ELSEVIER

Ceramics International 33 (2007) 827–835

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Microstructure and properties of TiC–Fe cermet coatings by reactive flame spraying using asphalt as carbonaceous precursor

Hui Yuan Liu, Ji Hua Huang [*], Chang Feng Yin, Jian Gang Zhang, Guo Biao Lin

School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

Received 27 September 2005; received in revised form 7 December 2005; accepted 21 January 2006

Abstract

A kind of agglomerated Ti–Fe–C compound spraying powder was prepared by heating a mixture of ferrotitanium and asphalt to pyrolyze the asphalt as carbonaceous precursor. The carbon by the pyrolysis of the asphalt acts as a reactive constituent as well as a binder in the compound powders. TiC–Fe cermet coatings were prepared by RFS of the compound powder. XRD, SEM, EDS and TEM were employed to analyze the microstructure of the cermet coating. In order to investigate the forming mechanism of the cermet coating, a quenching test was performed. The results show that the Ti–Fe–C compound powder has a very tight structure, which can avoid the problem that reactive constituent particles are separated during spraying. The TiC–Fe cermet coatings presents a typical morphology of thermal spraying coatings with two different laminated layers: the one is the composite layers in which the round fine TiC particles (<500 nm) are dispersed within a Fe matrix, the other is the paragentic layers of TiC and Ti_2O_3. The nucleation mechanism of the TiC in the two layers is homogeneous nucleation and heterogeneous nucleation, respectively. The TiC in the composite layers grows in the dissolution-precipitation mode that the smaller particulates dissolve and larger ones grow. The TiC–Fe cermet coating by RFS shows high hardness and wear resistance property: The surface hardness of the TiC–Fe cermet coating is 65 ± 6(HR30N). In the same fretting conditions, the wear area of Ni60 coating is much more than that of the TiC–Fe cermet coating.

Keywords: Reactive flame spray; TiC–Fe cermet coating; Precursor; Properties

1. Introduction

Thermally sprayed metal matrix coatings reinforced with hard particles, especially carbides particles, are widely used in many engineering applications for their high levels of wear resistance. By virtue of the higher hardness, lower densities and lower friction coefficients, thermal sprayed cermet coatings of TiC bonded with different metals promise to be an excellent replacement for the traditionally used WC or Cr_3C_2-based coatings, being potentially useful in many wearing resistant applications [1]. In the conventional thermal spraying processes, the TiC reinforced cermet coatings are prepared by directly adding TiC particles into the materials for spraying [2]. The hard phase particles in the coatings are usually large (more than 1 μm), unevenly distributed. Also, because the surface of added particles is usually not clean or polluted, the interface between the reinforced phases particles and the matrix is often a potential source of weakness. In another novel approach, the TiC-metal powder can be produced using self-propagating high-temperature synthesis (SHS). The drawback of SHS powder for spraying is the stringent conditions for spraying process, such as high spraying temperature, high spraying speed, etc. Usually, spraying TiC reinforced cermet coating by the powder needs expensive plasma-spraying device [3] or high velocity oxy-fuel (HVOF) device [4,5].

Reactive thermal spraying (RTS) is a novel technology combining the in situ reactive synthesis with thermal spraying, which is potentially useful in producing TiC-metal coating. The main feature of this technique is the ceramic phases, formed by an in situ reaction directly, are fine, spherical, and uniformly dispersed and have a clean interfacial structure with the metal matrix, which sharply increases the wear-resisting property of the coating, because fine-grained TiC can improve yield strength through dispersion and grain size mechanisms, and improve toughness by hindering crack propagation [6]. Also, in reactive thermal spraying, the reactions to synthesize the ceramic phases are exothermic, which provide a supplemental heat for spraying process, and enable TiC-metals

---

[*] Corresponding author. Tel.: +86 10 62334859.
E-mail address: Jihuahuang47@sina.com (J.H. Huang).

0272-8842/$32.00 © 2006 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2006.01.020

coatings to be prepared by a cheap oxyacetylene flame-spraying device [7].

According to the states of the reactive constituents to synthesize the ceramic phases, reactive thermal spraying can be classified into two processes, solid–gas RTS and solid–solid RTS. In the solid–gas RTS, the ceramic phases in coatings are synthesized by reactions of a solid constituent with a gas constituent. TiC reinforced cermet coatings were prepared by solid–gas RTS using ilmenite powder as the feed material and methane, propylene, and acetylene as the reactive gas [8,9]. Although solid–gas RTS has a simple process, it has been proved to be difficult to control the solid–gas reaction and its product during spraying. The solid–solid RTS synthesizes ceramic phases in coatings by reactions between two solid constituents. As an example, TiC reinforced cermet coatings can be prepared by reactive thermal spraying agglomerated compound powders of titanium (or titanium alloy), graphite, and other metals (Ni, Fe, etc.) [10]. In solid–solid RTS, the reactive product can be designed and controlled by adjusting the composition of the compound powders for spraying. Until the present, however, the powders used for solid–solid RTS have been prepared by simple mechanical blend and mechanical agglomeration adding a small mount of agglomerant [11]. Because of the strong airstreams of spraying gas and the lower bonding strength of the compound powders prepared by the methods above, the reactive constituent particles in the compound powders are liable to be separated during spraying, which leads to incomplete reaction, partial remaining of the reactive constituent particles in coatings, thus low hardness and wear resistance properties. It is evident that the compound powder in the solid–solid RTS is the key to obtaining a coating with high wear resistance.

