In Situ TiC-Reinforced Ni-Based Composite Coating Prepared by Flame Spraying Using Sucrose as the Source of Carbon

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A Ni-Ti-C composite powder for Reactive Thermal Spraying is made by heating a mixture of titanium, nickel, and sucrose to carbonize the sucrose, which is used as the source of carbon. The carbon obtained by pyrolysis of sucrose is a reactive constituent as well as the binder in the composite powder. The titanium and nickel particles are bound by the carbon to form granules of the composite powder. This powder feedstock was used to prepare in situ TiC-reinforced Ni-based composite coating by oxyacetylene flame spraying. The TiC-Ni composite coating is made of TiC, Ni, and some Ni_3Ti. In the coating, a mass of fine TiC particles is uniformly distributed within the metallic matrix. The microhardness and surface hardness of the coating are, respectively, 1433 $HV_{0.2kg}$ and 62 ± 6 (HR30N). The wear resistance is much better for the TiC-Ni composite coating than for the substrate and Ni60 coating.

1. Introduction

On account of the high melting temperature (3200 °C), high hardness (HV3200), and thermal stability of titanium carbide (Ref 1), different metallic matrix coatings reinforced with TiC hard particles have been widely investigated. So far, TiC-reinforced cermet coatings (e.g., TiC/Fe, TiC/Fe-Al, TiC/Al, TiC/Fe-Ni, TiC/Fe-Cr) have been investigated using various surface techniques such as thermal spraying, laser beam, tungsten inert gas melting process, and magnetron sputtering (Ref 2-8). Ni-based alloys have an excellent thermal stability and also good resistance to corrosion in the presence of air (Ref 9, 10). The TiC-reinforced Ni-based composite coatings are thus potential materials to wear resistance for many practical applications.

Thermal spraying is a practical and extensively used technique to prepare cermet coatings. In the conventional thermal spraying process, the TiC particles are directly added into a metallic binder to prepare cermet powders via sintering (Ref 11) or high-energy milling (Ref 12). Then the cermet powders are injected into a jet (e.g., plasma, oxyacetylene flame), heated, molten, and deposited to form a cermet coating. The hard phase particles in the coatings are usually large (more than 1 μm), and unevenly distributed. Besides, as the surface of the added TiC particles is usually not clean or polluted, the interface between the reinforced phase particles and metallic matrix is often a potential source of weakness. Employing a more recent method, the cermet powders containing TiC can be produced using self-propagating high-temperature synthesis (SHS). The drawback of SHS cermet powders is the stringent conditions required for the spraying process, such as high spraying temperature and high spraying speed. Usually, plasma (Ref 13) or high-velocity oxyfuel (HVOF) (Ref 8, 14) are required to spray the SHS cermet powders.

To get in situ TiC particles in cermet coatings, Reactive Thermal Spraying is used to produce TiC-reinforced composite coatings. Reactive thermal spraying is a novel technology combining the in situ reactive synthesis with thermal spraying. The main feature of this technique is that the ceramic phases, directly formed by an in situ reaction, are fine, spherical, and uniformly dispersed within the metallic matrix. These advantages can sharply increase the wear-resisting property of the coatings, because tiny TiC particles can improve yield strength through dispersion and grain size mechanisms, and improve toughness by hindering crack propagation (Ref 15). Furthermore, the chemical reactions to synthesize the ceramic phases are exothermic, which provides an additional heat source to the spraying process. The TiC-reinforced cermet coatings may thus be prepared by a cheap oxyacetylene flame spraying device (Ref 2).

Usually, the reactive raw material powders are firstly mixed up to make the composite feedstock for Reactive Thermal Spraying. Then the composite powders are sprayed and in situ TiC-reinforced composite coatings are synthesized and deposited simultaneously during spraying.

