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Synthesis of titanium carbide by induction plasma reactive spray ①

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Abstract: A novel method capable of sufficient mixing of titanium powder and methane of carbon source was developed in the synthesis of titanium carbide by induction plasma reactive spray. X-ray diffraction analysis, optical microscopy, scanning electron microscopy, and microhardness test were used to characterize the spray-formed deposit. The experimental results show that both primary carburization of the titanium particles inside the plasma flame and secondary carburization of the growing deposit on high temperature substrate contribute to the forming of titanium carbide. The transitional phase of TiC_{1-x} has the same crystal structure as TiC, but has a slightly low lattice constant. The deposit consists of fine grain structure and large grain structure. The fine grain structure, harder than large grain structure, shows grain boundary fracture.

Key words: induction plasma; carburization process; titanium carbide; phase constituent

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1 INTRODUCTION

Recently, thermal plasma synthesis and reactive plasma spray forming have received more and more attention for preparing refractory materials. Thermal plasma has several distinct characteristics in the chemical synthesis. An important characteristic is that a variety of different species reactions proceed at the same time, including excited species-atom, excited species-ion, atom-ion, etc. Thermal plasma reactors operated at temperatures as high as 10 000 ℃ dramatically increase reaction rate and decrease reaction time.

In 1993, Smith et al[1] used direct current plasma spray to synthesize and form the deposits of tungsten carbide and titanium carbide from tungsten powder and titanium powder, respectively. Because the particle velocity in direct current plasma is in the range of 100 - 500 m/s, the residence time of the particles inside the plasma flame is in the order of millisecond. The carburization of metal powder by an organic compound of carbon source like methane is very limited. In Smith's experiment, small fractions of WC and TiC were synthesized. As a result, the deposits obtained were W-WC and Ti-TiC composites, respectively.

In radio frequency induction plasma, electrical energy transferring to thermal energy is accomplished through an induction coil instead of electrodes[2]. Thus, the central feeding of powders and reactants into the plasma is allowed, which could significantly enhance the homogeneity of reactions. Also, the contamination from the erosion of electrodes in d. c. plasma is eliminated in the induction plasma. In addition, the volume of the induction plasma is large and the particle velocity is low, generally in the range of 30 - 50 m/s. Particle residence time in the induction plasma is 10 times longer than that in d. c. plasma. All of these are favorable for the chemical synthesis of ultrafine and pure ceramic powders[3, 4] as well as for the reactive spray forming of refractory materials[5-7]. In 1994, Soucy et al[3] investigated the mixing pattern of ammonia and a silicon source for the sake of increasing reaction probability and homogeneity during induction plasma synthesis of ultrafine Si_3N_4 powder. It was found that much fast mixing of the reactive sources occurred by the way of radial injection than by the way of axial injection. Three injection ports, 45° toward the upstream of the plasma flame, were developed.

Titanium carbide has very high hardness and good abrasive wear resistance. Titanium carbide films, coatings and composites were fabricated by a variety of techniques such as dense plasma focus device, high velocity oxy-fuel (HVOF) spray, d. c. plasma spray, vacuum plasma spray, and ion beam-assisted electron beam physical vapor deposition[8-14]. In this study, an innovative injection of titanium powder and methane of a carbon source was developed in the synthesis of titanium carbide by induction plasma reactive spray.

2 EXPERIMENTAL

The synthesis of titanium carbide by induction plasma reactive spray was conducted in a water-cooled

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stainless steel chamber operated at a low pressure. Schematic of the experimental set-up is shown in Fig. 1. The plasma was generated at the radio frequency of 3 MHz. Argon, at the flow rate of 40 L/min, was used as central plasma gas. A mixture of 90 L/min Ar and 9 L/min H_2 was used as sheath gas. The metal powder of titanium was axially injected into plasma through a water-cooled probe located at the position of the first turn of an induction coil.