This paper describes a novel process for preparing Ti–Fe–C system compound powder for RFS TiC reinforced cermet coating. The main feature of the process is that a carbonaceous precursor is used as the origin of carbon. The agglomerated Ti–Fe–C compound spraying powders are prepared by heating a mixture of ferrotitanium and asphalt to pyrolyze the asphalt. The carbon by the pyrolysis of the asphalt is a reactive constituent as well as a binder in the compound powders. Because the compound powder prepared by the novel process has a very tight structure, the aforementioned problems can be avoided. Furthermore, the use of asphalt as carbon precursor is a cheap alternative to the other methods using gaseous hydrocarbon precursors. Meanwhile the spraying device employed is cheap oxyacetylene flame spraying device. These result in considerable cost saving.

2. Experimental

In this experiment, the raw materials were asphalt used as the carbonaceous precursor and ferrotitanium powder, whose average particle size was 6 μm. The chemical composition of ferrotitanium powders is given in Table 1. According to the composition design, the coating contains 53 wt.% TiC and 47 wt.% metal matrix.

Table 1
Chemical composition (wt.%) of powders

Powders	Ferrotitanium
Fe	Balance
Ti	47.0
Al	1.72
Mn	1.9
Si	0.2
C	0.2
P	0.096
S	0.02
Cu	0.1

The compound spraying powder was prepared by a novel process. Firstly, ferrotitanium powder (76.3 wt.%) and asphalt (23.7 wt.%) were mixed at 300 °C. And then the mixture was pyrolized for 2 h under the temperature of 600 °C in the argon atmosphere, under which asphalt can be completely carbonized with the carbonization ratio of 31%. The product was a porous mass. Lastly, the Ti–Fe–C system compound powder was prepared by crushing the porous mass. The powder size employed for subsequent spraying was in the 48–104 μm range.

The TiC/Fe cermet coatings were synthesized and deposited onto low carbon-mild steel substrates (25 mm × 15mm × 3mm) by the ordinary oxyacetylene flame spraying of the compound powder. Prior to spraying, the substrates are grit-blasted on one side to clean and roughen the surfaces. Meanwhile, in order to investigate the forming mechanism of the TiC/Fe cermet coatings, the compound spraying powders were directly sprayed into quenching medium. The quenching medium employed in the test was water. The spray distance is 150 mm.

The phases present in the compound spraying powders and the TiC/Fe cermet coatings are identified using XRD with Cu Kα radiation. The cross-sections of the cermet coating and the powders after spraying into water were investigated using Leo-1450 scanning electron microscope (SEM) utilizing back-scattered electron (BSE) imaging and energy depressive X-ray spectroscopy (EDS). Sample for transmission electron microscope (TEM) observation were cut along the direction parallel to the cermet coating. It was mechanically thinned to 50 μm and then thinned by argon ion milling.

Microhardness test was performed on MH-6 machine with a 200 g load and a dwell time of 10 s. Surface hardness of the coatings were measured on HSRU-45 surface hardness machine with a 30 N load.

For wear testing, a ball-on-disk apparatus (OPTIMOL SRV) was used for the low-amplitude oscillating dry sliding tests in ambient condition at room temperature. The wear apparatus employed for the tests is shown in Fig. 1. The fretting conditions are summarized in Table 2. The Ni60 powder, which is a self-fluxing Ni based alloy, was sprayed for comparison. The chemical composition of Ni60 is 0.8C, 16Cr, 4.5Si, 3.5B, ≤15Fe and balance Ni (wt.%). The section areas of the tracks were measured by profilometry. Accordingly, the wear data of each specimen was presented numerically with the section

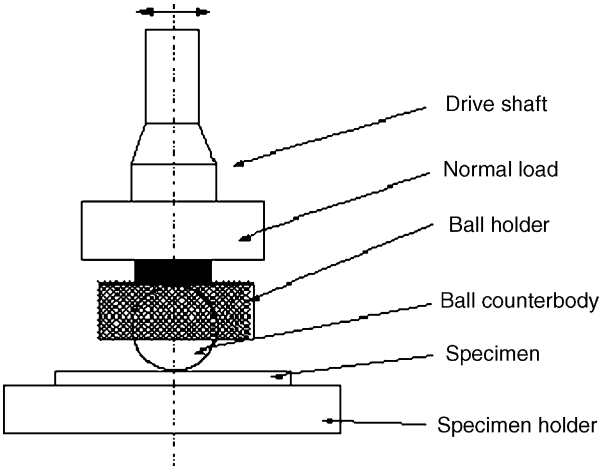


Fig. 1. Schematic view of the fretting apparatus.

Table 2
Fretting conditions used in the present study

Counterbody	GCr15 ball	Oscillating amplitude	1.5 mm
Diameter of ball	10 mm	Specimen temperature	Room (20 °C)
Normal load	20 N	Lubrication	None
Oscillating frequency	30 Hz	Fretting time	20 min

areas of the wear tracks, and schematically with the fretting track profiles.

3. Results and discussions

3.1. Characterisation of the compound spraying powder

Fig. 2 shows the XRD diffraction pattern of the Ti–Fe–C compound powder for RFS prepared by the novel process. The only phase can be detected in the XRD pattern is ferrotitanium. No TiC could be detected in the compound powder. Because the carbon in the compound powders prepared by pyrolysis of asphalt at 600 °C is amorphous, the peaks of carbon are also not found in the XRD pattern of the compound powder. In order to study the final product morphology as well as to better characterize them from the chemical composition, SEM and chemical analysis were used.

