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Investigation of Properties and Wear Behavior of HVOF Sprayed TiC-Strengthened Fe Coatings

Kirsten Bobzin, Thomas Schlaefer, Katharina Richardt, Thomas Warda, and Guido Reisel

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High-velocity oxyfuel (HVOF) sprayed carbide based coatings (such as Cr_3C_2/NiCr) are industrially well established for wear protection applications. Due to their high carbide content of typically 75 wt.% and more, they provide very high hardness and excellent wear resistance. Unfortunately, costs for matrix materials such as nickel underlie strong fluctuations and are normally well above the prices for iron. Therefore an alternative concept to conventional carbides is based on TiC-strengthened low-cost Fe-base materials, which are already used for sintering processes. Depending on the carbon content, the Fe-base material can additionally offer a temperable matrix for enhanced wear behavior. The sprayability of TiC-strengthened Fe-powders with a gaseous and a liquid fuel driven HVOF system was investigated in this study. The resulting coatings were analyzed with respect to microstructure, hardness, and phase composition and compared with galvanic hard chrome, NiCrBSi, and Cr_3C_2/NiCr (80/20) coatings as well as with sintered Fe/TiC reference materials. Furthermore, the Fe/TiC coatings were heat treated to proof the retained temperability of the Fe matrix after thermal spray process. Tribometer tests (pin-on-disk tests) were conducted to determine wear properties.

Keywords Fe-based coatings, HVOF spraying, TiC reinforcement, wear behavior

1. Introduction

Thermal spraying is a well-established technique for application of wear protection coatings. Often carbides (such as Cr_3C_2/NiCr) are used (Ref 1, 2). Increasing commodity prices of the typical wear protection materials are leading to an increase of coating costs. This can reduce the competitiveness of thermal spraying compared with other coating technologies. A further disadvantage with regard to competitiveness is created when carbide coatings are overdimensioned for the considered application (Ref 3). In this context the substitution of cost-intensive materials is discussed, and often Fe-based materials are mentioned (Ref 4, 5). Modern ferrous-based TiC-strengthened (Fe/TiC) coatings can be a very promising alternative to those carbide materials. With their advantageous wear properties (Ref 6) and lower material costs compared with conventional carbides, influenced by lower commodity prices of the alloy materials, cost-effective wear protection coatings can be realized.

Kirsten Bobzin, Thomas Schlaefer, Katharina Richardt and **Thomas Warda**, Surface Engineering Institute, RWTH Aachen University, Aachen, Germany; and **Guido Reisel**, Sulzer Metco WOKA GmbH, Barchfeld, Germany. Contact e-mail: warda@iot.rwth-aachen.de.

2. Experimental Procedure

For a classification of spraying results with TiC-strengthened Fe-based powders, the coatings were compared with the following reference materials and coating systems:

- Fe/TiC sinter materials (pressed powder and hardened sinter bodies)
- High-velocity oxyfuel (HVOF) sprayed Cr_3C_2/NiCr (80/20) coatings
- HVOF sprayed and remelted NiCrBSi coatings
- Galvanic hard chrome

The chemical composition of the Fe/TiC powders can be taken from Table 1. Two HVOF systems were used as coating techniques: a gaseous fuel driven system with hydrogen and oxygen (Diamond Jet Hybrid DJ 2600 from Sulzer Metco, Hattersheim, Germany) and a liquid fuel driven system with kerosene and oxygen (K2 from GTV GmbH, Luckenbach, Germany). Process parameters for Fe/TiC coatings can be taken from Table 2; parameters for Cr_3C_2/NiCr (80/20) and NiCrBSi coatings are listed in Table 3 (Ref 7).

2.1 Materials

Two different TiC-strengthened powders with a Fe-based matrix (Fe/TiC powders) in different particle fractions were used as spraying materials (Fig. 1 and 2; Table 1). The first Fe/TiC powder was manufactured by milling of turnings from a turning process of sintered

Table 1 Chemical composition of Fe/TiC powders

Hard phase 33% TiC, wt.%	Matrix 67% C, wt.%	Cr, wt.%	Mo, wt.%	Fe
100	0.75	13.50	3.00	Bal.