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As an example, TiC-reinforced composite coatings can be prepared by Reactive Thermal Spraying of composite powders of titanium (or titanium alloy), graphite, and other metals (Ni, Fe, etc.) (Ref 16). The reactive products can thus be designed and controlled by adjusting the composition of the composite powders for Reactive Thermal Spraying. Until now most of the composite powders used for Reactive Thermal Spraying have been prepared by simple mechanical blend or pelletization adding a small amount of agglomerant (Ref 5). Because of the low bond strength among raw materials in the composite powders prepared with such methods, the reactive constituents are liable to be separated and incompletely react with each other during spraying. Then some raw material particles may remain in the coatings, or graphite is lost during spraying (Ref 5). It results in an inhomogeneous coating microstructure with a small amount of TiC particles (Ref 17). In Ref 18, mechanical alloying of a Ni(Cr) prealloyed powder and Ti and C elemental powders was performed in a ball mill, and Ni-TiC coatings were prepared by reactive HVOF spraying of these metastable Ni-Ti-C powders. The milling cost too much time and small quantities of NiTi, TiO$_2$, and NiTiO$_3$ were also present in the coatings, although in situ TiC particles were synthesized during the spraying.

Liu et al. (Ref 2) reported that a composite feedstock powder with high bond strength among raw materials had been prepared by precursor carbonization process using asphalt as the carbonaceous precursor. It can be noticed too that the carbon obtained from the carbonization of asphalt is used as a reactive constituent as well as the binder in the composite powder. However, the temperature of pyrolysis of asphalt is 550 °C, at which a few TiC particles may be formed in the feedstock powder. Also, owing to the large amount of impurity present in commercial asphalt, its composition is difficult to control enough accurately to precisely design the coating composition.

This article is concerned with a novel precursor carbonization process to prepare Ni-Ti-C composite powder for Reactive Thermal Spraying. The main characteristic of the process is that sucrose, a carbonaceous precursor, is used as the source of carbon. The feedstock powder was prepared by heating a mixture of titanium powder, nickel powder, and sucrose to pyrolyze the sucrose. The sucrose can be pyrolyzed completely at 350 °C and the products obtained after carbonization are pure. Raw material particles are bounded by the carbon, which allows avoiding separation of Ti and C during spraying. A cheap oxyacetylene flame spraying device was employed to prepare in situ TiC-reinforced Ni-based cermet coating by reactive flame spraying (RFS).

2. Materials and Experiments

In this experiment, the raw materials are titanium powder (97% Ti, $d < 50$ μm), Ni powder (99% Ni, $d < 2.5$ μm), and sucrose (C$_{12}$H$_{22}$O$_{11}$) as carbonaceous precursor. First, the raw materials were mixed with

alcohol to be milled for 24 h in a miller. They were milled with the ratio of 4:1 of balls to powders (in weight). Second, the mixture was held at 350 °C for 3 h in a nitrogen atmosphere for the sake of completely carbonizing the sucrose. Finally, the product after carbonization was crushed in a centrifugal mill and sieved mechanically to get the composite feedstock powder in the size range of 40-60 μm. Liu (Ref 19) studied the influence of carbon titanium atomic ratio on the microstructure, porosity, and properties of a TiC/Fe coating. They found that both the size of agglomerated area of TiC particles in the coating and the porosity of the coating increase with the increase of the C/Ti atomic ratio. When the C/Ti atomic ratio is 1, the surface hardness of the coating is the highest. Based on research about the influence of Ni content on the microstructure and properties of TiC/Ni coating, it is found that a Ni content above 40 wt.% is good for decreasing the oxidation of Ti (Ref 20). The composition of the mixture before carbonization and composite powder after carbonization are shown in Table 1.

The Ni-Ti-C composite powder was sprayed onto substrates (low-carbon steel) by oxyacetylene flame spraying equipment. The spraying parameters are listed in Table 2. Prior to spraying, the substrates were grit-blasted on one side to clean and roughen the surfaces.

X-ray diffraction (XRD) with Cu-Kα radiation, Leo-1450 scanning electron microscope (SEM), and transmission electron microscope (TEM) were employed to analyze the composition and microstructure of both the composite powder and coating. A microhardness test was performed on a MH-6 machine with a 200 g load and a dwell time of 10 s. The surface hardness of the coatings was measured on a HSRU-45 surface hardness machine with a 15 N load. For comparison purpose, a ball-on-disk apparatus (Optimal SRV oscillating friction and wear tester) was employed to evaluate the wear-resisting property of the TiC-Ni composite coating, the substrate, and a Ni60 coating prepared by the same flame spraying. The substrate was made of medium carbon steel and the chemical composition of the Ni60 self-fluxing alloy coating was 0.8C, 16Cr, 4.5Si, 3.5B, ≤15Fe, and balance Ni (wt.%). The Ni60 coating is a widely used hard facing in many industrial applications for their good wear resistance and surface hardness above HRC60. A schematic