Fig. 3 shows the SEM micrograph of cross section of a compound particle. It may be seen that the obtained products consist of ferrotitanium particles, which are in the range of 5–10 μm, and carbon, with which the internal porosity between individual ferrotitanium powder particles are stuffed. Furthermore, the carbon acts as a binder between ferrotitanium powder particles. Because the amorphous carbon, generated by pyrolysis asphalt at 600 °C, has strong adsorptive capacity with ferrotitanium particles, the compound powder prepared by the novel process has a very tight structure and high bond strength. In addition, the result of chemical analysis reveals that the corresponding Ti/C atomic ratio of the final product was very close to 1.

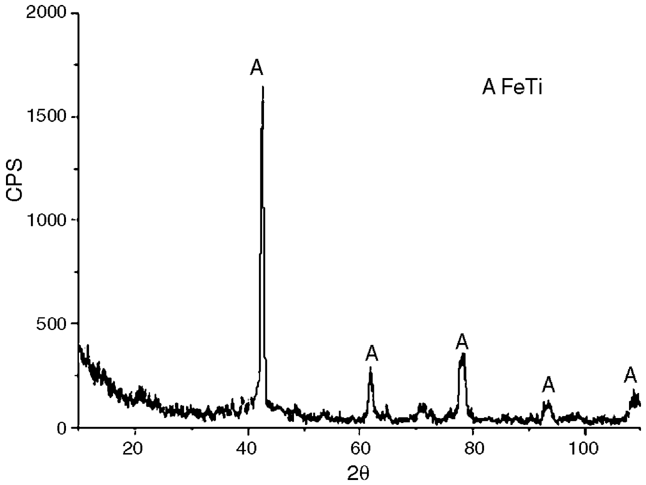


Fig. 2. XRD diffraction pattern of the Ti–Fe–C compound powder for RFS.

3.2. Microstructure of the TiC–Fe cermet coating

After being injected into the flame, the reactive spraying compound powder as a in situ reaction system is ignited by the oxygen–acetylene flame. The reaction leading to the formation of titanium carbide can be represented by the following equation:

$$\mathrm{FeTi} + \mathrm{C} = \mathrm{TiC} + \mathrm{Fe}$$

In the XRD pattern of the TiC–Fe cermet coating prepared by RFS of the compound powder (Fig. 4), the only phases can be detected are TiC, Fe and a little of Ti_2O_3 in the final product. It indicates the novel process can avoid some problems in the spraying process due to the lower bonding strength among reactive constituent particles, such as the problem that reactive constituent particles were separated during spraying, which leads to incomplete reaction of components and remaining of FeTi or carbon.

The cross-section image of the TiC–Fe cermet coating by RFS is shown in Fig. 5a and b. Fig. 5a is backscatter micrograph

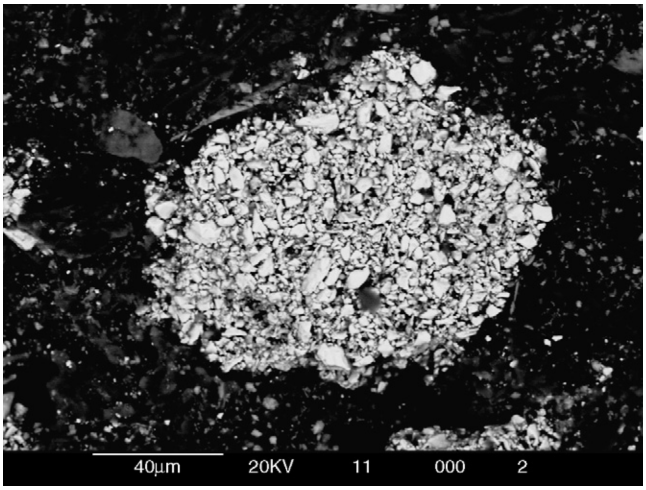


Fig. 3. SEM micrograph of cross-section of the Ti–Fe–C compound powder for RFS.

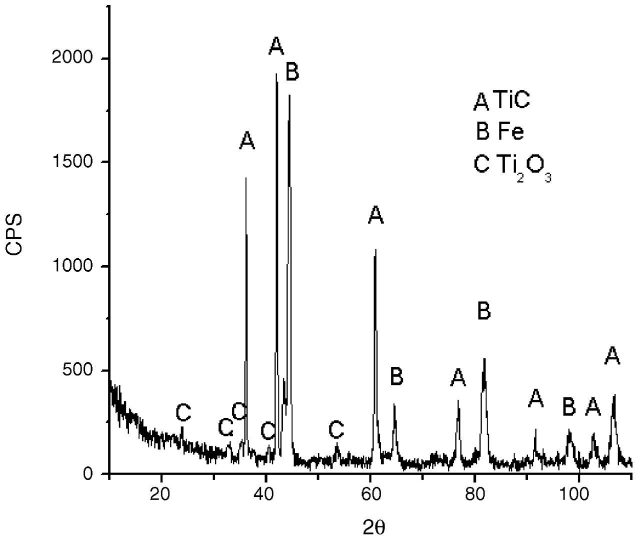


Fig. 4. XRD diffraction pattern of the TiC–Fe cermet coating by RFS.

of the TiC–Fe cermet coating by RFS; Fig. 5b shows secondary electron micrograph of the same area. Form Fig. 5, it may be seen that the coating present typical morphology of thermal spraying coating with different layers. The layers of the coating are very thin, as indicated that the spraying powder prepared by this method wholly melt in the spraying process. Meanwhile, the microstructure shows good inter-layers cohesion with very little porosity, and the interface does not reveal any debonding showing that the coating adhesion is good.

