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# TiC-Fe coatings prepared by flame spray synthesis process①

LIU Chang-song(刘长松), HUANG Ji-hua(黄继华),
ZHAO Yong(赵 勇), LIU Mu(柳 牧), YIN Sheng(殷 声)
*School of Materials Science and Engineering,*
*University of Science and Technology Beijing, Beijing 100083, P. R. China*

**Abstract:** A new process, flame spray synthesis (FSS), has been developed for producing ceramic-containing composite coatings. By combining self-propagation high-temperature synthesis (SHS) and flame spraying, the cermet-based material was synthesized and deposited simultaneously. TiC-Fe coatings were deposited from commercial ferrotitanium, iron and graphite powders by the flame spraying synthesis process. Microstructure analyses revealed that TiC was synthesized during spraying, and that submicron and round TiC particles were dispersed within an iron matrix. Flame-spray synthesized coatings were composed of alternate soft and hard layers, whose hardness were 3.0 ~ 6.0 GPa and 11 ~ 13 GPa, respectively.

**Key words:** Ti-C; coatings; flame spray; SHS **Document code:** A

## 1 INTRODUCTION

It is generally accepted that wear resistance is a consequence of a specific favorable combination of hardness and toughness. Because of their brittle nature, pure hard ceramic materials cannot be used for all protective coatings. Fine-grained multiphase coatings composed of hard materials 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. Multilayer coatings in which interfaces are parallel to the substrate interface can also limit crack propagation, thus increasing the toughness[1].

Multiphase coatings composed of mixed hard phases and metals have been currently produced by plasma spraying mixtures of metal and ceramic powders, metal-coated ceramic powders and agglomerated metal and ceramic powders[2]. In many cases, however, these plasma-sprayed multiphase coatings are not composed of lamellae containing finely dispersed hard phases. They can contain angular particles of a size larger than the lamella thickness.

In order to obtain a homogeneous microstructure and to ensure good wettability of the ceramic particles by the metal matrix, thus improving the bonding between the metal matrix and the ceramic particles, a so-called plasma spray synthesis, or reactive plasma spraying process has been developed for producing ceramic-containing composite coatings[3~5]. However, plasma spraying units are too expensive for the Chinese thermal spraying factories where the flame spray technique is widely used[6].

It is noted that SHS is an in-situ technique for preparing materials because of the following advantages: high purity of products, low energy requirements, short reaction time and relative simplicity of process. When the reaction between reagents is initiated, it will maintain without any other energy[7].

Considering the national conditions of China, TiC-based coatings were prepared by a new process, called Flame Spray Synthesis (FSS) combining SHS and flame spraying in this study. The TiC-Fe composites in the process were produced by the exothermic reaction between ferrotitanium, iron and graphite. The microstructure and characteristics of the coatings are described below.

## 2 EXPERIMENTAL

Commercial ferrotitanium, iron and graphite powders were used as raw materials for 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 (Fig.1).

The raw materials 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

**Table 1** Chemical composition of commercial raw materials (%)

| Material | Composition/ % | | | | | | |
|---|---|---|---|---|---|---|---|
| | Ti | Si | Al | S | P | C | Fe |
| Ferrotitanium | 65.12 | 1.5 | 0.51 | 0.022 | 0.025 | 0.15 | Balance |
| Iron | | | | | | | >99 |
| Graphite | | | | | | 99.5 | |

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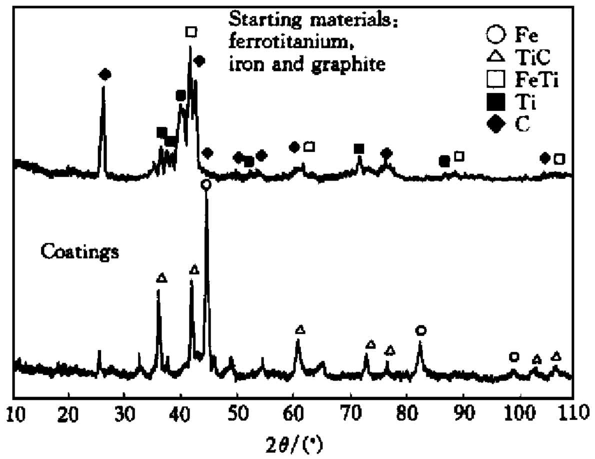


**Fig.1** X-ray diffraction patterns of raw materials and coatings

carbon during spraying. For this purpose, the calculated carbon titanium atomic ratio corresponds to 1.2. The batch was adjusted to obtain 60 %( volume fraction) TiC phases in the spray synthesized coatings. After the solid micropellets were agglomerated, they were then sieved to - 150 ~ + 300 mesh. The resultant powders were flame sprayed on 10 cm × 10 cm × 0.8 cm mild steel substrates with the process parameters listed in Table 2.

**Table 2** Flame spraying parameters

| Oxygen pressure/ MPa | Acetylene pressure/ MPa | Protective gas pressure/ MPa | Spray distance/ mm |
|---|---|---|---|
| 0.8 | 0.09 | 0.5 | 150 |

Scanning Electron Microscopy (SEM) was carried out on polished samples. X-ray diffraction with copper $K_{\alpha}$ radiation was used to characterize the reaction products and coatings. Vickers microhardness measurements were conducted under a 0.5 N load.

## 3 RESULTS AND DISCUSSION

The fundamental reaction in the flame spray synthesis of TiC-Fe coatings takes place exothermically between titanium and graphite. When iron is added into the mixture, it will promote the reaction between elements by dissolving them in an iron bath[8]. Thus, a temperature as low as 1 200 ℃, corresponding to the melting point of ferrotitanium, is obtained to initiate the dissolution of carbon[5,8]. 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 1 600 ℃[9]. This is why ferrotitanium was used to take the place of titanium. In this case, iron plays a role not only as a diluent but also as a reactant.