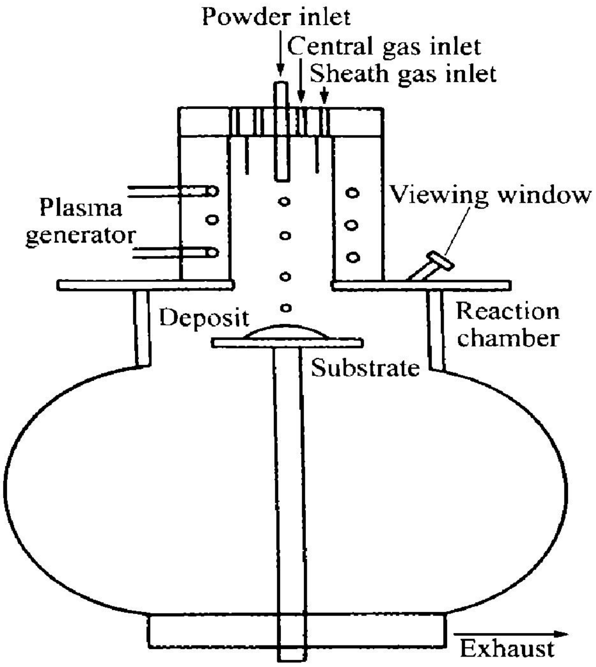

Fig. 1 Schematic of experimental set-up used for induction plasma reactive deposition

An innovative method for injecting carbon source into the plasma was invented. Methane, instead of Ar inert gas, was used as powder carrier gas. Only in this way could the goal of sufficient contact of the carbon source with the metal powder be achieved. Substrate used was graphite disc with 100 mm in diameter and 5 mm in thickness. Before each experiment, the graphite substrate was sprayed with boron nitride for easy removal of the deposit from the substrate after cooling. Plasma spray conditions are given in Table 1. Principal plasma spray parameters such as plasma power and carrier gas flow rate were varied. Each run of the deposition experiment last 10 - 20 min, and the peak height of the deposits with the shape of mountain varied from 5 to 10 mm.

Diamond saw was used to cut the deposit for cross-section examination. X-ray diffraction analysis was made on Rigaku Geigerflex instrument, using Cu K_α line at the scanning speed of 2°/min. The area of the sample exposed to X-ray is about 2 mm × 5 mm. Microstructure examination was made on Leitz Metallux optical microscope and also on JSM-840A scanning electron microscope. Vicker's microhardness was measured under the test load of 3 N in 15 s.

Table 1 Plasma spray conditions for reactive deposition of titanium carbide

Plasma power/kW	Powder feed rate/ $(g \cdot min^{-1})$	Methane flow rate/ $(L \cdot min^{-1})$	Chamber pressure/kPa	Spray distance/mm
40 - 50	5	1 - 2	26	200

3 RESULTS AND DISCUSSION

3.1 Synthesis of titanium carbide

The morphology of starting titanium powder is shown in Fig. 2. The powder consists of irregular particles, appearing sponge. When the powder was injected into the plasma, the particles were heated and melted. Meanwhile, methane was decomposed into a variety of active species like C, CH, CH_2, CH_3, etc. These species, reacted with titanium particles, resulted in the forming of titanium carbide inside the plasma. When methane was used as the powder carrier gas, the carburization of the particles was highly effective and homogeneous because the contact of the active species with titanium was long and sufficient.