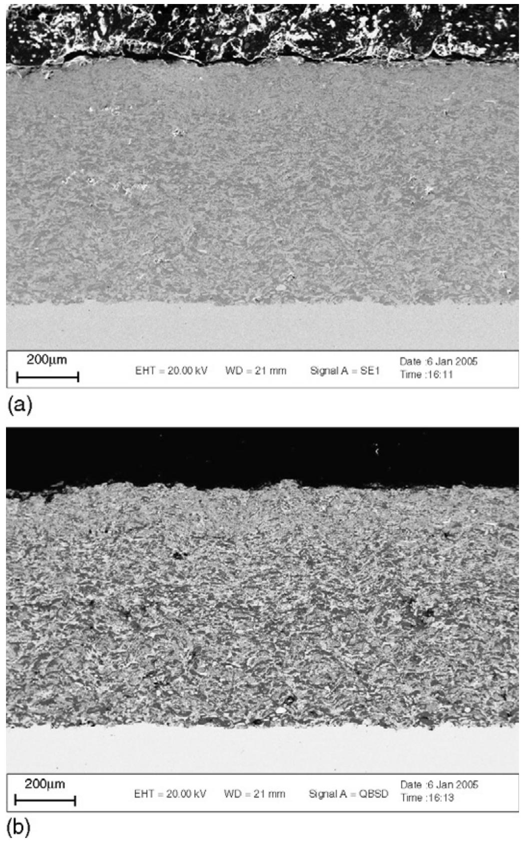


Fig. 5. SEM micrograph of cross-section of the TiC–Fe cermet coating By RFS: backscatter (a) and secondary electron (b).

Table 3
EDS of the different areas in the TiC–Fe cermet coating by RFS

Area	Element (at.%) area			
	C	Ti	Fe	O
TiC particle in A# layer	43.29	53.29	2.52	0.90
Binder phase in A# layer	0.92	1.17	97.18	0.73
A# layer	25.98	29.12	44.10	0.80
B# layer	15.03	44.74	0.90	39.33

Fig. 6 shows typical morphology of a TiC–Fe cermet coating by RFS. Form Fig. 6a, the coating consists of two different laminated layers, A# layer and B# layer. Fig. 6b and c shows their morphology, respectively. According to the results of XRD (Fig. 4) and SEM–EDS (Table 3), in the A# layer, the white area is iron binder and the gray round particles are the TiC phases. The fine TiC particles, as the reinforcement particles, are uniformly distributed in the metallic matrix. So A# layers was called the composite layers. Form Fig. 6b, in the A# area, the particle size of TiC is very fine below 500 nm. Formation of nanoscale TiC particles in metal matrix is due to extremely high cooling rate during solidification after spraying particles impinging on the substrate. Fig. 7a shows a bright field TEM image of the round TiC in the composite layer. The selected area diffraction parameter (SADP) in the [−1 1 2] direction shows that the round TiC has the same crystal structure as NaCl, as shown in Fig. 7b. The calculated lattice parameter of TiC carbide (NaCl type) is approximately 0.4314 nm, which is slightly lower than the standard lattice parameter, 0.4328 nm. SEM-EDS measurement (Table 3) indicates that titanium and carbon content is very high, but Ti/C atomic ratio slightly lower than 1, resulting in the smaller lattice parameter [12]. And form Fig. 6c, two different phase can be found in the B# layers. According to the results of XRD (Fig. 4) and SEM–EDS (Table 3), the B# layers are composed of TiC and Ti_2O_3, and is named the paragentic layers of TiC and Ti_2O_3. Because the atomic number of oxygen in Ti_2O_3 is larger than that of carbon in the TiC, the colour of Ti_2O_3 is lighter than that of TiC in the SEM micrograph (back-scattered electron image).

3.3. The quenching test

Fig. 8a shows a top view of the Ti–Fe–C compound spraying powder prepared by the novel process. From Fig. 8a, we can see that the compound powder is irregular, and range from 60 to 100 μm in size. Fig. 8b shows a SEM micrograph of the Ti–Fe–C compound powder after spraying into quenching medium (water). The quenched powders exhibiting a good spherical shape indicate that the Ti–Fe–C compounds powder by the novel process can melt sufficiently under the synergism of oxyacetylene flame and heat of in situ reaction.

Fig. 9 shows the cross-section of the Ti–Fe–C compounds powder directly sprayed into quenching medium (water). From Fig. 9a we can see that the spherical quenched particles have

