C_2-NiCr is lower than WC-Co. These facts caused the lower wear resistance ratio of WC-Co to Cr_3C_2-NiCr for wet conditions in comparison to the dry ones.

Interesting phenomena has been shown for the results of pin-on-disc test (Fig. 7-8). Wear resistance of Cr_3C_2-NiCr coating in comparison to WC-Co was 100 times lower. Possible reason for this result should be a semibrittle behavior of the Cr_3C_2-NiCr (Fig.5b).

Cr_3C_2-NiCr coating shows 4,3 times higher wear resistance by both dry and wet conditions in comparison to NiCrBSi coating because the influence of hardness. But the ratio was lower in the case of pin-on-disc test because of the influence of the higher fracture toughness of NiCrBSi coating.

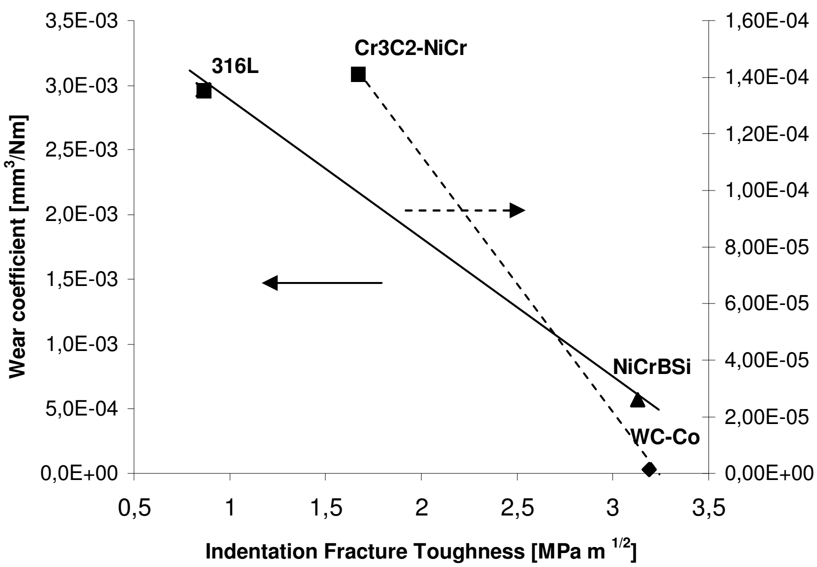

Figure 8 The wear coefficient of HVOF thermally sprayed coatings after pin-on-disc test as a function of the fracture toughness

Further, it can be seen that for non-cermets coatings the NiCrBSi coating has higher wear resistance in comparison to 316L. This is due to the higher hardness and fracture toughness (Fig. 8). At the NiCrBSi and 316L stainless steel coating the wear was caused by plowing, cutting for dry and wet abrasion conditions and fatigue and delamination process for pin-on-disc was determined. The NiCrBSi coating has higher hardness and fracture toughness as well. These conclusions lead to the results shown in (Fig. 6-8) where wear resistance of the NiCrBSi coating is 2 times higher for dry conditions while 2,7 times for wet conditions than of 316L steel coating. The difference in wear resistance for wet and dry abrasion conditions should be due to further mentioned phenomenon that liquid career acts as a lubricant and modifies the mechanics of the abrasive particle contact. At dry conditions rolling of the abrasives in the contact with particularly large plastic deformation in the surface layer for 316L coating has been occurred (Fig.3d). There is also an important role of changes in coefficient of friction for dry and wet conditions where the lower coefficient of friction for wet conditions causes predominant effect of cutting and plowing (Fig. 4d). While for dry and wet abrasion it seems that hardness plays a predominant role, the results obtained from pin-on-disc test show that fracture toughness also takes place in case of non-cermets coatings. (Fig. 5c) shows formation of cracks in the NiCrBSi coating but the lower fracture toughness of the 316L coating involves extending of the dramatic delamination process between individual splats and cracks initiation and propagation which involves 5,7 times lower wear resistance in comparison with NiCrBSi coating.

Conclusions

For all HVOF thermally sprayed coatings the high wear resistance in the three and two body abrasion was determined. Cermet coatings exhibited superior wear resistance in comparison to non-cermets. Wear mechanism changes from three body abrasion causing cutting, plowing, plastic deformation and the indentation of the abrasive tips particles mechanisms to the two body abrasion under wet conditions where predominantly cutting and plowing mechanisms has been observed. Though different fracture toughness of tested coatings was measured it has been observed that the hardness was the major factor which influenced the wear resistance. A different situation was examined for two body abrasion carried out by pin-on-disc test, where predominantly high cycles fatigue, plastic deformation and cracks initiation and propagation, which can result in the delamination in splats boundaries, take place. For these wear mechanisms the value of the fracture toughness instead of the hardness was determined as a dominant factor to the wear resistance.

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