Reactive thermal spraying of TiC-Fe composite coating by using asphalt as carbonaceous precursor

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By virtue of the higher hardness, lower densities and lower friction coefficients, thermal sprayed composite coatings of TiC bonded with different metals promise to be an excellent replacement for the traditionally used WC or Cr₃C₂-based coatings, being potentially useful in many wearing resistant applications [1]. In the conventional thermal spraying processes, the TiC reinforced composite coatings are prepared by directly adding TiC particles into the materials for spraying. The hard phase particles in the coatings are usually large (more than 1 μ m), unevenly distributed. Also, because the surface of added particles usually is not clean or is polluted, the interface between the reinforced phases particles and matrix is often a potential source of weakness [2]. Another drawback directly adding TiC particles into the materials for spraying is the stringent conditions for spraying process, such as high spraying temperature, high spraying speed, etc. Usually, spraying TiC reinforced composite coatings by directly adding TiC particles into the spraying materials needs expensive plasmas praying device.

Reactive thermal spraying (RTS) is a novel technology combining the in-situ reactive synthesis with thermal spraying, which is potentially useful in producing TiC-metals coatings. The main feature of this technique is the ceramic phases, formed by an in-situ reaction directly, are fine, spherical, and uniformly dispersed and have a clean interfacial structure with the metal matrix, which increases sharply the wear-resisting property of the coating, because fine-grained TiC can improve yield strength through dispersion and grain size mechanisms, and improve toughness by hindering crack propagation [3]. Also, in reactive thermal spraying, the reactions to synthesize the ceramic phases are exothermic, which provide a supplemental heat for spraying process, and enable TiC-metals coatings to be prepared by a simple flame spraying device.

According to the states of the reactive constituents to synthesize the ceramic phases, reactive thermal spraying can be classified into two processes, solid–gas RTS and solid–solid RTS. In the solid–gas RTS, the ceramic phases in coatings are synthesized by reactions of a solid constituent with a gas constituent. TiC reinforced composite coatings were prepared by solid–gas RTS using ilmenite powder as the feed material and methane, propylene, and acetylene as the reactive gas [4]. Although solid-gas RTS has a simple process, it has been proved to be difficult to control the solid-gas reaction and its product during spraying. The solid-solid RTS synthesizes ceramic phases in coatings by reactions between two solid constituents. As an example, TiC reinforced composite coatings can be prepared by reactive thermal spraying agglomerated compound powders of titanium (or titanium alloy), graphite, and other metals (Ni, Fe etc) [5–8]. In solid–solid RTS, the reactive product can be designed and controlled by adjusting the composition of the compound powders for spraying. Until now, however, the powders used for solid-solid RTS have been prepared by simple mechanical pelletization adding a small mount of agglomerant or even not. Because of the strong dispersing effect of spraying gas jet and the lower bonding strength of the compound powders prepared by the mechanical pelletization, the reactive constituent particles in the compound powders are liable to be separated during spraying, which leads to incomplete reaction, partial remaining of the reactive constituent particles in coatings, thus bad coating properties. It is evident that the compound powders in the solid-solid RTS are the key to obtaining a coating with high properties.

This paper describes a new process, precursor carbonization-composition process, to produce Ti–Fe– C system compound powders for reactive flame spraying TiC reinforced composite coatings. The main feature of the process is that a carbonaceous precursor is used as the origin of carbon to prepare agglomerated compound spraying powders by carbonization.