Table 2 Spraying parameters for Fe/TiC coatings with milled as well as agglomerated and sintered powders

	H_2/O_2-HVOF system	Kerosene/ O_2-HVOF system
Standoff distance, mm	250-280	300-500
O_2/H_2 ratio	0.28-0.36	…
Air/fuel ratio, λ	…	1.0-1.5
Gas flow rate, SLPM	680-880	…
Mass flow rate, g/min	…	1100-1400
Transversal speed, mm/s	500	500
Powder feed rate, g/min	14-36	40-80

Table 3 Spraying parameters for Cr_3C_2/NiCr (80/20) and NiCrBSi coatings using the liquid fuel driven HVOF system

	Cr_3C_2/NiCr (80/20)	NiCrBSi
Standoff distance, mm	400	300
Air/fuel ratio, λ	1.0	1.16
Oxygen, SLPM	850	800
Kerosene, L/h	24	20
Transversal speed, mm/s	1500	1667
Powder feed rate, g/min	100	100
Nozzle, mm	200/11	150/11

Source: Ref 7

Fe/TiC components. This was investigated with regard to the aspect of whether such turnings can be processed further in a thermal spraying process. The second one was an optimized Fe/TiC powder produced with a newly developed manufacturing route by Sulzer Metco WOKA GmbH (Barchfeld, Germany). The manufacturing route is explained in detail in Sect 3.1 "Fe/TiC Powders."

For application of the coatings, 1.0037 steel substrates with dimensions of 60 × 40 mm^2 and a thickness of 5 mm and 1.4301 steel substrates with a diameter of 20 mm and a thickness of 7 mm were used. Before spraying, samples were grit blasted with F24 grit at a pressure of 6 bar and degreased.

2.2 Structural and Properties Characterization of Powders and Coatings

Beside metallographic analysis, surface roughness measurements, glow discharge optical emission spectrometric (GDOES) measurements, and x-ray diffraction (XRD) measurements were also conducted. The parameters used for these measurement techniques are:

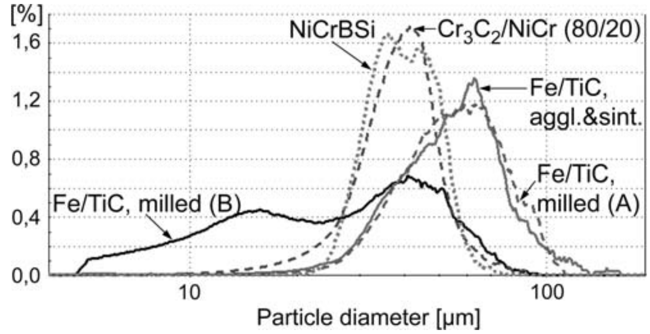

Fig. 1 Fractions of powders used in this study

GDOES: JY 5000 RF (HORIBA Jobin-Yvon GmbH, Muenchen, Germany)

- Chamber pressure: 700 Pa
- Cathode power: 35 W
- Sputter diameter: 4 mm
- Excitation mode: RF

XRD: Seifert X-Ray Diffractometer 3000:

- Cu anode
- Voltage: 40 kV
- Current: 40 mA
- Step size: 0.05°
- Step scan: 0.05 s

Furthermore, Fe/TiC coated samples (nine samples coated with the gaseous fuel driven HVOF system and nine samples coated with the liquid fuel driven HVOF system) were heat treated at 1080 °C with a subsequent quenching in order to investigate the effect of temperability of the Fe-base matrix. Before spraying experiments, the powders were analyzed with an optical particle analyzing system (Morphologi G2, Malvern Instruments Ltd., UK) and with scanning electron microscopy (SEM) (Fig. 2) with regard to particle size distribution and particle morphology. The sintered Fe/TiC reference samples were analyzed with XRD, with GDOES, and metallographically. The wear behavior was investigated by pin-on-disk tests with a CSM HT Tribometer (CSM Instruments, Freiburg, Germany) at room temperature without any lubricants. As a counterpart Al_2O_3 spheres with a diameter of 6 mm were used.