Table 1 Characteristics of the powders (wt.%)

Mixture before carbonization		Powder after carbonization	
Ti powder	34.9	Ti	42.4
Ni powder	38.7	Ni	47
Sucrose	26.4	C	10.6

Table 2 Flame spraying parameters

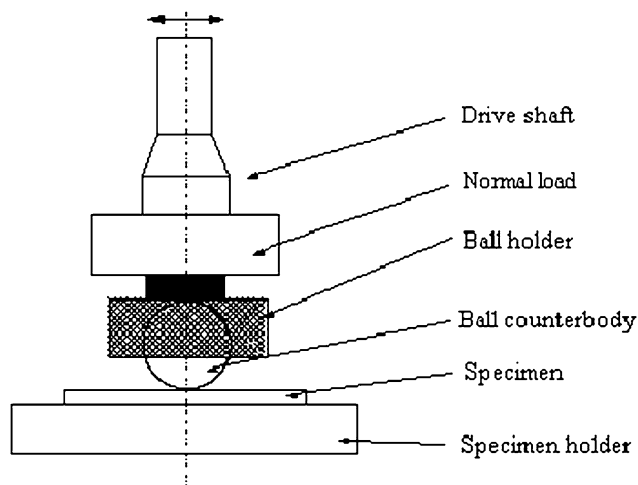| Oxygen pressure, MPa	Acetylene pressure, MPa	Protective gas pressure, MPa	Spray distance, mm
0.8	0.1	0.4	170

Fig. 1 Schematic illustration of Optimal SRV friction and wear tester

Table 3   Conditions of wear-resisting property test

Counter body	GCr15ball	Oscillating amplitude	1.5 mm
Diameter of ball	10 mm	Specimen temperature	20 °C
Normal load	20 N	Lubrication	None
Oscillating frequency	30 Hz	Fretting time	20 min

illustration of the Optimal SRV friction and wear tester is given in Fig. 1. The upper ball slides right and left reciprocally against the stationary discs (polished specimen). The upper ball was made of GCr15 steel, whose composition was 0.95-1.05C, 0.15-0.35Si, 0.25-0.45Mn, 1.40-1.65Cr, ≤0.10Mo, ≤0.025P, ≤0.025S, ≤0.30Ni, ≤0.25Cu, and balance Fe (wt.%). The hardness of the GCr15 steel ball was above HRC65. All the fretting conditions are summarized in Table 3. The wear volume loss of the lower disc was determined by using a Talysurf 5P-120 profilometer.

3. Results and Discussion

3.1 Characterization of the Ni-Ti-C Composite Powder for RFS

Figure 2 shows the XRD diffraction pattern of the Ni-Ti-C composite powder for RFS. The only phases that can be detected in this pattern are titanium and nickel, which indicates that the formation of TiC does not happen during the carbonization process. The peaks of carbon are also absent in the XRD pattern of the composite powder. Figure 3 shows the XRD diffraction pattern of the carbon obtained by pyrolysis of sucrose at 350 °C for 3 h in a nitrogen shielding gas. It can be seen that the carbon has a noncrystalline structure: it is neither graphite nor diamond carbon, but instead amorphous. As a result, the peaks of carbon can not be found in the XRD pattern of the composite powder (Ref 21).
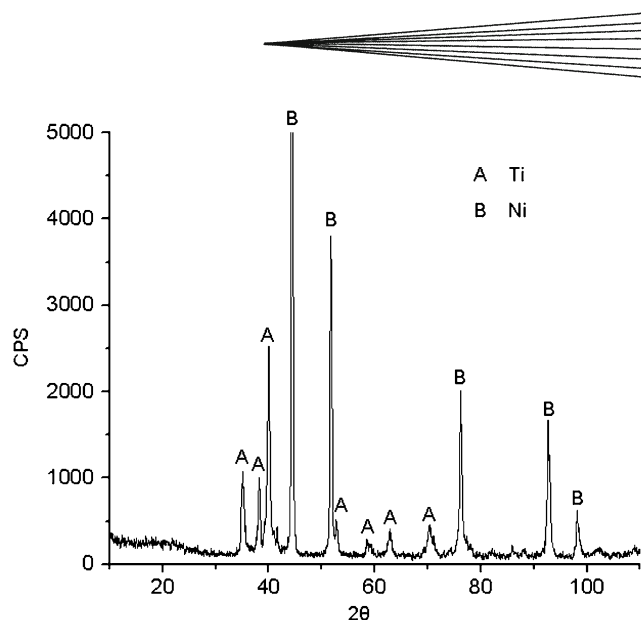