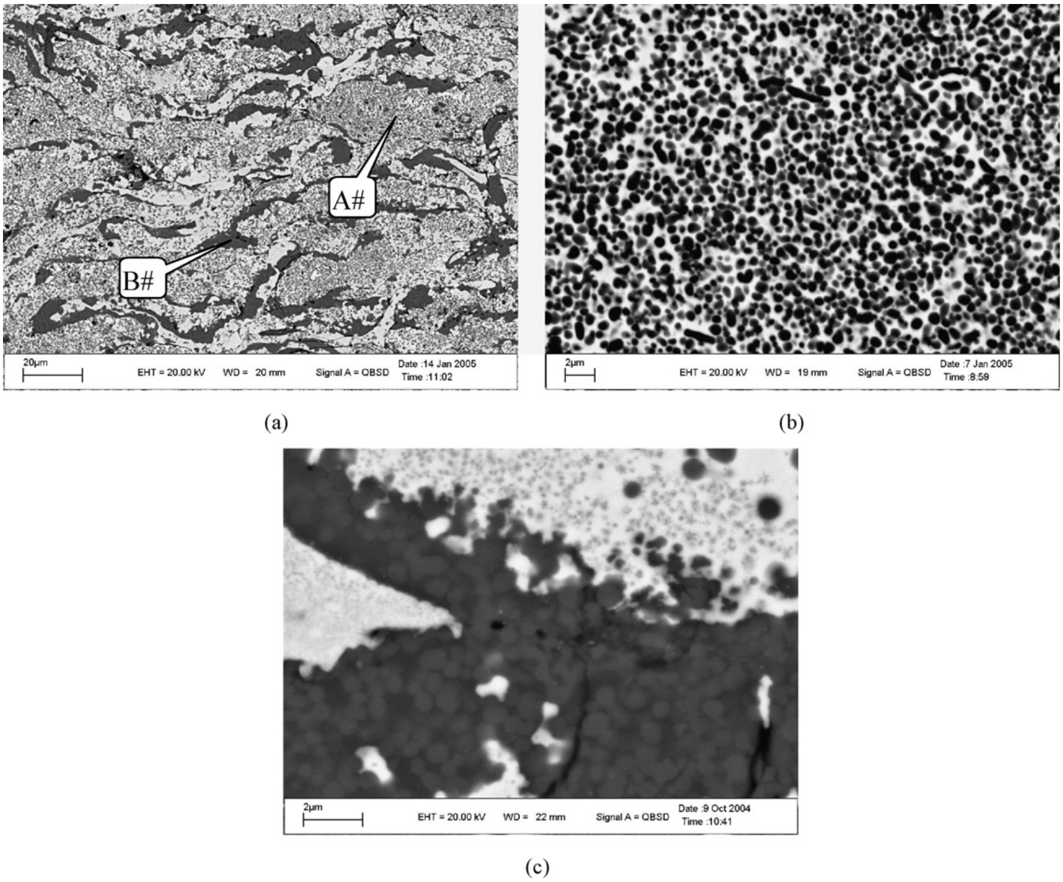


Fig. 6. Typical morphology of the TiC–Fe cermet coating by RFS: general (a), A# layer (b) and B# layer (c).

similar microstructure. Fig. 9b and c shows two typical microstructure of the quenched particles. According to the results of XRD and EDS, in Fig. 9b. The dark fine spherical-like particles are titanium carbide, <500 nm in diameter, whereas the surrounding brighter region is the Fe matrix. It indicates that the reactive constituent particles, in the Ti–Fe–C compound powders by the novel process, can react sufficiently during spraying. After the spraying particles impact on the substrate, the spraying particles of this type becomes A# laminated layers (the composite layers) in the cermet coating. From Fig. 9c,

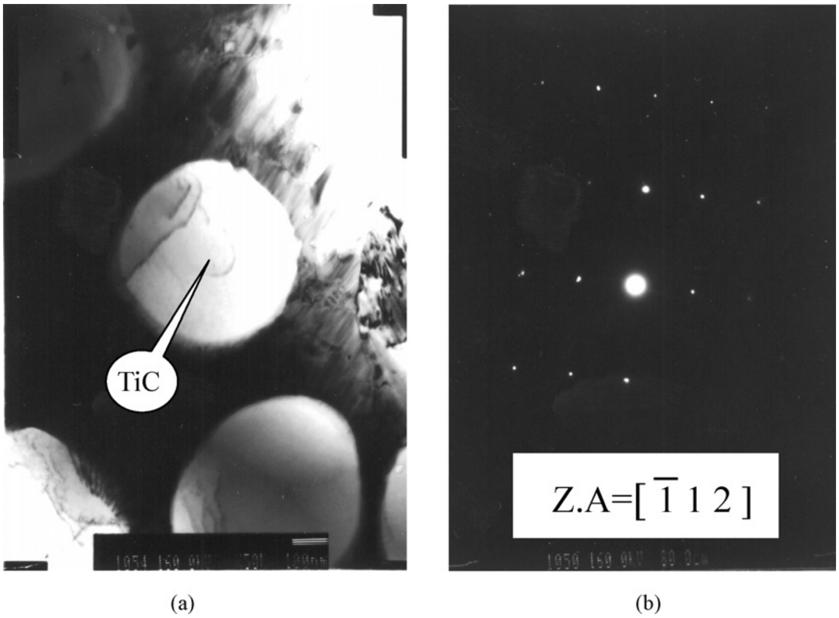
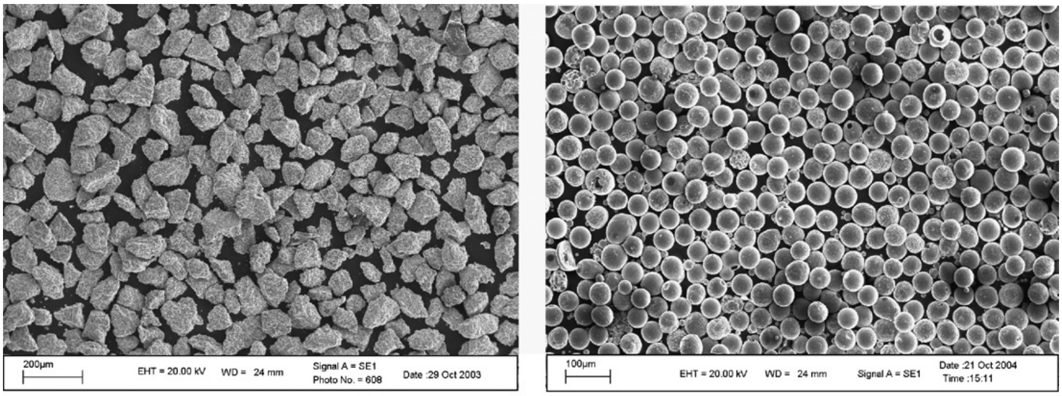


Fig. 7. Bright field TEM images of the TiC–Fe cermet coating by RFS: TiC (a) and selected area diffraction (SAD) patterns of TiC in the [−1 1 2] direction (b).

