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The influence of composition and process parameters on the microstructure of TiC-Fe coatings obtained by reactive flame spray process

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It has been proved that TiC-Fe fine-grained multiphase and multilayer coatings, composed of alternate TiC-rich and TiC-poor lamellae with different microhardness, can be obtained by reactive flame spray technology using ferrotitanium and graphite as the starting materials. This study was undertaken to assess the influence of composition and process parameter on the microstructure of the coatings. It is found that parameters related to the melting and reaction of the reactive micropellets are the factors influencing the hardness of TiC-rich layers. A high hardness can be favored by more titanium reacted with graphite (that is, less Fe content and more C/Ti atomic ratio within the reactive micropellets), smaller micropellets and properly longer spray distance. Among all the variables considered, Fe content (or the expected TiC content) and spray distance are the main parameters to affect the microstructure of the coatings. Because the hardness of the stacking multiphase layers containing very fine and rounded TiC particles depend on the composition and process parameters, the TiC-Fe coatings could be tailored to meet different applications, particularly those needed resistance to crack propagation. © *2002 Kluwer Academic Publishers*

1. Introduction

It is generally accepted that wear resistance is a consequence of a specific favorable combination of hardness and toughness. Fine-grained multiphase coatings composed of hard particles dispersed in a metal matrix would be tougher and more resistant to crack propagation than pure ceramic coatings while ensuring wear resistance imparted by the hard ceramic phase. Titanium carbide possesses so high a hardness that it has been considered for the development of wear-resistant coating materials. However, its brittleness and the difficulty to homogeneously and finely disperse within a tough metal matrix have so far limited its application in the hard surfacing industry [1].

Up to now multiphase coating composed of mixed hard phases and metals have been produced by many methods including hot pressing and plasma spraying mixtures of metal and ceramic powders, metal-coated ceramic powders and agglomerated metal and ceramic powders [2]. However, many of these engineered thermal spray powder production methods need many intermediate manufacturing steps, which increase the cost of powders over the constituent raw materials by a factor of four or more, thus making some engineered powders production less economical. In addition, the cohesion between the ceramic phases and the matrix may be relatively weak. Also, the hard particles within the coatings are usually large (more than 1 μm), unevenly distributed, and angular. Using a process called Reactive Plasma Spray Process (RPSP), TiC-Fe coatings containing very fine TiC particles have been obtained by plasma spraying mixtures of ferrotitanium and graphite powders. The process eliminates many intermediate powder manufacturing steps and involves the synthesis of hard phases during their deposition by plasma spray. These ceramic phases, being directly formed by an *in situ* reaction, should have stronger cohesion with the metal matrix and should result in an improvement in wear resistance. Because it is not necessary to reach a temperature as high as the melting point of TiC, the decomposition or dissociation of TiC can be avoided [3–5].

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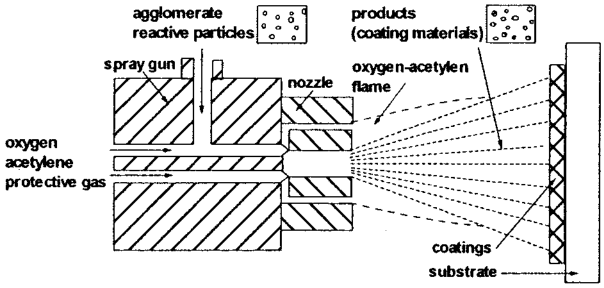

Figure 1 Schematic view of the reactive flame spray process.

It is shown that the reaction occurring during reactive plasma spraying involves a Self-Propagation High-Temperature Synthesis (SHS) process. The characteristic of the coatings essentially does not almost vary with the increasing energy of plasma arc provided that the reaction of the reactive spray powder is ignited. Considering that the plasma spray gun, is inconvenient and expensive compared with oxyacetylene flame spray equipment, and the reaction of Fe-T-C system can be ignited by the oxyacetylene flame, a new process RPSP, Reactive Flame Spray Process (RFSP), has been developed for TiC-Fe cermet coatings [6–8]. The schematic view of the reactive flame spray process is shown in Fig. 1.

