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A New Process for Preparing Fine-ceramic-containing Composite Coatings——Flame Spray Synthesis

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Abstract: Flame spray synthesis (FSS), a combination of the flame spray technology and Self-propagation High-temperature Synthesis (SHS) was developed for preparing fine-ceramic-containing composite coatings. It can simplify the preparations of powder to synthesize and deposit the desired materials in one step. The preliminary results obtained from TiC-Fe cermet coatings by FSS process are reported. The peculiar microstructure of the composite coatings, which contains very fine (<1μm) and round TiC and alternate TiC-rich (Hv = 11–13 GPa) and TiC-poor layers (Hv = 3.0–6.0 GPa), is expected to play an important role in their tribological properties.

Key words: Self-propagation High-temperature Synthesis (SHS); flame spray; flame spray synthesis (FSS); TiC-Fe cermet coating

1 Introduction

Thermally sprayed metal matrix coatings reinforced with hard carbide particles are wear-resistant materials for many applications. It has been observed that the wear-resistance of a coating varies with the distribution, volume fraction, and morphology of the carbide particles. It is improved when fine carbide particles are embedded in a tough metallic matrix, where the carbides act as bearings for the sliding surfaces, reducing friction coefficients,preventing adhesive metal transfer, or resisting the metal removal from erosive particles [1–3]. The plasma spraying technique has been successful in depositing cermet-type coatings. However, it is not an effective process in producing a well dispersed structure of very fine and spherical hard particles in large amounts without the decomposition [4]. In addition, many of these engineered spray powder production methods increase the cost of powders over the constituent raw materials by a factor of four or more, thus making some engineered powder production less economical. Also, the cohesion between the carbide phases and the matrix may be relatively weak, allowing the particles to fragment during thermal spray processing [5].

Self-propagation High-temperature Synthesis (SHS) is a combustion process in which an exothermic, self-sustaining chemical reaction proceeds layer by layer into the reaction volume, gradually transforming the reactant powder mixture into the desired products. It is one of the in-situ techniques of preparing materials with the following advantages: the higher purity of products, the low energy requirements, the short time of reaction and relative simplicity of the process. These carbide phases, being formed in-situ directly from the metal matrices, should have stronger cohesion with the matrix and should result in improved wear resistance [6].

A process, combining SHS and thermal spraying, called plasma spray synthesis (PSS), has been developed for producing ceramic-containing composite coatings [7–10]. During spraying, the products, as the coating materials, are synthesized by an exothermic reaction and soon are deposited to the expected coatings, which have the characteristics of the materials by in-situ SHS. However, the complicated equipment causes the costs of the process to be still great.Instead of the plasma equipment, TiC-Fe composite coatings were obtained by a new process, called flame spray synthesis combining SHS and flame spraying. In this study, the microstructure and characteristic of these coatings are described.

2 Experimental

Commercial ferrotitanium, iron and graphite powders were used as the starting materials for the preparation of micropellets and spray powders. **Table 1** gives the chemical analyses of these powders. X-ray diffraction analysis showed that ferrotitanium mostly consists of Ti and FeTi (see **figure 1**).

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 ex-

Table 1 Chemical composition of commercial starting powders (mass fraction in %)

Materials	Ti	Si	Al	S	P	C	Fe
Ferrotitanium	65.12	1.5	0.51	0.022	0.025	0.15	balance
Iron				Fe > 99			
Graphite				C > 99.5			

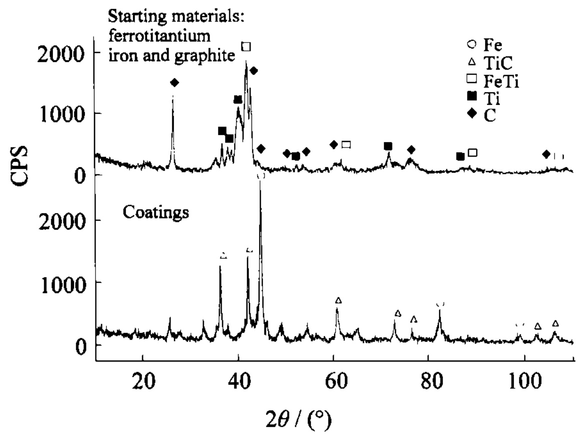

Figure 1 X-ray diffraction pattern of starting materials and coatings.