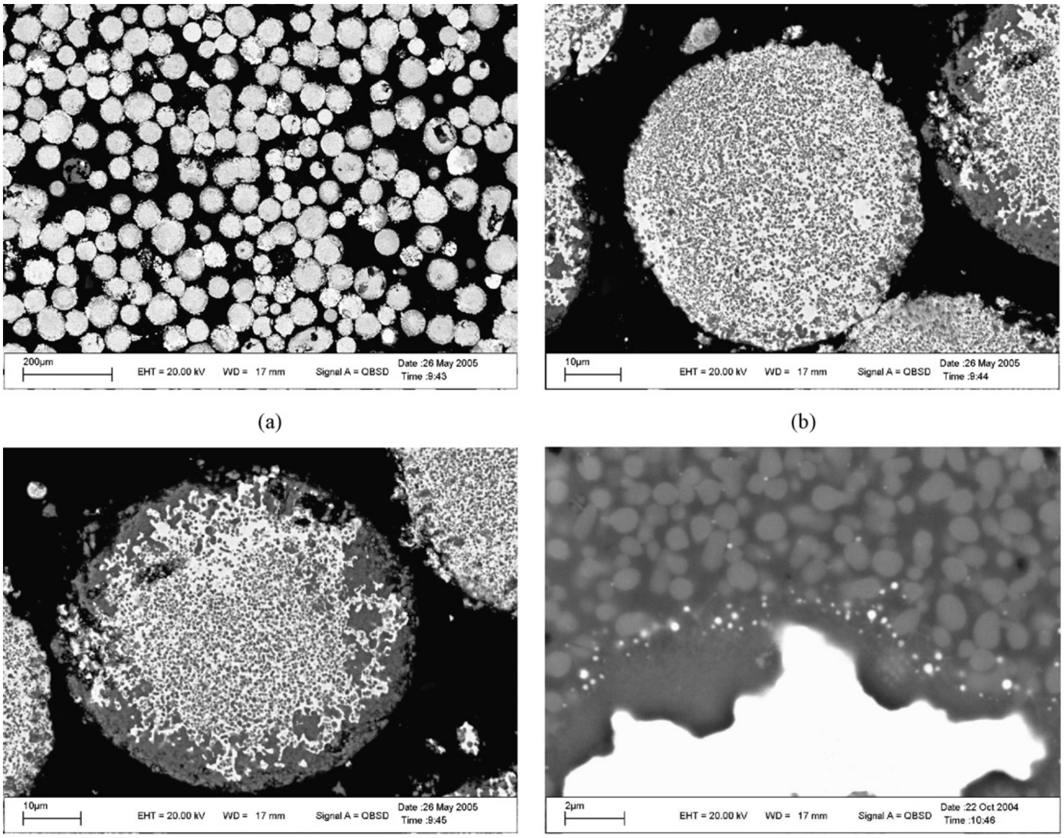


(a) (b)

Fig. 8. SEM micrographs of the Ti–Fe–C compound spraying powder (a) and the powders after spraying into quenching medium (water) (b).

there is the dark area in the surface of some quenched particles. Fig. 9d shows the SEM micrograph of the dark area in the surface of the quenched particles. Meantime, according to the results of XRD and EDS, the dark area in the quenched particles has homogeneous phase composition and microstructure with B# layers in the cermet coating. Therefore, it is considered to form B# laminated layers during spraying.

From the quenching test, we can see that the Ti–Fe–C compound powder by the novel process can wholly melt during spraying. It indicates that TiC particles precipitate and grow in the Ti–Fe–C ternary molten droplets. During the flight of molten droplets in the air, it is inevitable that the surface of the molten droplets contact with oxygen. Titanium is prone to oxidation, leading to the formation of titanic oxide particles in the surface of the molten droplets. The titanic oxide particles can serve as the crystal nucleus of heterogeneous nucleation for the TiC carbide. Meantime, because of large undercooling on surface of molten droplets during spraying, TiC particles



(a) (b)

(c) (d)

Fig. 9. SEM micrograph of cross-section of the Ti–Fe–C compound powders after spraying into quenching medium (water) for RFS: general (a), single quenched particles (b and c) and dark area of quenched particles (d).