This study was aimed at determining which factors could control the peculiar microstructure of reactive-flame-sprayed TiC-Fe coatings. For this purpose the influence of both the composition of the spray powders and the deposition parameters on the coating microstructure were examined.

2. Material and experimental procedure

Commercial ferrotitanium, iron and graphite powders were used as the starting materials for the preparation of micropellets and spray powders. Table I gives the chemical analyses of these powders.

TABLE I Chemical composition of commercial starting powders

Material	Element (wt%)						
Ferrotitanium	Ti	Si	Al	S	P	C	Fe
	65.1	1.5	0.51	0.02	0.02	0.15	Bal.
Iron	Fe						
	>99						
Graphite	C						
	>99.5						

The starting ferrotitanium and iron powders were separately milled in alcohol and then mixed together. The batch compositions were prepared by adding graphite and binder. The mixture contains a slight excess of carbon to compensate the loss of carbon during spraying. For this purpose, the calculated atomic ratio of carbon to titanium corresponded to 1.2. The batch was adjusted to obtain 40, 60 and 80 vol% TiC phases in the spray-synthesized coatings. After solid micropellets were agglomerated, they were sieved into two size fractions (−150 ∼ +200 and −200 ∼ +300 mesh). Table II gives the chemical compositions of the reactive micropellets and spraying characteristics. The resulting powders were flame sprayed on $10 \times 10 \times 0.8$ cm^3 mild steel substrates. Prior to spraying, some micropellets were treated in a neutral atmosphere at 1148 K to evaluate their behavior upon spraying.

Scanning electron microscopy and X-ray diffraction were used to characterize the microstructure of the reactive spray powders and the coatings. Microhardness measurements were carried out by indenting material areas with a diamond tip under a 50 gf load. Sliding wear tests were done at room temperature with a ball-on-disc device, namely the rotating AISI 52100 steel ball mated against the stationary coated disc.

3. Results and discussions

The fundamental reaction in the reactive flame spraying of TiC-Fe coatings takes place exothermically between the titanium and graphite. When iron is added into the mixture, iron will promote the reaction between elements by dissolving them in an iron bath. Thus, a temperature as low as 1200°C, corresponding to the melting point of ferrotitanium is obtained to initiate the reaction between titanium and carbon [5]. It is worth mentioning that the starting reaction temperature is lower than by using pure elements, namely titanium and graphite, whose reaction is initiated at approximately 1600°C. This is why ferrotitanium was used to take the place of titanium. In this case, Fe within ferrotitanium plays a role not only as a diluent but also as a reactant.

After being injected into the flame, the reactive micropellets (comprising ferrotitanium, graphite and iron) are ignited to form TiC and iron, irrespective of their composition, as shown in Fig. 2. Other than the dominant phases, namely TiC and Fe, a small amount of Ti_xO_y are also identified. The proportion of Ti_xO_y increases with increasing amount of titanium in the

TABLE II Composition and characteristics of reactive micropellets

	Material (wt%)				
Sample	Ferrotitanium	Graphite	Iron	Theoretical TiC volume content	Powder or spraying characteristics
1	60	12	28	60	Regular spraying conditions[a]
2	36	7	57	40	Regular spraying conditions
3	82	28	0	80	Regular spraying conditions
4	62	10	28	60	C/Ti atomic ratio 1.0
5	58	14	28	60	C/Ti atomic ratio 1.4
6	60	12	28	60	−200 ∼ +300 mesh micropellets
7	60	12	28	60	Heat treated micropellets
8	60	12	28	60	Spray distance 70 mm
9	60	12	28	60	Spray distance 125 mm
10	60	12	28	60	Spray distance 250 mm

[a] Unless otherwise specified, the –150 ∼ +200 mesh micropellets were sprayed with spray distance = 170 mm.