3. Results and Discussion

3.1 Fe/TiC Powders

Results of the optical particle analysis are shown in Fig. 1. It can be clearly seen that through air separation (Air Separator Turboplex 50 ATP, Hosokawa Alpine AG, Augsburg, Germany) of the milled Fe/TiC powder (B) a particle size distribution was reached (A), which is very close to that of agglomerated and sintered Fe/TiC powder.

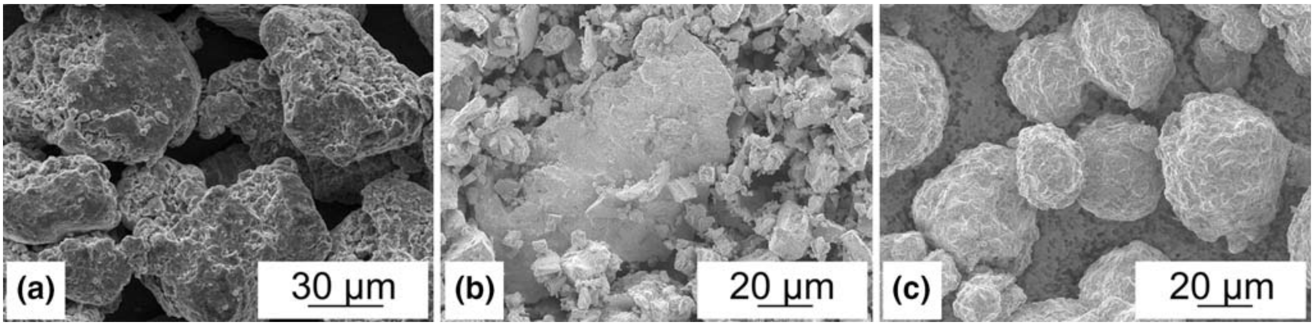

Fig. 2 Scanning electron micrographs of powders used. (a) Milled Fe/TiC (A). (b) Milled Fe/TiC (B). (c) Agglomerated and sintered Fe/TiC

Figure 2 shows that the agglomerated and sintered Fe/TiC powder predominantly consists of spherical particles, whereas the milled Fe/TiC powder is angular. The agglomerated and sintered Fe/TiC powder was produced with a newly developed sintering process. The feed material therefore consisted of 33 wt.% TiC hard phase and 67 wt.% Fe-based matrix (matrix composition: 82.75 wt.% Fe, 13.50 wt.% Cr, 3.00 wt.% Mo, 0.75 wt.% C). This feed material was homogenized in an attritor and was subsequently spray dried. Hydrogen was used for releasing purposes. The sintering process took place at 1280 °C in a vacuum atmosphere; the feed materials were located in an Al_2O_3 annealing box. Finally, the sintering cake was crushed, ground, and sieved. Using this process route, it was possible to manufacture spherical Fe/TiC powder without large quantities of oversize or undersize grains. Other investigated manufacturing routes have led to unsatisfactory results. For example, during experiments in a hydrogen atmosphere at 1220 °C, no sintering effect could be realized. Sintering on a graphite plate in a vacuum atmosphere at 1280 °C has led to an inhomogeneous distribution of carbon because of diffusion effects between sintering cake and graphite plate as well as to a strong adherence of the sintering cake to the plate (Ref 8).

3.2 Fe/TiC Coatings

Differences between the Fe/TiC powders can also be seen in cross-sectional micrographs of the coatings (Fig. 3a, b). Coatings produced with the milled Fe/TiC powder (both fractions) clearly show oxides (GDOES measurements show up to 3% of oxygen in the coating). This phenomenon can be seen when a gaseous-driven HVOF system was used as well as when liquid fuel driven HVOF system (Fig. 3a) was used. In contrast, coatings produced with agglomerated and sintered powder show only few oxides with distinctly smaller dimensions (Fig. 3b). The black areas in the micrographs represent breakouts of hard phases, which occurred during sample preparation. The roughness of the Fe/TiC coatings was determined to be about $R_a = 6$ µm (as-sprayed, average of 5 measurements per sample); the microhardness in the as-sprayed condition was up to 714 HV 0.1 (average of 10 measurements per sample, see also Fig. 5). A deposition efficiency (DE) of up to 50% was reached.