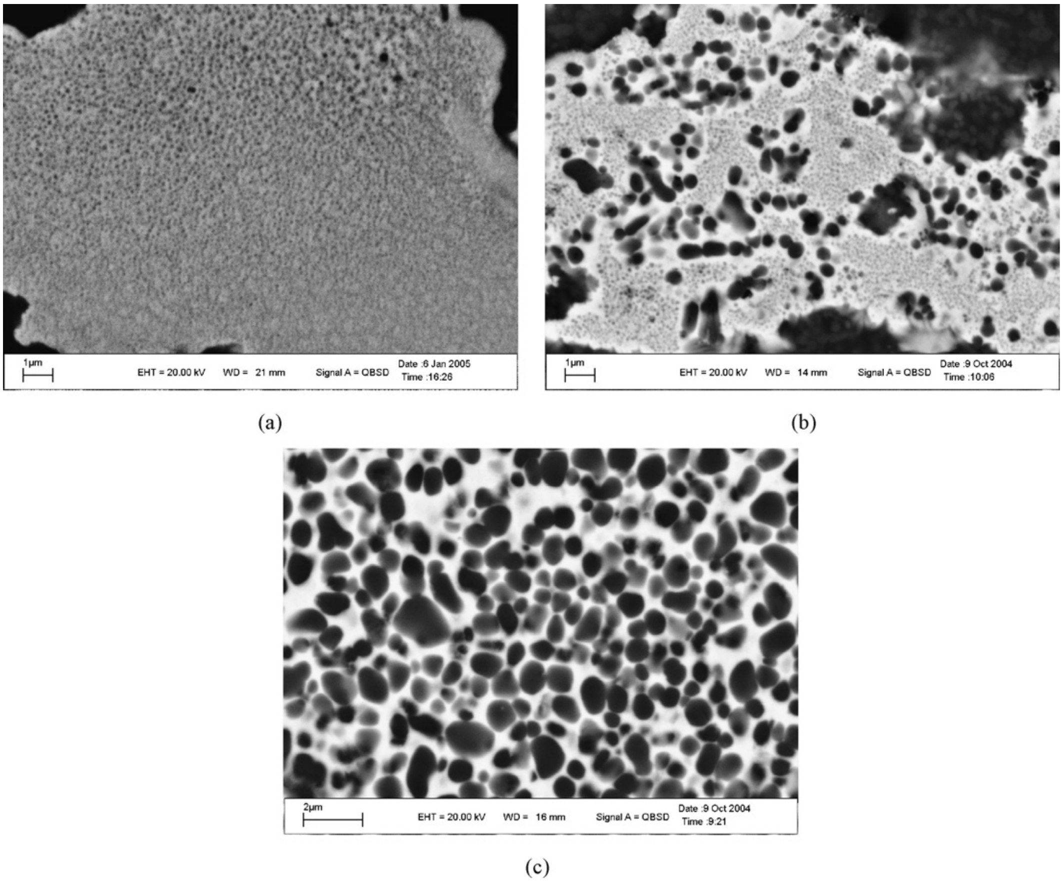


Fig. 10. Microstructure of TiC particles at different growth stages.

sharply grow around the oxide particles in the surface of molten droplets before impinging on the substrate, which results in formation of the area of the paragentic layers of TiC and Ti_2O_3. In the middle of the molten droplets, however, there is not crystal nucleus of heterogeneous nucleation, and there is a supersaturation over the equilibrium concentrations, the nucleation mode of the round fine TiC particles is homogeneous nucleation. Fig. 10 shows microstructures of TiC particles at the different growth stages. The TiC in the composite layers grows in the dissolution-precipitation mode that the smaller particulates dissolve and larger ones grow.

3.4. Properties of the TiC/Fe cermet coating

Table 4 shows the microhardness and surface hardness of the TiC–Fe cermet coating by RFS. The results show that the microhardness of the A# and B# layers is 1636 and 1893, respectively. And the surface hardness of the coating is the great higher than that of substrate.

The fretting track profiles of the coatings in different tested areas are shown in Fig. 11. The wear areas of the TiC–Fe cermet coating and Ni60 coating are illustrated in Fig. 12. The track depths of the TiC–Fe cermet coating are about 5–10 μm; however, the track depths of Ni60 coatings are as large as 30–

Table 4
Hardness of the TiC–Fe cermet coating

	Microhardness ($HV_{0.2\ kg}$)		Surface hardness (HR30N)
	A#	B#	
TiC–Fe cermet coating	1636	1893	65 ± 6
Substrate	–		18 ± 5

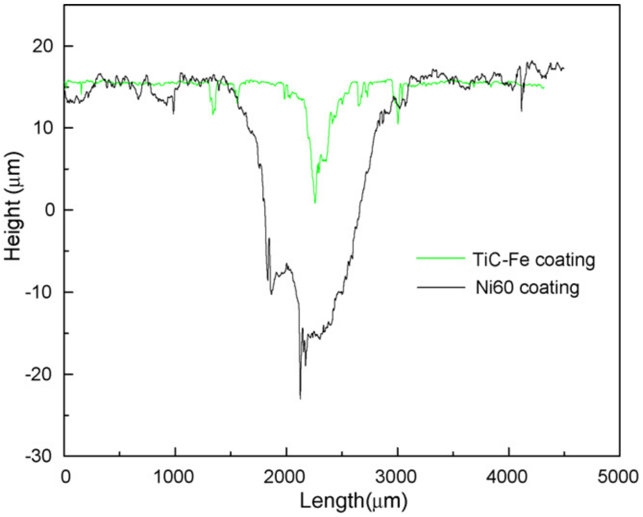


Fig. 11. Fretting track profiles of the TiC–Fe cermet coating and the Ni60 coating.

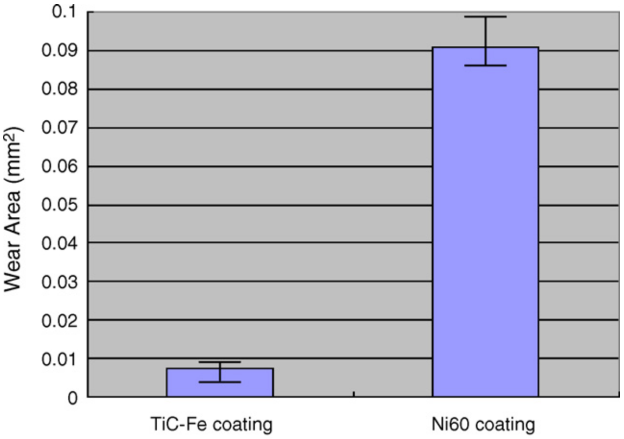


Fig. 12. Wear area of the two coatings investigated.