cess 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 60% (volume fraction) TiC phase in the spray synthesized coatings. After the solid micropellets were agglomerated, they were then sieved to −150 — +300 mesh. The resulting powders, which were made of grains in the micron size range, were flame sprayed on 10 cm×10 cm×0.8 cm mild steel substrates with the process parameters shown in **table 2**.

Table 2 Flame spraying parameters

Oxygen pressure / MPa	Acetylene pressure / MPa	Protective gas pressure / MPa	Spray distance/ mm
0.80	0.09	0.50	150

3 Results and Discussions

After being injected into the flame, the reactive micropellets (comprising ferrotitanium, graphite and iron) as a SHS reaction system were ignited by the oxygen-acetylene flame. The combustion initiation is all-insided, the combustion front, while contracting, moved to the center and the process was much more efficient. The extra-bright particles in the spray stream revealed that the following reaction happened during the spraying process:

$$FeTi + Ti + 2C + Fe \rightarrow 2TiC + 2Fe .$$

Figure 1 gives the X-ray diffraction patterns of starting materials and coatings. As expected, figure 1 confirmed that TiC and Fe were the main constituents synthesized during the reaction of agglomerated powders through the flame. The reaction seemed to be complete since FeTi and Ti phases were not observed. C was difficult to identify although the calculated atomic ratio of carbon to titanium corresponds to 1:1.2 in the reactive micropellets. The extra graphite up to 20% (molar fraction) here could be oxygenated by the oxygen-acetylene flame. It is noted that TiC is usually a stoichiometric compound characterized by a face-centered cubic lattice identified by a single lattice parameter, *a*. However, this carbide can also exist over a wide range of substoichiometries, forming TiC_x (x=0.47–0.97). The properties,such as melting temperature, hardness *etc.*, of TiC_x depend strongly on the value of x [11].

A correlation can be established between the value of the lattice parameter of TiC_x and the atomic ratio of the combined carbon to titanium (that is, the value of x); see **figure 2** [12]. The lattice parameter of a crystalline compound can be directly correlated to the value of the interplanar spacing, *d*, and the corresponding 2θ angles of the peaks identifying its characteristic XRD pattern.

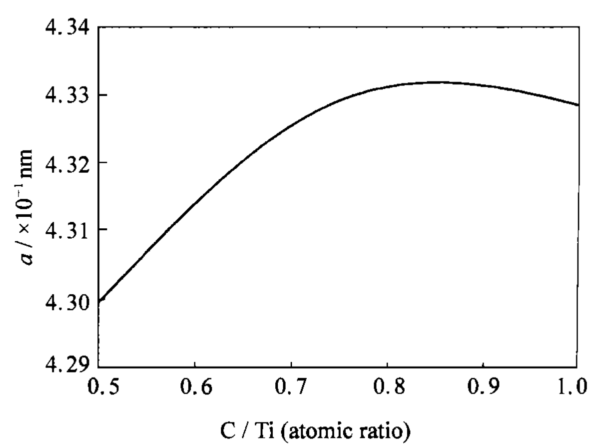

Figure 2 Lattice parameter *a* of TiC_x as a founction of the C/ Ti atomic ratio.