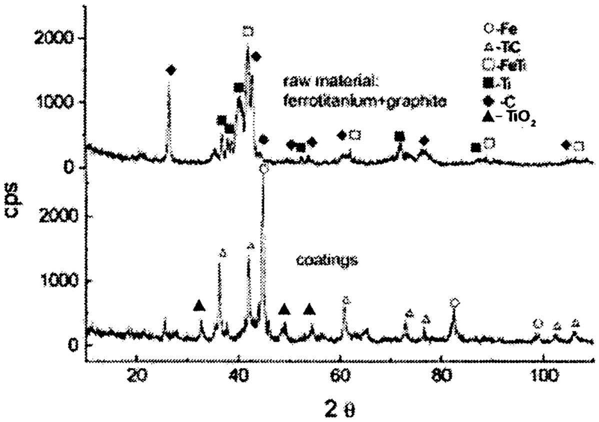

Figure 2 XRD pattern of the spray powders and coatings.

micropellets. It is shown that, when iron is added to dilute the concentration of titanium within the micropellets, the iron in excess absorbs the heat liberated by the reaction of titanium with graphite, thus the combustion temperature reduces, and titanium is prevented from oxidation.

SEM photograph (Fig. 3) reveals that the reactive-flame-sprayed TiC-Fe coatings are composed of alternate, laminated TiC-rich and TiC poor layers. These layers contain very fine ($<1\ \mu$m) and rounded TiC particles dispersed in an iron-based matrix (Fig. 4). Microhardness measurement shows that the TiC-rich and TiC poor layers have a hardness 11.9–13.7 GPa and 3.3–6.0 GPa respectively. Obviosly, The proportion and the microhardness of TiC-rich layers within the TiC-Fe coatings are two of the most important factors to affect the wear resistance of the coatings. So the effects of the variable on the characteristics of the TiC-rich layers are emphasized on study.

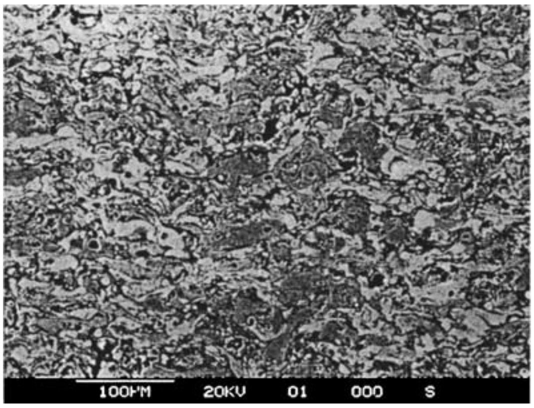

Figure 3 SEM photograph with low magnification of the reactive-flame-sprayed TiC-Fe coatings.

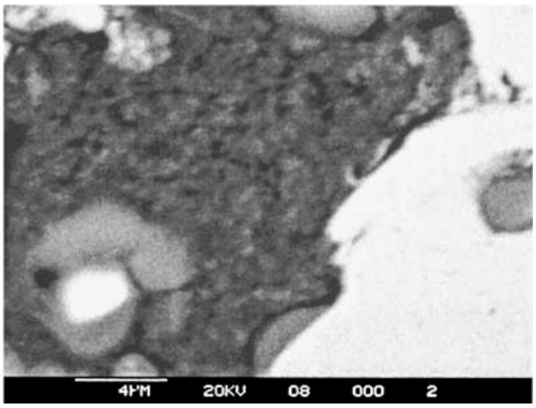

Figure 4 SEM photograph with high magnification of the TiC-rich layers within these TiC-Fe coatings.