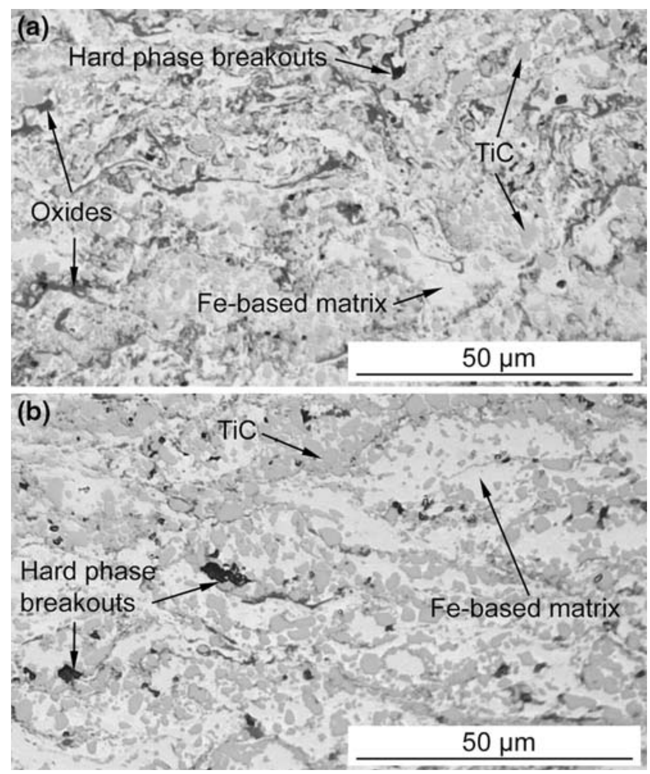

Fig. 3 Cross-sectional micrographs of Fe/TiC coatings sprayed with kerosene-driven HVOF system. (a) Coating produced with milled powder. (b) Coating produced with agglomerated and sintered powder

3.3 Phase Analyses of Fe/TiC Coatings

Phase analyses (Fig. 4) show that through the coating process a change in the phase composition of the Fe-based matrix can occur. By comparing the XRD results with other investigations from literature (Ref 9-11), the assumption can be stated that within the sprayed coatings an incomplete transformation from γFe (austenite) to αFe