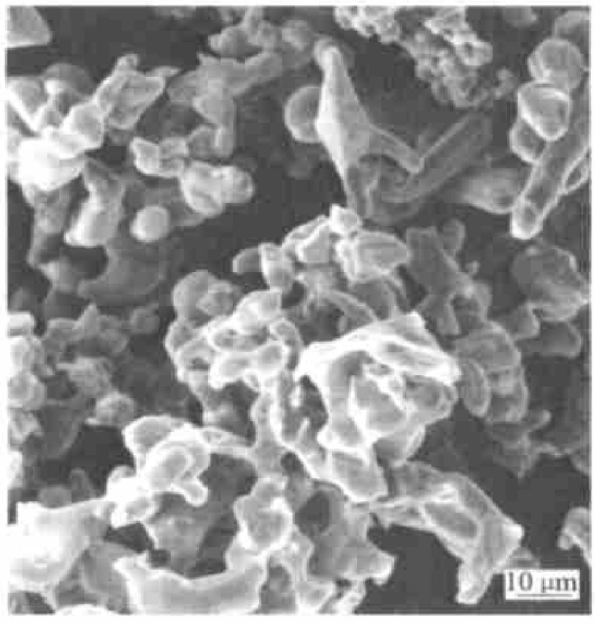

Fig. 2 SEM micrograph of starting titanium powder

X-ray diffraction patterns obtained from the cross-section of the reactive plasma spray-formed deposit and from titanium carbide standard are shown in Fig. 3. It is found that the major phase in the deposit is TiC_{1-x} with $0 < x < 1$. Because each peak of TiC_{1-x} is corresponding to the left one of TiC and 2θ values of the corresponding peaks of the two phases (Table 2) are extremely close, it is

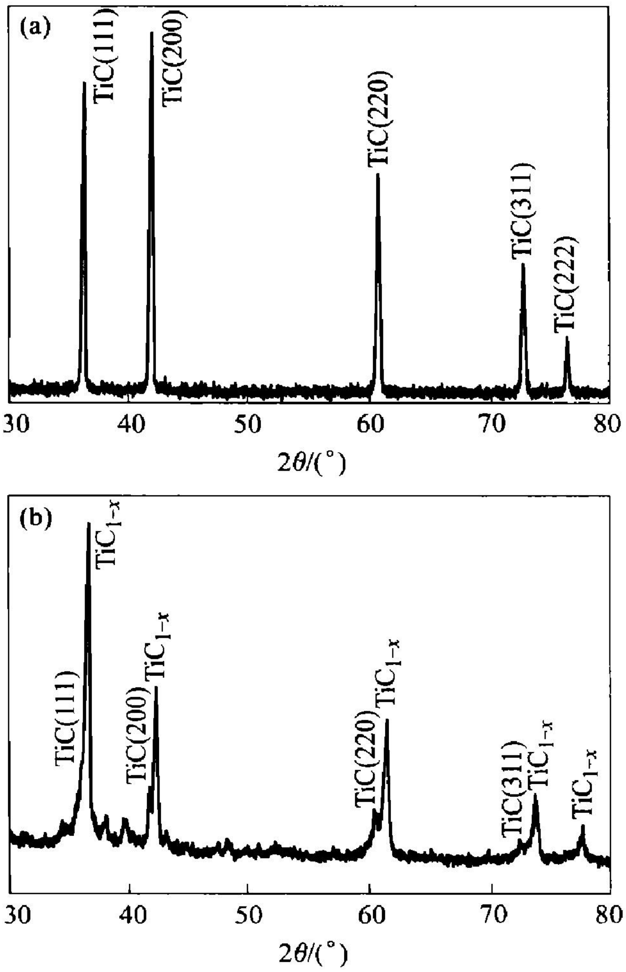

Fig. 3 X-ray diffraction patterns from TiC standard and from central region of reactive plasma spray-formed deposit with thickness of approximately 10 mm and surface temperature of 1 700 ℃ during deposition

Table 2 Crystal plane index and corresponding 2θ values of TiC and TiC_{1-x}

hkl	111	200	220	311	222
2θ (TiC)	35. 89	41. 66	60. 44	72. 35	76. 08
2θ (TiC_{1-x})	36. 40	42. 34	61. 46	73. 70	77. 70
d space (TiC)	2. 500	2. 165	1. 531	1. 305	1. 250
d space (TiC_{1-x})	2. 466	2. 133	1. 508	1. 284	1. 228

believed that the two phases have the same crystal structure, i. e., NaCl type fcc structure, but have slightly different lattice constants, according to Brag's diffraction law. The lattice constant of TiC is 4. 330 Ù and the calculated lattice constant of TiC_{1-x} is 4. 266 Ù.