Fig. 2 XRD diffraction pattern of the Ni-Ti-C composite powder for RFS
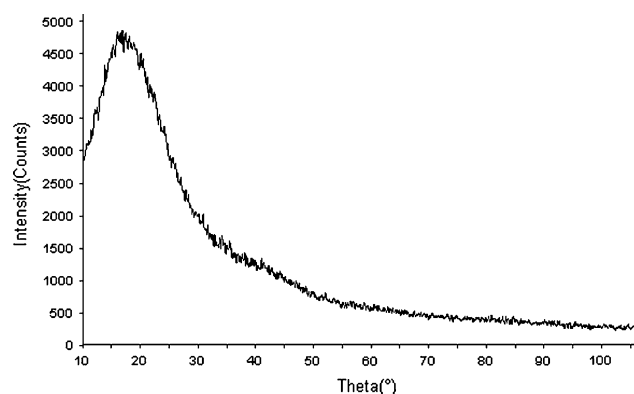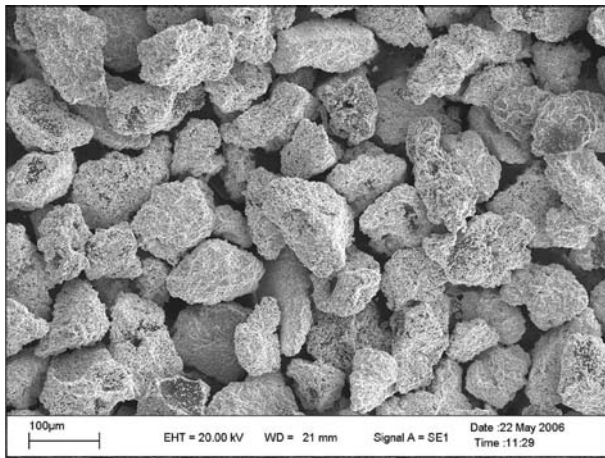

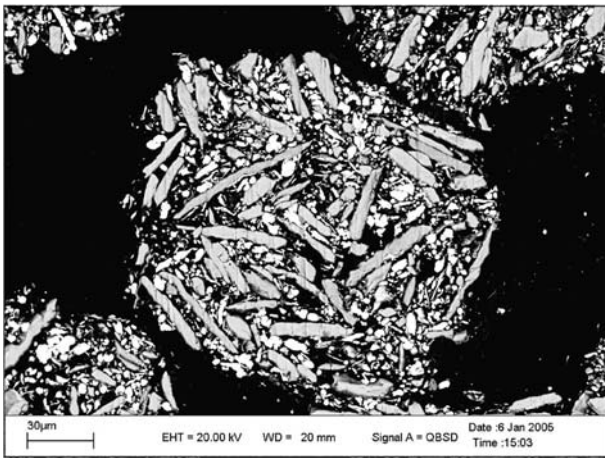**Fig. 3** XRD diffraction pattern of the carbon obtained by pyrolysis of sucrose

A top view of the composite powder is shown in Fig. 4(a). The size of the composite powder lies in the range of 60-100 μm and the shape is irregular. A cross section of the composite powder is represented in Fig. 4(b). The white areas hold for clavate titanium and fine nickel particles, and the black areas among them hold for carbon obtained from carbonization of sucrose. The clavate titanium and fine nickel particles are bound by the carbon, which is a reactive constituent as well as the binder in the composite powder, to form granular feedstock for spraying. Every single composite powder granule can be recognized as an independent reactive unit during spraying.