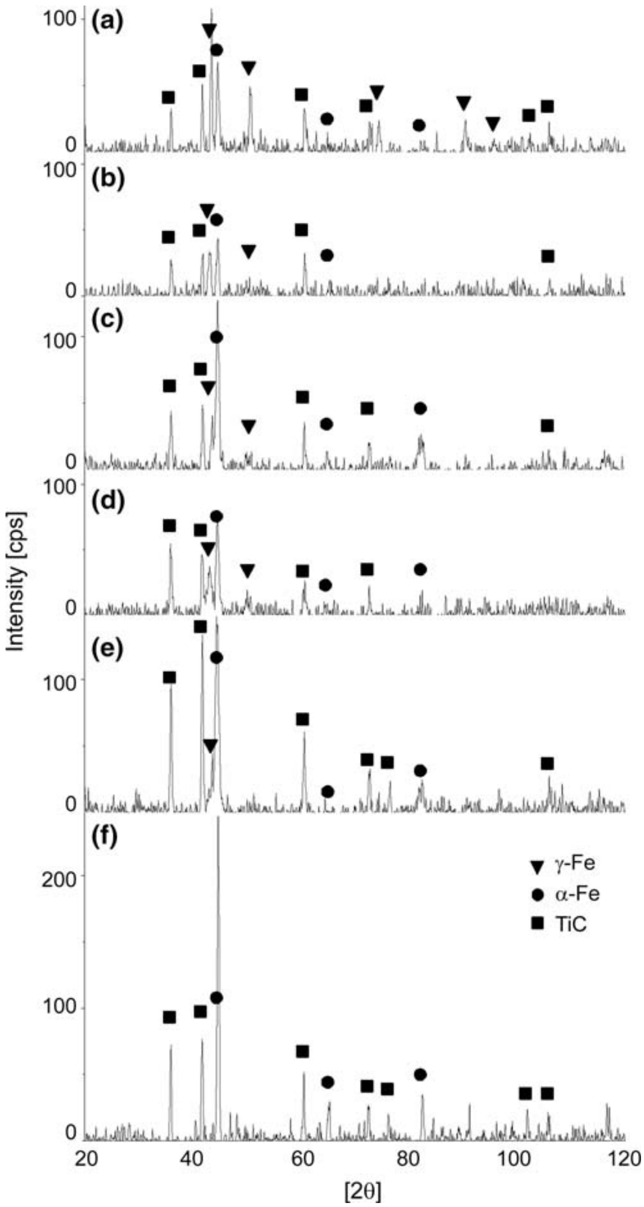

Fig. 4 Results of XRD measurements. (a) Coating produced with a liquid fuel driven HVOF system with milled Fe/TiC powder after heat treatment. (b) Coating produced with a liquid fuel driven HVOF system with milled Fe/TiC powder before heat treatment. (c) Coating produced with a gaseous fuel driven HVOF system with milled Fe/TiC powder after heat treatment. (d) Coating produced with a gaseous fuel driven HVOF system with milled Fe/TiC powder before heat treatment. (e) Reference Fe/TiC sample (hardened). (f) Reference Fe/TiC sample (pressed powder). XRD parameters: Cu anode, voltage 40 kV, current 40 mA, step size 0.05°, step scan 0.05 s

(ferrite) occurs, and thus residual austenite remains within the Fe matrix. The formation of residual austenite is, according to Ref 12, possible using this material (Fig. 4e). The microhardness values (300-400 HV 0.005) of the Fe matrix in as-sprayed conditions indicate also that the microstructure consists of austenite. XRD measurements of the Chair in Composite Materials (Ref 13) (Chemnitz

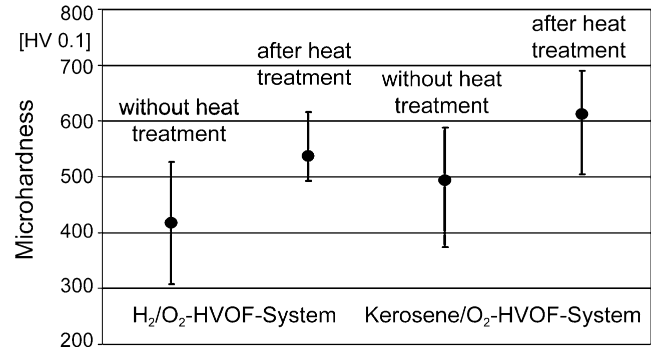

Fig. 5 Results of microhardness measurements with heat treated and untreated Fe/TiC coatings sprayed with the milled powder

University of Technology) on Fe/TiC-coated samples confirm the existence of austenite in the coatings. Within the diffractogram of the pressed Fe/TiC reference samples no γFe can be found (Fig. 4f).

3.4 Heat Treatment of Fe/TiC Coatings

For determination of the remaining temperability of the carbonaceous Fe-based matrix with a carbon content of 0.75 wt.%, part of the samples was heat treated at 1080 °C and then quenched in N_2 at 1 bar. The parameters were chosen with reference to the heat treatment of sintered components made of Fe/TiC. Results of the hardness measurements can be seen in Fig. 5. In these initial tests the achieved increase in microhardness was about 25-30%. For the gaseous HVOF system, this means an increase of 130 ± 80 HV 0.1 compared with the untreated samples. In case of the liquid fuel driven HVOF system, the values rose by 150 ± 80 HV 0.1. As a result of a subsequent variation of the spraying parameters, it was possible to achieve an even higher as-sprayed hardness of up to 714 HV 0.1 with the liquid fuel driven HVOF system.