X-ray diffraction analysis on the top surface and the bottom region of the spray-formed deposit was also made, as shown in Fig. 4. Great difference in the phase constituents of the two regions of the deposit was found . On the top surface of the deposit ,

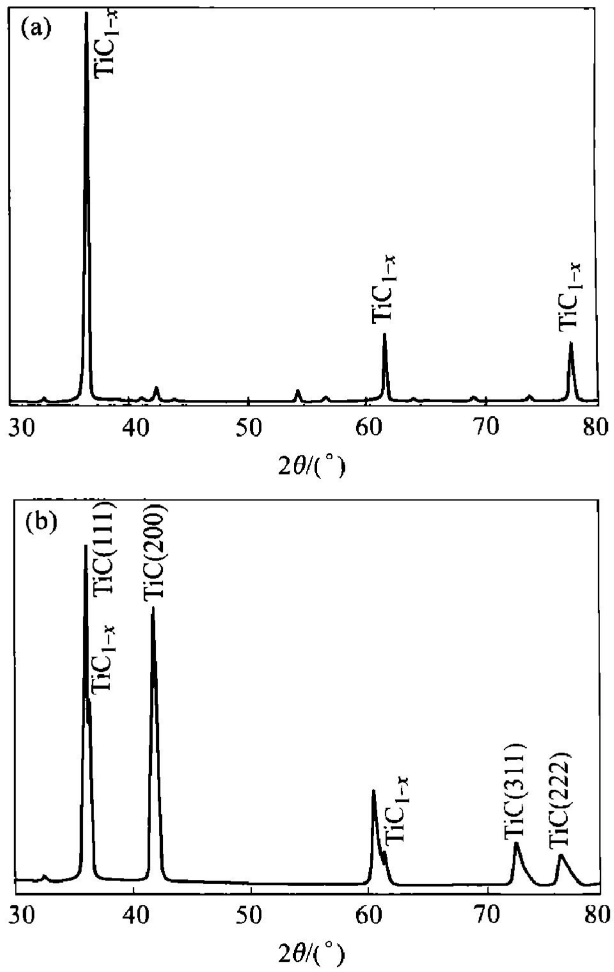

Fig. 4 X-ray diffraction patterns obtained from top surface and bottom region of deposit

TiC_{1-x} phase is dominant. On the bottom region of the deposit, however, the major phase is TiC and the minor phase is TiC_{1-x}.

At the spray distance of 200 mm, the plasma flame was close to the substrate. When deposition last more than 10 min, substrate temperature reached as high as 1 700 ℃. At such a high temperature, the phase of TiC_{1-x} can be further converted into the phase of TiC if carbon is available. In fact, the free carbon decomposed from methane was found everywhere in the deposition chamber and surely involved into the deposit during deposition. Consequently, secondary carburization happens in the deposit on the high temperature substrate, based on the X-ray diffraction analysis result.

3. 2 Microstructure of plasma spray-formed deposit

Optical micrographs taken from the central region and the bottom region of the deposit are shown in Figs. 5(a) and (b). There are two different features illustrated in Fig. 5(a), i. e., fine grain structure and large grain structure. In Fig. 5(b), only fine grain structure can be seen. Also, two different fracture patterns were found on the fracture surface of the reactive spray-formed deposit, as shown in Figs. 6(a) and (b). Grain boundary fracture was found in the