35 μm. According to the results of tests after the same process, the wear area of Ni60 coating is much more than that of the TiC–Fe cermet coating. It can be concluded that the wear resistance property of the TiC–Fe cermet coating is superior to that of the Ni60 coating. The superior wear resistance property of the TiC–Fe cermet coating is attributed to the peculiar microstructure of the cermet coating, containing very fine and round TiC in the metal matrix. In the present method, TiC-reinforced phase are introduced into the metal matrix by the direct reaction between titanium and carbon. Furthermore, the reinforced phase reacted in situ may be more compatible with the matrix and the phase boundaries may be cleaner as compared with other composites produced conventionally [13]. The TiC particles in the matrix would increase the toughness by limiting crack propagation [6]. Meanwhile, because a number of ultra-fine and thermally stable TiC particles uniformly distributed on the matrix of Fe alloy, the yields strength is increased through dispersion strengthening, grain size mechanisms and modify the plasticity of the exposed surface [14].

4. Conclusion

On the basis of a novel process of preparing Ti–Fe–C compound powder, the TiC–Fe cermet coating was prepared by RFS of the compound powder. The following conclusions can be drawn from the present investigation:

(1) A kind of agglomerated Ti–Fe–C compound spraying powder was prepared by heating a mixture of ferrotitanium and asphalt to pyrolyze the asphalt as carbonaceous precursor. The carbon by the pyrolysis of the asphalt was a reactive constituent as well as a binder in the compound powders. The Ti–Fe–C compound powder has a very tight structure, which can avoid the problem that reactive constituent particles were separated during spraying.

(2) The TiC–Fe cermet coating can be prepared by RFS of the Ti–Fe–C compound powder prepared by the novel process. The TiC–Fe cermet coating by RFS presents typical morphology of thermal spraying coating with two different laminated layers: the one is the composite layer in which the round fine TiC particles are dispersed within the Fe matrix. The other is the paragentic layers of TiC and Ti_2O_3. From SEM micrographs, the cermet coatings have good inter-layers cohesion and coating adhesion with very little porosity.

(3) According to the result of the quenching test, the Ti–Fe–C compounds powder by the novel process can melt wholly and react sufficiently during spraying. TiC particles precipitate and grow in the Ti–Fe–C ternary molten droplets. The nucleation mechanism of the TiC in the composite layers and the paragentic layers of TiC and Ti_2O_3 is homogeneous nucleation and heterogeneous nucleation, respectively. The TiC in the composite layers grows in the dissolution-precipitation mode that the smaller particulates dissolve and larger ones grow.

(4) The TiC/Fe cermet coating by RFS shows high hardness and wear resistance property: the surface hardness of the coating is 65 ± 6(HR30N). In the same Fretting conditions, the wear area of Ni60 coating is much more than that of the TiC/Fe cermet coating. It can be concluded that the wear resistance property of the TiC–Fe cermet coating is superior to that of the Ni60 coating.

Acknowledgement

This work was supported by the Innovative Fund for Outstanding scholar of Henan Province (No. 0421001000).

References

[1] S. Economou, M. De Bonte, J.P. Celis, R.W. Smith, E. Lugscheider, Tribological behaviour at room temperature and at 550 °C of TiC-based plasma sprayed coatings in fretting gross slip conditions, Wear 244 (2000) 165–179.

[2] S. Economou, M. De Bonte, J.P. Celis, R.W. Smith, E. Lugscheider, Processing, structure and tribological behaviour of TiC-reinforced plasma sprayed coatings, Wear 220 (1998) 34–50.

[3] R. Licheri, R. Orru, G. Cao, A. Crippa, R. Scholz, Self-propagating combustion synthesis and plasma spraying deposition of TiC–Fe powders, Ceram. Int. 29 (2003) 519–526.

[4] M. Jones, A.J. Horlock, P.H. Shipway, D.G. McCartney, J.V. Wood, Microstructure and abrasive wear behaviour of FeCr–TiC coating deposited by HVOF spraying of SHS powders, Wear 249 (2001) 246–253.

[5] M. Jones, A.J. Horlock, P.H. Shipway, D.G. McCartney, J.V. Wood, A compoarison the abrasive wear behaviour of HVOF sprayed titanium carbide and titanium boride-based cermet coatings, Wear 251 (2001) 1009–1016.

[6] C.S. Liu, J.H. Huang, Sh. Yin, TiC–Fe coatings prepared by flame spray synthesis process, Trans. Nonferrous Metals Soc. China 10 (2000) 405–407.

[7] Zh.W. Li, C.S. Liu, J.H. Huang, Synthesis and deposition of TiC–Fe coatings by oxygen–acetylene flame spraying, J. Mater. Sci. Technol. 19 (2003) 161–164.

[8] P.V. Ananthapadmanabhan, P.R. Taylor, Titanium carbide–iron composite coating by reactive plasma spraying of ilmenite, J. Alloys Compd. 287 (1999) 121–125.

[9] R. Knight, R.W. Smith, M.A. Lawley, Spray forming R&D at Drexel University, Int. J. Powder Metall. 31 (1995) 205–210.

[10] G. Cliché, S. Dallaire, Sythnesis and deposition of TiC–Fe coatings by plasma spraying, Surf. Coat. Technol. l46 (1991) 199–206.

[11] J.H. Huang, C.S. Liu, Q.K. Dang, A study on reactive flame spraying for TiC/FeAl composite coating, Powder Metall. Technol. 20 (2002) 219–222.

[12] M. Eslamloo-Grami, Z.A. Munir, The mechanism of combustion synthesis of titanium carbonitride, J. Mater. Res. 9 (1994) 431–435.

[13] X.L. Wu, In situ formation by laser cladding of a TiC composite coating with a gradient distribution, Surf. Coat. Technol. 115 (1999) 111–115.

[14] C.S. Liu, J.H. Huang, Sh. Yin, New process for the fine-ceramic-coating: flame spray synthesis, J. Univ. Sci. Technol. Beijing 7 (2000) 214–217.