3.2 Microstructure of the TiC-Ni Composite Coating Prepared by RFS

The chemical reaction taking place in the Ni-Ti-C ternary system at the ideal state of equilibrium can be represented by the following equation: $Ti + Ni + C = TiC + Ni$ with the final products TiC and Ni. At nonequilibrium

(a)

(b)

Fig. 4 SEM micrograph of the Ni-Ti-C composite powder for RFS: top view (a) and cross section (b)

Fig. 5 XRD diffraction pattern of the TiC-Ni composite coating prepared by RFS

conditions, the reactions between Ti and Ni take place, and the intermediate products Ni_3Ti or NiTi are present (Ref 9). In the XRD diffraction pattern of the TiC-Ni composite coating synthesized and deposited by RFS of the composite powder (Fig. 5), the phases that can be detected are TiC, Ni, and some Ni_3Ti. It indicates that the RFS is a typical nonequilibrium processing technology, leading to an incomplete reaction between Ti and C in the Ni-Ti-C ternary system to form some Ni_3Ti. Nonetheless, there is no trace of titanium powder in the composite coating, which reveals that the specific structure of the composite powder granule allows preventing the raw material particles from separating each other during spraying.

Figure 6(a) is a secondary electron image of a cross section of the TiC/Ni composite coating. The composite coating shows good interlayer cohesion with very little porosity. Also the interface between coating and substrate does not reveal any debonding, showing that the coating adhesion is good. Figure 6(b) is a backscattered electron image of the same area in the TiC/Ni composite coating. It can be seen that the coating presents a typical morphology
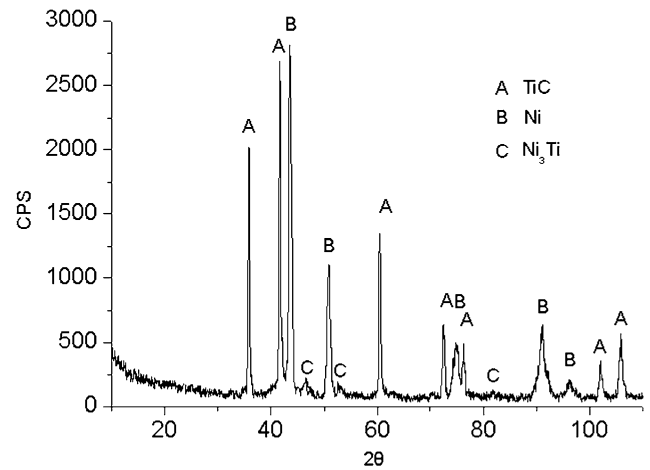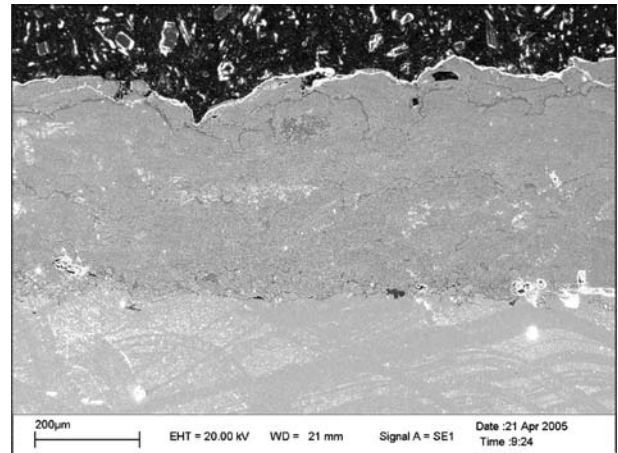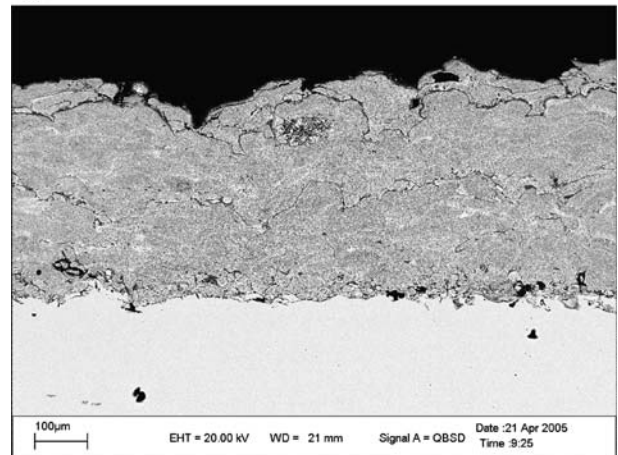

(a)

(b)

Fig. 6 SEM micrograph of cross section of the TiC/Ni composite coating prepared by RFS: secondary electron image (a) and backscattered electron image (b)

of thermal-sprayed coating with superposition of layers. The layers in the coating are very thin, which indicates that the composite powder could completely melt under the combined action of the exothermic reactions and the oxyacetylene flame during the spraying process.