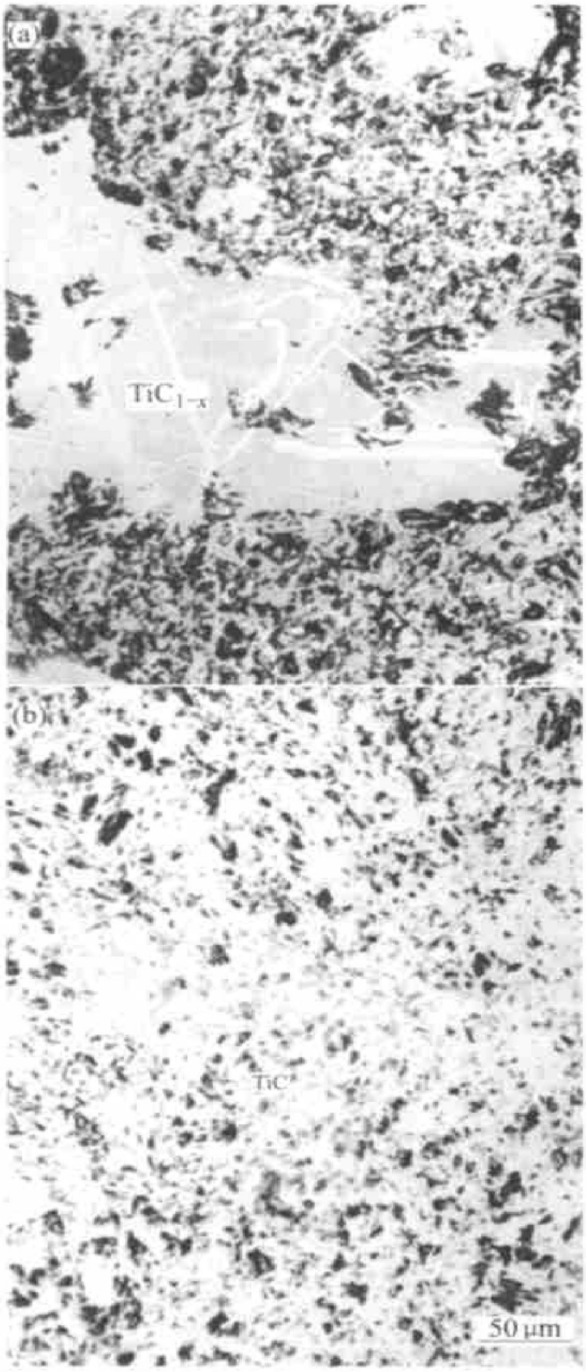

Fig. 5 Optical micrographs of cross-section of reactive plasma spray-formed deposit
(a) —From central region; (b) —From bottom region

fine grain structure region, as shown in Fig. 6(a). Cleavage fracture was found in the large grain region, as shown in Fig. 6(b). The fine grain region has Vicker's microhardness (Hv_{300}) of 1 990 ± 180, much harder than the large grain region.

Because the temperature of the deposit on the substrate was gradually increased to 1 700 ℃ during deposition, obvious grain growth would not occur at the beginning of the deposition. After a few minutes of deposition, rapid grain growth occurred in the central region mainly consisting of TiC_{1-x} where less carbon was present, but not in the bottom region where more carbon was present and TiC was formed. The high microhardness found in the fine grain region

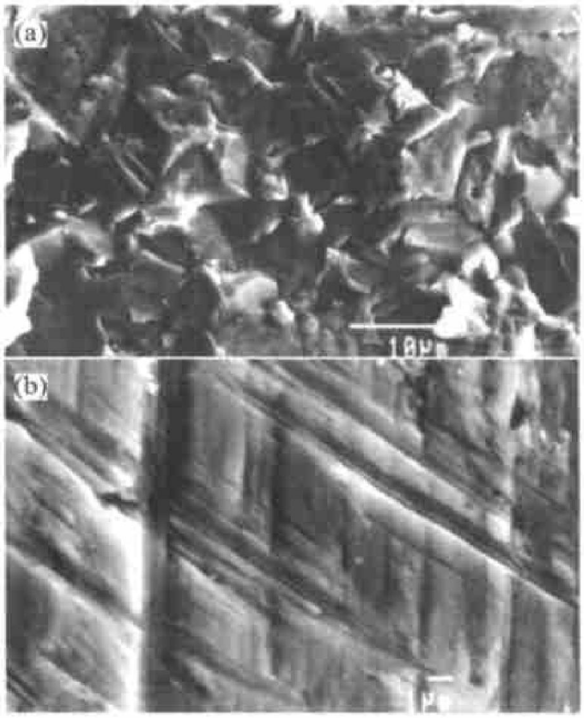

Fig. 6 SEM micrographs of fracture surface of reactive plasma spray-formed deposit
(a) —From fine grain area; (b) —From large grain area

at the bottom of the deposit confirms the secondary carburization happened on the substrate.

4 CONCLUSIONS

Induction plasma reactive spray can be used to form titanium carbide deposit directly from metal titanium powder. The use of methane as powder carrier gas is important for ensuring the sufficient contact of the titanium powder and the carbon source. The first carburization occurs inside the plasma flame, resulting in the synthesis of the transitional phase of TiC_{1-x}. The second carburization takes place on high temperature substrate, resulting in the conversion of TiC_{1-x} phase into TiC phase. The reactive spray-formed deposit consists of fine grain structure and large grain structure. The large grains result from the rapid grain growth in the region where TiC_{1-x} is the major phase.

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