3.5 Wear Behavior

Wear properties of the investigated coatings were determined by pin-on-disc tests with following parameters:

- Three samples per coating system
- Sliding speed: 100 mm/s
- Sliding distance: 1000 m
- Diameter of wear track: 11 mm
- Pressing-on force: 5 N
- Without any lubricants at room temperature

The results can be seen in Fig. 6. The width and depth of the wear tracks were determined using a laser profilometer from UBM Messtechnik GmbH (Ettlingen, Germany) and additionally an optical microscope. For determination of the wear volume, wear tracks were assumed to be segments of a circle; hence, the wear

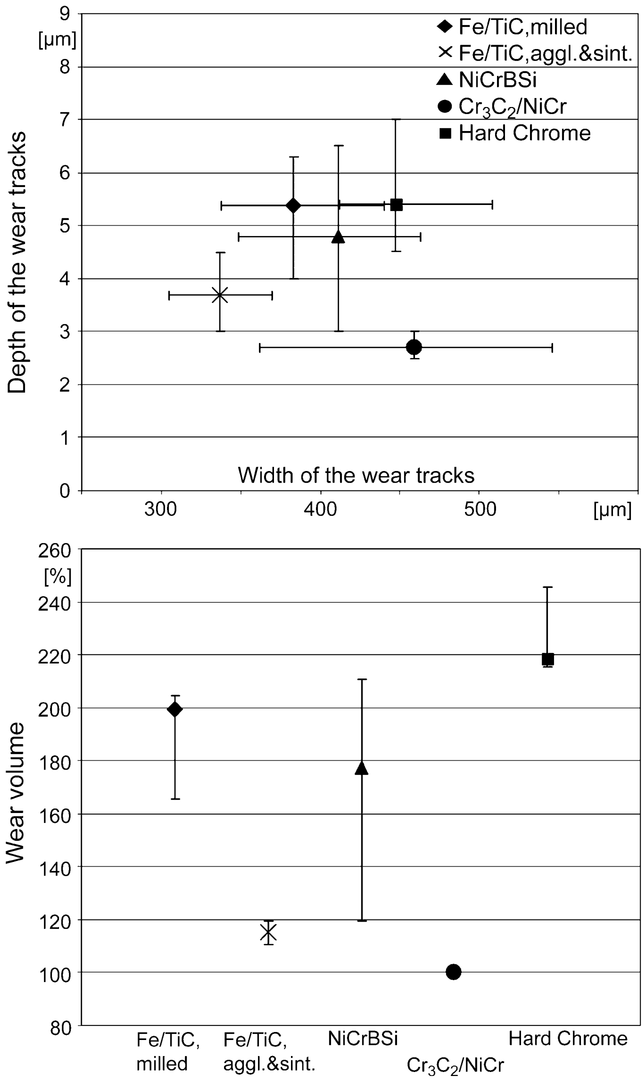

Fig. 6 Results of wear tests (pin-on-disk tests). The upper diagram shows the depth of wear tracks (vertical lines) as a function of the width of wear tracks (horizontal lines), in the lower diagram the wear volume is shown (Cr_3C_2/NiCr (80/20) coatings were taken as reference and scaled to 100%). Test parameters: Al_2O_3 sphere with a diameter of 6 mm as counterpart, sliding speed 100 mm/s, sliding distance 1000 m, diameter of wear track 11 mm, pressing-on force 5 N, without any lubricants, room temperature

volume was a kind of torus. From the upper diagram in Fig. 6 one can see that the Cr_3C_2/NiCr (80/20) coated samples show the lowest track depth (2.7 µm). The highest values (about 5 µm) reach coatings of galvanic hard chrome, remelted NiCrBSi and Fe/TiC (sprayed with milled powder). In contrast to the milled powder, the wear depth in coatings produced with agglomerated and sintered Fe/TiC powder is lower (around 3.7 µm). It shows also the most narrow wear track of all investigated coatings (except for the sintered and hardened Fe/TiC reference sample). Comparing the wear volumes of the different coating systems, it can be stated that coatings