A typical microstructure of the TiC/Ni composite coating prepared by RFS is presented in Fig. 7(a). Obviously the coating is formed by superposition of layers but these layers look identical, and the interface between them is indistinct. From the further magnified backscattered electron image shown in Fig. 7(b), it is found that a mass of fine particles is dispersed within the metallic matrix. These layers can be called the composite reinforcement layers. The microstructure of the TiC/Ni composite coating is extremely uniform without any TiC-rich or TiC-poor layer. Figure 7(c) shows the hard phase particles in the composite reinforcement layers. The Ni metallic binder appears to be white and the TiC phases appear to be gray round particles. In the composite reinforcement layers, fine TiC particles are uniformly distributed within the metallic matrix and their size is small, below 500 nm. Figure 8(a) shows a bright-field TEM image of a spherical TiC particle in a composite reinforcement layer. Electron diffraction pattern along the $[\bar{1}12]$ direction of selected areas indicates that the TiC has a face-centered cubic (FCC) crystal structure, as shown in the Fig. 8(b). The formation of submicron-scale TiC particles in the metallic matrix may be due to an extremely high cooling rate during particle solidification after impingement on the substrate (Ref 22).

3.3 Properties of the TiC-Ni Composite Coating Prepared by RFS

Table 4 shows the microhardness and the surface hardness of the TiC-Ni cermet coating prepared by RFS. As the layers forming the TiC-Ni coating look identical, the microhardness of the composite reinforcement layers was measured 30 times to get an average value. The obtained coating microhardness is about 1433 $HV_{0.2kg}$, while it was reported that the microhardness of both: (i) induction clad Ni-based composite coating reinforced with micro- and nanoWC particles (Ref 23) and (ii) in situ TiC-TiB$_2$/Ni cermet coating by laser cladding (Ref 24) was below 1000 $HV_{0.2kg}$. At the same time, the surface hardness of the TiC-Ni composite coating (resulting from the average 30 measurements) is much higher than that of the substrate. This high coating hardness may be attributed to the presence of many in situ fine TiC particles and few intermetallic Ni$_3$Ti in the metallic matrix. The high cooling rate during particles solidification (mentioned in section "Microstructure of the TiC-Ni Composite Coating Prepared by RFS") may also promote to decrease the Ni alloy grain size and thus enhance the coating hardness.

The wear resistance of the TiC-Ni composite coatings prepared by RFS was measured and compared with wear resistance of both substrates and Ni60 coatings prepared with the same flame spraying equipment. The fretting track profiles of the three specimens are plotted in Fig. 9. The metal substrate has a narrow track with a maximum
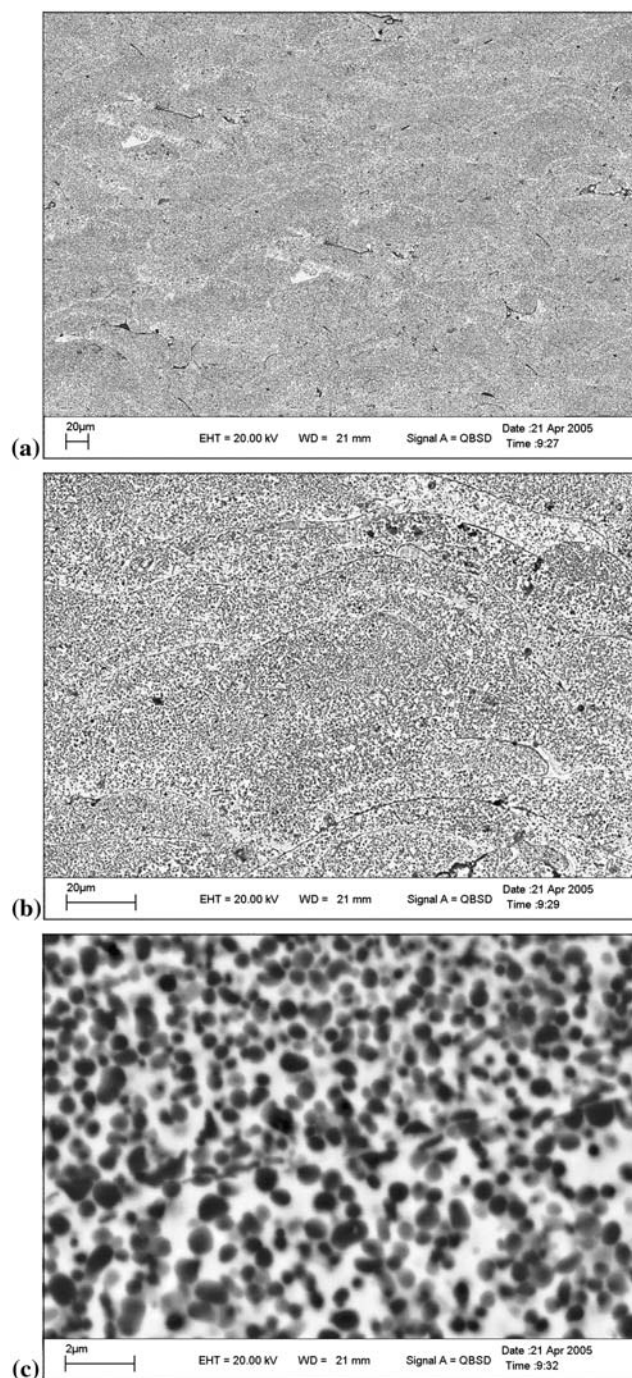