The values of parameter a were calculated from the measured diffraction patterns of three samples. The final value of *a* for each diffraction run was extrapolated for 2θ angles approaching 180° since large Bragg angles are much more sensitive to small changes in cell dimension. To this aim, for each value of the measured d spacing, the value of $[d\{h^2+k^2+l^2)^{1/2}]$ was plotted against the corresponding value of $[1/2\theta\cos^2\theta/\theta+\cos^2\theta/\sin\theta]$. The resulting points are distributed around a straight line, whose parameters can be calculated by the least squares method. The intercept with the ordinate axis is the final value of a for that diffraction run [13].

For the present case, d values were measured for only 7 of the 10 lines characteristic of the TiC pattern. In fact, two of the remaining peaks (corresponding to the [2 2 2] and [4 0 0] planar directions) fall very close to some of the peaks generated by Fe, making their attribution unreliable; the last peak (plane [5 1 1]) was not clearly detected by the instrument. In **figure 3**, the construction of the $[d\{h^2+k^2+l^2\}^{1/2}]$ versus $[1/2(\cos^2\theta/\theta + \cos^2\theta/\sin\theta)]$ plot used to calculate the lattice parameter of the coatings for a single diffraction run is illustrated.

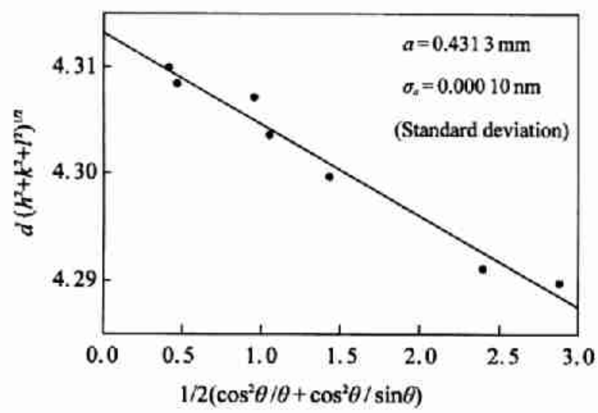

Figure 3 Example of the $[d\{h^2+k^2+l^2\}^{1/2}]$ versus $[1/2(\cos^2\theta/\theta + \cos^2\theta / \sin\theta]$ plot for one particular XRD run.

The average value of a calculated from the three samples is 0.431 3 nm. Thus the corresponding value of x (C/Ti atomic ratio) calculated from the curve in figure 2 is about 0.59, which is close to that of commercial SHS and plasma densified (PD) Ni-Cr-40%TiC (volume fraction) spray powders [13], as shown in **table 3**. From the Ti-C phase diagram (**figure 4** [12]), when the values of x are 0.59, 0.62 and 0.63, the melting points of TiC_x are about 2 600, 2 800 and 2 900 K, respectively. This results show that the stoichiometry of the titanium carbide present in the above three powders does not differ significantly. Therefore, the coatings produced by the three techniques have almost the same microhardness and other mechanical and wear properties.

Figure 5 gives the SEM photograph of the TiC-Fe coatings fabricated by flame spray synthesis process. They are composed of laminated dark, gray and white

Table 3 Lattice parameter and C/Ti atomic ratio for FSS, SHS and PD powders

Power	Lattice parameter a / nm	Standard deviation σ_a / nm	C/Ti ratio / x
FSS	0.431 3	0.000 10	0.59
SHS	0.431 7	0.000 12	0.63
PD	0.431 6	0.000 11	0.62

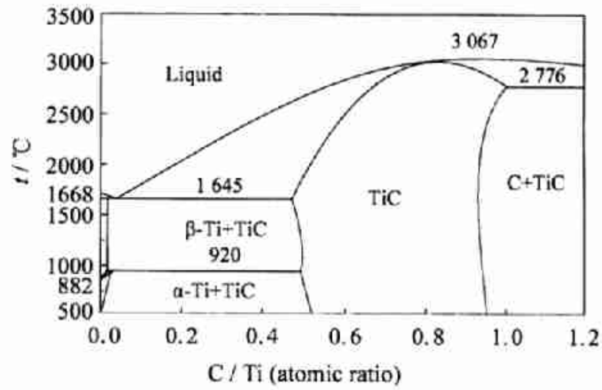

Figure 4 Ti-C phase diagram.