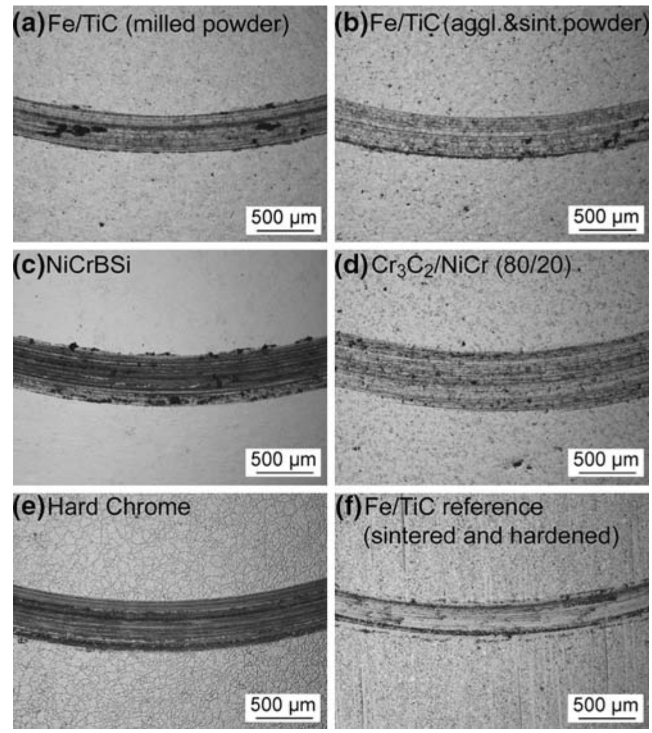

Fig. 7 Wear tracks of HVOF sprayed Fe/TiC coatings and investigated reference samples. Test parameters: Al_2O_3 sphere with a diameter of 6 mm as counterpart, sliding speed 100 mm/s, sliding distance 1000 m, diameter of wear track 11 mm, force 5 N, without any lubricants, room temperature. (a) Fe/TiC coating (milled powder). (b) Fe/TiC coating (agglomerated and sintered powder). (c) NiCrBSi coating. (d) Cr_3C_2/NiCr (80/20) coating. (e) Galvanic hard chrome. (f) Fe/TiC sinter body (hardened)

produced with the agglomerated and sintered Fe/TiC powder show similar wear behavior as HVOF sprayed Cr_3C_2/NiCr (80/20) coatings, which were taken as reference for this consideration. The wear volume of Fe/TiC coatings sprayed with the milled powder is comparable with those ones of remelted NiCrBSi and galvanic hard chrome coatings. It is approximately two times higher than that of Cr_3C_2/NiCr (80/20) coatings. The light-optical microscope (LM) micrographs of the wear tracks of the investigated coating systems can be seen in Fig. 7(a)-(f).

4. Conclusions and Outlook

Spraying tests with TiC-strengthened Fe-based materials were performed and analyzed within the framework of this work. The analysis included metallographic investigations such as micrographs and microhardness measurements and XRD and GDOES analyses. Furthermore, Fe/TiC coated samples were heat treated. Thus it was possible to raise the microhardness by up to 30%. The structure of the coatings was dependent on the powder used: coatings sprayed with milled Fe/TiC powder clearly contained more oxides compared with coatings sprayed with agglomerated and sintered Fe/TiC powder. The microhardness of Fe/TiC coatings (as-sprayed) was up to 714 HV 0.1, the roughness (as-sprayed) about $R_a = 6$ μm. In pin-on-disk tests, coatings with agglomerated and sintered Fe/TiC powders showed similar wear behavior as Cr_3C_2/NiCr (80/20) coatings. The depth and width of the wear tracks as well as the wear volume of coatings produced with milled Fe/TiC powders can be compared with galvanic hard chrome and remelted NiCrBSi coatings.

These results underline the potential of the Fe/TiC coatings as a low-cost alternative to conventional carbides with regard to wear resistance. On the basis of current raw material prices, up to 50% of material costs could be saved by using such Fe/TiC materials compared with Cr_3C_2/NiCr (80/20).

Currently, the machinability of HVOF sprayed Fe/TiC coatings by turning and the wear behavior of Fe/TiC coated pistons (interaction of coating and sealing ring) are investigated as well as the corrosion properties.

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