Fig. 7 SEM backscattered micrograph of the TiC/Ni composite coating prepared by RFS: typical microstructure (a); the composite reinforcement layers (b); and the submicron-scale TiC particles (c)

depth of 80 µm; the Ni60 coating has a lower track depth of about 30 µm; however, the TiC-Ni composite coating has the smoothest track with the smallest depth, less than 10 µm. Wear volume loss tests were done in the same conditions for the three types of specimens. Five tests were performed on five samples for each type of specimen
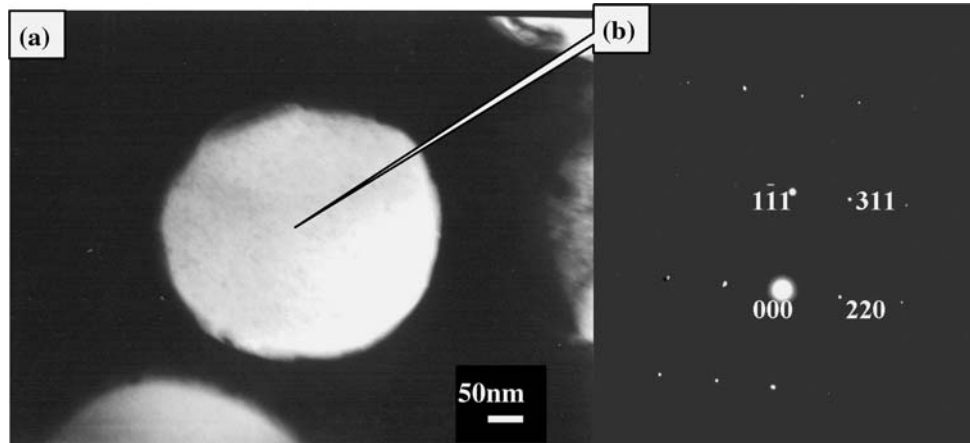
Fig. 8 Bright-field TEM images of the TiC/Ni composite coating prepared by RFS: submicron-scale TiC (a) and selected area electron diffraction pattern of TiC, [112] zone axis (b)
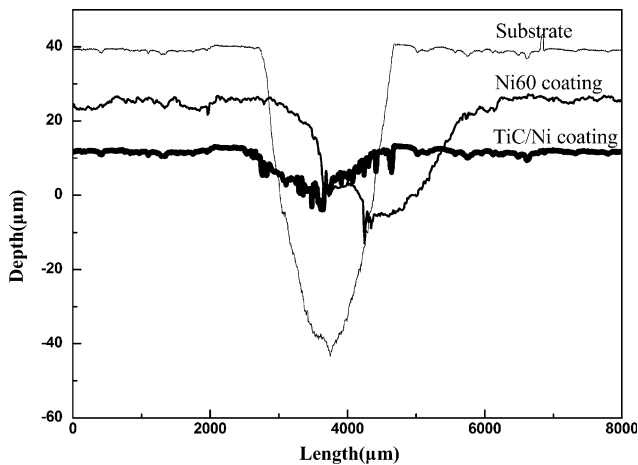