In this experiment, the raw materials are asphalt used as the carbonaceous precursor and ferrotitanium powder, which contains 47 wt% Ti and 53 wt% Fe and has an average particle size of 7 μ m. The ferrotitanium powder (76.3 wt%) and asphalt (23.7 wt%) are mixed at 300 °C. Ti–Fe–C system compound powder was prepared by carbonizing the mixture of ferrotitanium powder and asphalt at 600 °C. The powder size employed for subsequent spraying is in the 60–100 μ m range. The TiC/Fe composite coatings were synthesized and deposited onto low carbon-mild steel substrates by reactive flame spraying of the compound powder. Prior to spraying, the substrates are grit-blasted on one side



Figure 1 XRD diffraction pattern of Ti–Fe–C compound powder for RFS.

to clean and roughen the surfaces. X-ray diffraction, SEM and EDS were employed to study the microstructures of the compound powder and the coatings. Vickers Micro-hardness tests are performed with a 1 kg load and a dwell time of 5 s.

Fig. 1 shows the XRD diffraction pattern of Ti–Fe– C compound powder for RFS prepared by the precursor carbonization- composition process. The only phase can be detected in the XRD pattern is ferrotitanium. No TiC to be detected in the compound powder. Because the carbon in the compound powders prepared by carbonization of asphalt at 600 $^{\circ}$ C is amorphous, the peaks of carbon are also not found in the XRD pattern of the compound powder.





(b)

Figure 2 SEM back-scattered micrographs of Ti–Fe–C compound powder for RFS: top view (a) and cross-section (b).



Figure 3 XRD diffraction pattern of the TiC–Fe compound coating by RFS.





(b)



Figure 4 SEM Back-scattered micrograph of the TiC–Fe compound coating by RFS: general (a), the TiC-poor layer (b) and the TiC-rich layer (c) views.

Fig. 2a and b show two SEM back-scattered micrographs of Ti-Fe-C compound powder for RFS prepared by the precursor carbonization-composition process. Fig. 2a shows a top view of the compound powder. From Fig. 2a, we can see that the size of the compound powder is in the 60–100 μ m range and the shape of the compound powder is irregular. In order to study the final product morphology as well as to better characterize them from the chemical composition, SEM and chemical analysis were used. Fig. 2b shows the SEM micrograph of cross-section of a compound particle. It may be seen that the obtained products consist of ferrotitanium particles, which are in the range of 5-10 μ m, and carbon, which surrounds ferrotitanium particles and acts as a binder. Because the undefined structure carbon, generated by carbonizing asphalt at 600 °C, has strong adsorptive capacity with ferrotitanium particles, the compound powder prepared by the precursor carbonization-composition process has very tight structure. In addition, chemical analysis result revealed that the corresponding Ti/C atomic ratio of the final product was very close to 1.

In the XRD pattern of the TiC/Fe composite coating synthesized and deposited by reactive flame spraying of the compound powder (Fig. 3), the phases can be detected are TiC and Fe, no other phase is observed in the final product. It indicates that the reactive constituents in the compound powder prepared by the precursor carbonization–composition process have completely reacted during spraying, no raw material powders remaining in the coating.

The cross-section Back-scattered image of the TiC-Fe compound coating by RFS is shown in Fig. 4a. The coating consists of alternate, laminated microareas as following: the layers of TiC-poor microareas and the layers of TiC-rich microareas distributed with the TiC particles. In the two different layers, the TiC content of the two layers is 50.9 wt.% and 91.5 wt.% respectively. The Microhardness of the two layers is 783 and 988 respectively. The SEM micrograph of TiC-poor and TiC-rich layers are shown in Fig. 4b and c. In the

TiC–Fe compound coating, the iron binder appears to be white and the titanium carbide phases appear to be gray round particles. From Fig. 4b, we can see that the fine TiC particles are uniformly distributed in the metallic matrix of the TiC-poor layer. Because TiC particles are formed "*in-situ*" and the particle residence time in the flame is only a few milliseconds, the mean size of the TiC particles is very fine below 500 nm. And from Fig. 4c, we can see that the TiC-rich layer is composed of clustering TiC particles.

Under the same wear testing conditions, the wear resistance of the TiC/Fe composite coating synthesized and deposited by reactive flame spraying of the compound powder prepared by precursor carbonization– composition process is about 12 times as good as that of the Ni60 coating.

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