The hardness of these hard lamellae is found to be related to the composition of the micropellets. Fig. 5a shows that a 30% increase in hardness is achieved when the Fe content reduces from 70 to 50 wt%. There may be a more increase when the Fe content is 30 wt%. However, these coatings contain lots of titanium oxides (Fig. 2), which result in many large pores and a badly adherent strength. It is noted that the weight loss due to wear of the coatings with Fewt% = 50 and with Fewt% = 70 is 0.014 mm^3 and 0.262 mm^3, respectively, that is, the wear resistance of the before is about 18 times better than that of the latter. Compare with the influence of Fe content on the hardness of TiC-rich layer, the C : Ti atomic radio within the reagents seems to have less effects on it. As shown in Fig. 5b, almost no improvement is obtained when increasing the C : Ti atomic ratio from 1.0 to 1.4.

Other process parameters related to the fabrication of the reactive micropellets also have an influence on the microhardness of TIC-rich lamellae. As shown in Fig. 5c, using smaller micropellets ($-200 \sim +300$ mesh) instead of larger ones ($-150 \sim +200$ mesh) brings about an increase in hardness of the hard layer by 10%. It should be pointed out that, when the reactive micropellets are heat treated before spraying in N_2 atmosphere at 1073 K for 2 hours, the reaction between titanium and graphite has already taken place during the heat treating process (Fig. 6). Therefore, coatings fabricated by spraying these heat treated reactive micropellets contain many pores and are very loose. However, the TiC crystals dispersed in TiC-rich layers, prepared by reactive plasma spraying these sintering the micropellets, can grow by an Ostwald ripening mechanism from submicron up to micron size, and the hardness of the hard lamellae increased by 15% [3]. This can be explained as following. In the case of reactive plasma spraying, the plasma are can melt or partially melt ceramic. However, oxyacetylene flame used in this study cannot melt ceramic, such as TiC, with high melting temperature.

The spray distance strongly modifies the hardness of the TiC-rich layer. Fig. 5d indicates that an increase in hardness is obtained when the spray distance is raised from 70 to 170 mm and there is a fast increase between 125 mm and 170 mm. However, when the spray distance is raised up to 250 mm, there is a decrease in hardness compare to one at 170 mm. It is noted that TiC can also exist over a wide range of substoichiometries. The chemical formula of TiC_x ($x = 0.47$–0.97) is preferred. The properties, such as melting temperature, hardness and others, of TiC_x are strongly dependent on the value of x [9], which can be calculated using XRD data (detailed calculate process was shown in [10]). By means of neasuring the value of x (combined C/Ti ratio) of TiC_x synthesized in the coatings with different spray distance, we can conclude that the reaction of Fe-Ti-C system happens step by step during the reactive spray powder flying, and that TiC-Fe materials were mainly synthesized where the spray distance is 125–170 mm. If