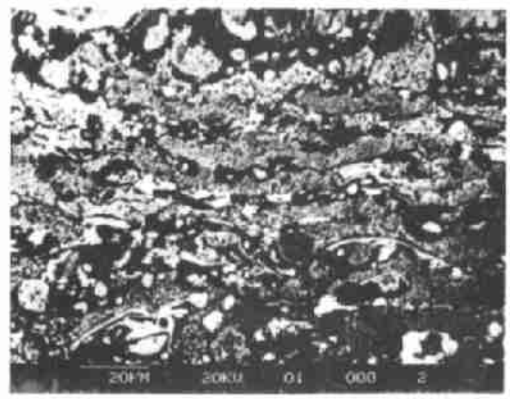

Figure 5 SEM of flame spray synthesized TiC-Fe coatings.

layers alternately. These layers have microhardness values of 11–13 GPa for dark areas and 3.0–6.0 GPa for others. The alternate hard and soft layers would increase the toughness by limiting crack propagation.

The hardness, X-ray analysis and energy dispersive spectrometry revealed that the dark layers are TiC-rich ones, which contain very fine (<1 μm) and round TiC crystals dispersed in an iron-based matrix, as shown in **figure 6**. The microstructure of these coatings was considerably finer than that of the traditional combustion synthesized specimen (about 15 μm) [14]. The rapid cooling of layers while depositing on the substrates can

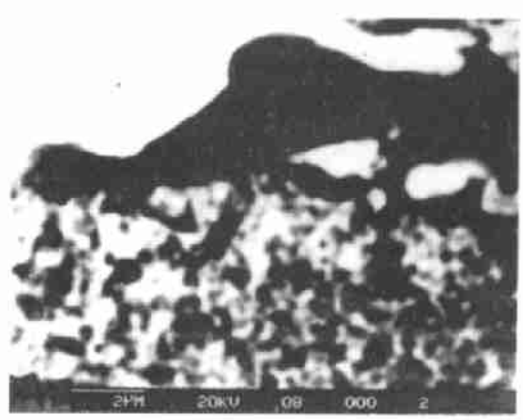

Figure 6 SEM of TiC-rich lammella within flame spray synthesized TiC-Fe coatings.

be responsible for the formation of submicron carbide particles. The grey or white layers should also contain TiC but to a lesser extent. Indeed, the pseudobinary TiC-Fe phase diagram predicts that iron can contain 3.8% (mass fraction) TiC at the eutectic temperature [15]. Consequently, those TiC-poor layers have a hardness between 3.0 and 6.0 GPa. Fine-grained carbides can achieve an increase in yield strength through dispersion and grain size mechanism, and modify the plasticity of the exposed surface.

Qualitative adhesion tests (scratching and peeling) performed on the coatings indicate that the inter bondings are great firm and massive removal of the coatings was not observed.

4 Conclusions

Flame spray synthesis is a new process for the preparation of fine-ceramic-containing composite coatings. It can eliminate many intermediate steps during the traditional powder-manufacturing, and can synthesize and deposit the desired materials in one step. The preliminary results reveal that these coatings, which are composed of alternate ceramic-rich and ceramic-poor layers, contain very fine and round ceramic particles and have the similar compound carbon/titanium atom ratio compared with the commercial SHS and PD Ni-Cr-40% (volume fraction) TiC spray powders. With the peculiar structure and the higher compound carbon/titanium atom ratio, these coatings is expected to play an important role in the wear-resistance applications.

Although the FSS process is new and requires further detailed evaluation, its economization, simplicity and peculiar structure will help it to be considered as a promising technique for the production of coatings to resistant sliding-wear with low stress and where the plasma equipment is not popular.

Acknowledgment

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