After injected into the flame, the reactive micropellets (comprising ferrotitanium, graphite and iron) form TiC and iron according to the following reaction:

$$FeTi + Ti + 2C \rightarrow 2TiC + Fe \quad (1)$$

Fig.1 gives the X-ray diffraction patterns of starting materials and coatings.

Although the calculated carbon titanium atomic ratio corresponds to 1.2 in the reactive micropellets, the coatings mostly consists of TiC and Fe, and C is difficult to be identified. However, when the synthesis was conducted in an electric arc furnace where rapid heating and cooling could be obtained in an attempt to simulate conditions of spraying, an excess of carbon within the matrix would be found[10]. The loss up to 20 %( mole fraction) of graphite here could be the oxygenated carbon during spraying process.

Fig.2 shows the back scattered SEM image of TiC-Fe coatings fabricated by flame spray synthesis process. It is found that these coatings are composed of alternate, laminated dark, gray and white layers. X-ray analysis shows that the coatings mostly consists of TiC and Fe. The dark areas have microhardness values in the range of 11 ~ 13 GPa. Therefore, the dark layers would be TiC-rich, containing very fine and rounded TiC crystals dispersed in an iron-based matrix, as shown in Fig.3. As a matter of fact, the compositional analysis performed by energy dispersive spectroscopy with X-ray microanalysis revealed that they are titanium rich while the white areas seem to be rich in iron. The iron-rich layers should also contain TiC but to a lesser extent. Indeed, the pseudobinary TiC-Fe phase diagram predicts that iron can contain 3.8 % TiC at the eutectic temperature. As a result, those iron-rich layers have a hardness of 3.0 ~ 6.0 GPa. The Ti content of those gray areas will be varied with the shades of color, so their hardness varies between 7.0 and 10 GPa.

The presence of iron-rich layers within coatings could result from inadequate micropellet fabrication or their partial breaking-up when they enter the flame.

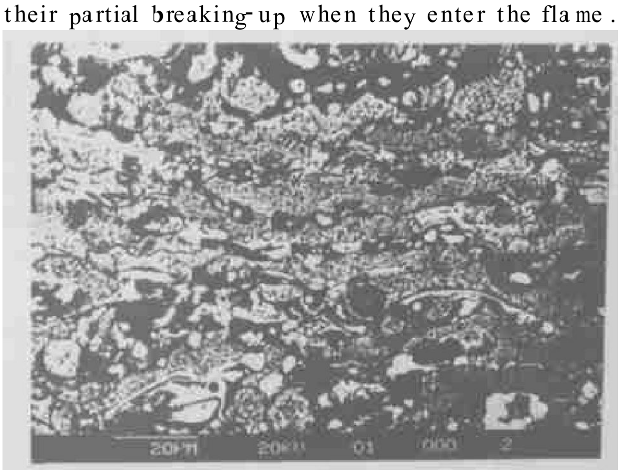

**Fig.2** Back scattered SEM image of flame spray synthesized TiC-Fe coatings

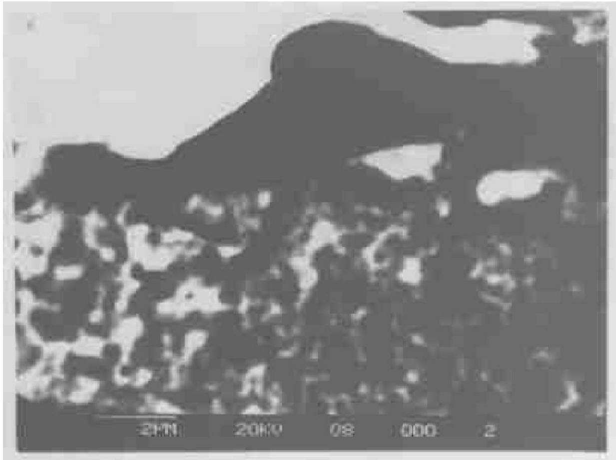


**Fig.3** Back scattered SEM image of TiC-rich lamellae within flame spray synthesized TiC-Fe coatings

Iron-rich micropellets or fragments of them are responsible most likely for the formation of iron-rich layers in coatings.

It is noted that TiC grains within the TiC-rich layers are very fine ( $<1$ μm) and round. When TiC is combustion synthesized from pure Ti and C mixture with a molar ratio of 1.0 and without any metal addition, it is composed of agglomerated angular grains with a size about 15 μm. This can be explained as follows. With the addition of iron, the combustion temperature becomes lower and the grain size becomes smaller since the grain growth of TiC is an exponential function of the combustion temperature; also, when the layers are deposited on the substrate, the rapid cooling prevent the growth of TiC grains.

The peculiar microstructure of the composite coatings, containing very fine and round TiC composed of alternate TiC-rich and TiC-poor layers, is expected to play a major role in their tribological properties[11]. Fine-grained carbides can achieve an increase in yield strength through dispersion and grain size mechanisms, and modify the plasticity of the exposed surface. What's more, alternate hard and soft layers would increase the toughness by limiting crack propagation.

## 4 CONCLUSIONS

1) A new process, flame spray synthesis (FSS), has been developed for preparing coatings containing hard ceramic phases without a need to reach the melting point of these ceramics.

2) TiC-Fe coatings were deposited by the flame spray synthesis process. The flame-spray-synthesized coatings were composed of alternate soft and hard layers, whose hardness is 3.0 ~ 6.0 GPa and 11 ~ 13 GPa, respectively.

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