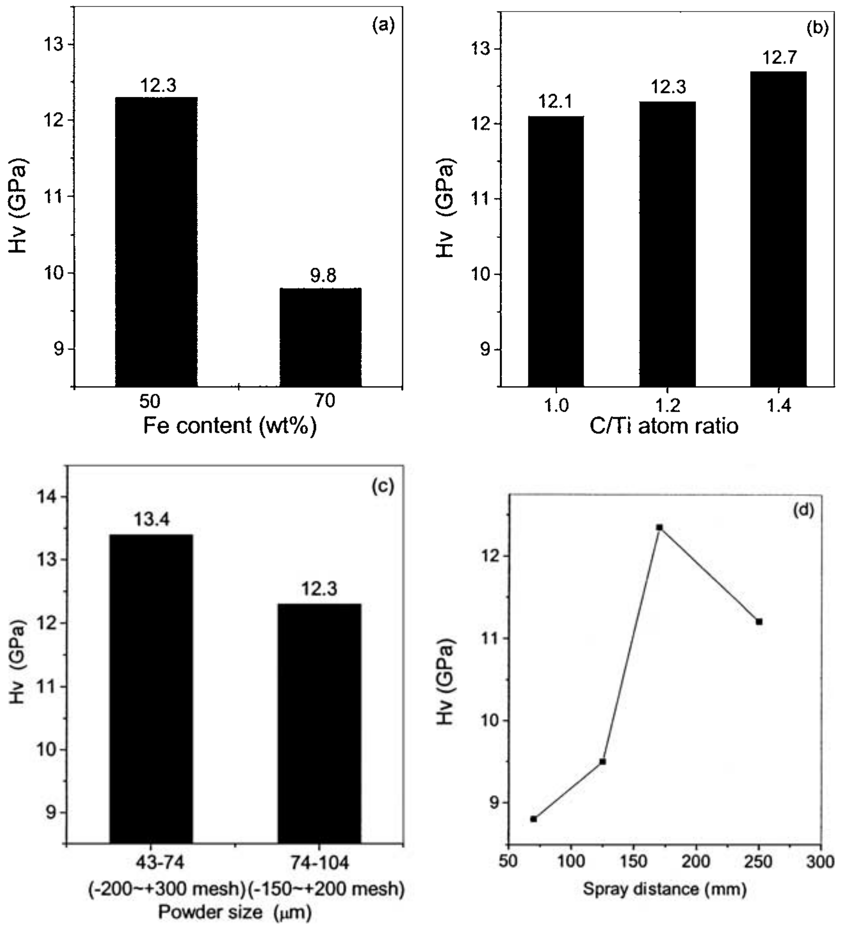

Figure 5 Microhardness of TiC-rich layers as a function of Fe content within micropellets (a), C/Ti atomic ratio of micropellets (b), spray powder size (c), and spray distance (d).

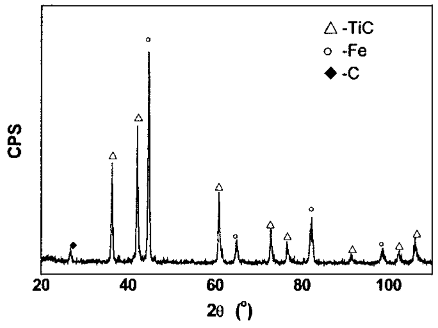

Figure 6 X-ray analysis of reactive micropellets that are heat treated before spraying in N_2 atmosphere at 1073 K for 2 hours.

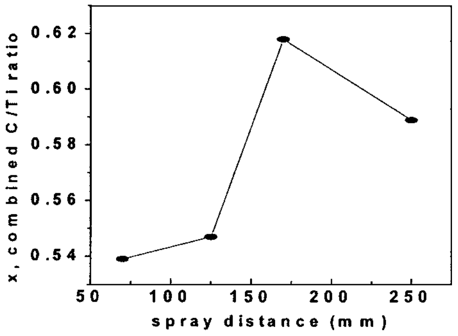

Figure 7 Value of x of TiC_x as a function of spray distance.

the spray distance is longer than 170 mm, the oxidation reaction will be dominant, thus TiC_x synthesized will be decarbonized. As mentioned before, the hardness of TiC_x is strongly dependent on the value of x, so the influences of spray distance on the microhardness of TiC_x-rich layers (Fig. 5d) and on the value of x (Fig. 7) show the same tendency.

The variation in hardness of TiC-rich lamellae within TiC-Fe coatings obtained by reactive flame spraying seems to be related to factors influencing the melting and reaction of the reactive micropellets rather than those influencing their cooling rate, which is concluded in reference [3] by S. Dallaire. As shown in Fig. 5, obviously, a high hardness can be favored by more titanium reacted with graphite, smaller reactive micropellets and properly longer spray distance. All of these have a strong effect on the melting and reaction of the reactive micropellets.

4. Conclusions

The composite TiC-Fe coatings have been obtained by reactive oxyacetylene flame spraying micropellets comprising ferrotitanium, graphite and iron. The microstructural features responsible for an increase in hardness of the TiC-rich layers depend on factors influencing the melting and reaction of the reactive micropellets. More titanium reacted with graphite, smaller reactive micropellets and properly longer spray distance can favor a high hardness. Because the hardness and the stacking multiphase layers containing very fine and rounded TiC particles depend on the composition and process parameters, the TiC-Fe coatings could be tailored to meet different applications.

Acknowledgements

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