Fig. 9 Fretting track profiles of the TiC/Ni composite coating, Ni60 coating, and metal substrate
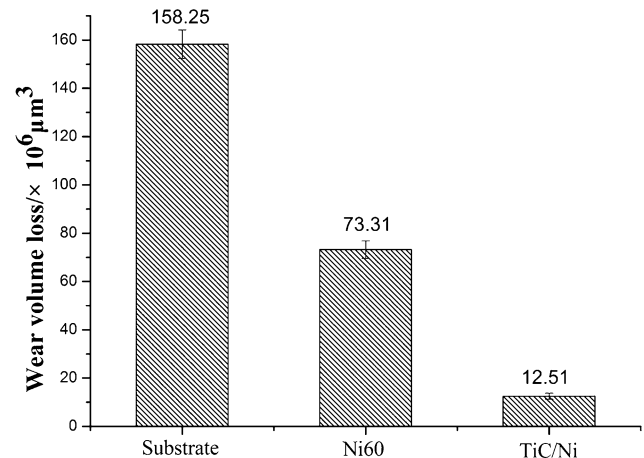

Fig. 10 Wear volume loss of specimens at the same wear conditions on a Optical SRV friction and wear tester

**Table 4 Hardness of the TiC-Ni composite coating prepared by RFS**

	Microhardness ($HV_{0.2kg}$)	Surface hardness (HR30N)
TiC-Ni composite coating	1433	62 ± 6
Substrate	–	18 ± 5

and the average value was deemed to be the wear volume loss of this type of specimen. The results compared in Fig. 10 show that the wear volume loss of medium carbon steel substrate is much larger than for any other coating. It can indeed be concluded that the wear-resisting property of the TiC-Ni composite coating is about 6 and 11 times better than the Ni60 coating and the substrate, respectively. Besides, the wear volume loss of TiC/Fe coating prepared by reactive flame spray using asphalt as source of carbon was about 1/5 of that for the Ni60 coating (Ref 25), so the wear resistance of TiC-Ni coating made using

sucrose as source of carbon is better. This enhanced wear resistance may be due to the following reasons. The in situ TiC may be more compatible with the metallic matrix and the phase boundaries may be cleaner as compared with other composites produced conventionally (Ref 17). The TiC particles in the matrix could increase the toughness by limiting crack propagation (Ref 26). Meanwhile, because a number of ultra-fine and thermally stable TiC particles are uniformly distributed in the metallic matrix of Ni alloy, the yield strength may increase through dispersion strengthening and grain size mechanisms (Ref 27). The plasticity of the coating may be improved.

4. Conclusions

Based on a novel process for preparing Ni-Ti-C composite powder, in situ TiC-reinforced Ni-based composite coating was prepared by RFS of the composite powder.
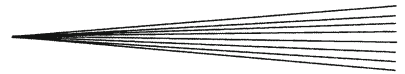
The following conclusions can be drawn from the present investigation:

1. A Ni-Ti-C composite powder for Reactive Thermal Spraying, using titanium powder, nickel powder, and sucrose as raw materials, was made. The main feature of this technique is that sucrose, as carbonaceous precursor, is used as source of carbon. The Ni-Ti-C composite powder was prepared by heating a mixture of titanium powder, nickel powder, and sucrose to pyrolyze the sucrose. The carbon obtained from carbonization of the sucrose was a reactive constituent as well as the binder in the composite powder. The titanium and nickel particles were bound by the carbon to form spraying feedstock granules.

2. The Ni-Ti-C composite powder can well melt under the combined action of exothermic reactions and an oxyacetylene flame to form TiC-Ni composite coating. The coating is composed of TiC, Ni, and some Ni_3Ti, and is formed by superposition of identical composite reinforcement layers. The microstructure of the coating is extremely uniform without any TiC-rich or TiC-poor layer. In the composite reinforcement layers, a mass of fine TiC particles is uniformly distributed within the metallic matrix and the TiC particles size is below 500 nm.

3. The microhardness of the TiC-Ni composite coating reaches 1433 $HV_{0.2kg}$ and the surface hardness is 62 ± 6 (HR30N). The wear resistance of metal substrate and Ni60 coating is, respectively, about one twelfth and one sixth of that for the TiC-Ni composite coating.

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