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**PLASMA SPRAYING OF CARBON-COATED TiC POWDERS IN AIR
AND INERT ATMOSPHERE**

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ABSTRACT

An important carbon loss occurs during the plasma spraying of TiC in air and, in a lesser extent, in an inert atmosphere. Moreover, an increase of the oxygen content is observed in coatings sprayed in air. In the present study, different carbon coatings have been applied on TiC powders by an agglutination coating technique in order to control both the carbon stoichiometry and the oxygen content within sprayed coatings. The effects of the carbon crystalline form (graphite or carbon black) and of the coating thickness deposited on TiC particles on the chemical composition and microstructure of plasma-sprayed coatings are investigated. An increase of both combined and free carbon content and a decrease of the oxygen contamination are observed in coatings sprayed in air with the carbon black-coated TiC powders. On the other hand, graphite coatings applied on TiC particles have a less significant effect on the composition of coatings sprayed in air or in the inert atmosphere. Severely decarbonized and oxidized zones are found within coatings sprayed in air.

1. INTRODUCTION

TiC coatings are of interest in various applications [1,2] and in particular in fusion reactors [3-6]. Indeed, TiC has a high melting temperature, a low atomic number, a good resistance to thermal shocks and a good chemical and physical sputtering resistance under bombardment by the high energetic particle fluxes in the plasma environment. Deposition of such coatings by plasma spraying permits to obtain thick coatings that can potentially survive for a long period of time in the very aggressive plasma environment. However, an important carbon loss occurs during plasma spraying in air and, in a lesser extent, in an inert atmosphere bringing about the formation of substoichiometric TiC coatings [7-10] whose mechanical properties and melting temperature are lowered [11-13]. Moreover, a significant increase of the oxygen content has been observed when coatings are sprayed in air [8,15,16].

In the present study, a carbon coating is applied on the surface of the TiC starting powders in order to limit the carbon loss occurring during plasma spraying and to protect the TiC particles against oxidation when spraying is performed in air. The effect of the carbon crystalline form (graphite or carbon black) and of the carbon coating thickness on the chemical composition and microstructure of the TiC coatings sprayed in air or in an inert atmosphere is examined. Moreover, the formation of severely oxidized and decarbonized zones within coatings sprayed in air is investigated by Auger electron spectroscopy (AES).

2. EXPERIMENTAL

The starting powders were obtained from a commercial Cerac TiC powder 99.5% pure (-325 mesh +10 μm) sieved by using an Alpine jet sieve sizer and an Alpine zigzag air classifier. The resulting particle size distribution measured with a Hiac Royco PA-720 particle size analyzer is shown in Figure 1. Most of the sieved particles are comprised

between 25 and 50 μm . These sieved particles were then covered with graphite or carbon black coatings. For this purpose, a Lonza KS-2.5 graphite powder (2- μm mean particle size) and a Fisher carbon black powder were used.

The carbon coatings were applied on the TiC particles using an agglutination process described elsewhere [17]. In this technique, an organic binder is first applied on the TiC core particles. These binder-coated particles are then introduced with the appropriate amount of fine carbon powders into a cylinder tilted relatively to his rotation axis. The cylinder rotation induces a tumbling movement to the powders insuring a good particle mixing. Upon heating the cylinder, the binder reaches a viscous state which allows the fine carbon powders to stick on the surface of the TiC core particles forming a thin coating.

In the present study, 3.5 wt.% polyethylene glycol (PEG) (molecular weight 3350) was used as binder and was applied on the TiC core particles by heating the rotating cylinder loaded only with the TiC particles and the PEG. However, 7 wt.% binder was required to coat TiC particles with 9 wt.% graphite. A small quantity (1 wt.%) of aluminum stearate was added to graphite and carbon black powders to avoid the formation of agglomerates during the tumbling process. TiC particles were coated with 1, 3 and 9 wt.% carbon. It is worth noting that the carbon loss measured in TiC coatings sprayed in argon is about 3 wt.% [8]. Figures 2.a and 2.b show examples of TiC particles coated with 1 wt.% graphite and carbon black.

Plasma spraying was carried out with a Plasmadyne SG100 spray gun at a power of 30 kW (600 A x 50 V) in air and in an inert atmosphere composed mainly of nitrogen and argon. The arc gas was a mixture of 50 l min^{-1} argon and 2.7 l min^{-1} hydrogen. An argon flow rate of 5.7 l min^{-1} was used as powder feed gas. The carbon-coated particles were injected radially at the exit of the plasma gun at a feed rate ranging from 6 to 10 g min^{-1} and the stand-off distance was 12 cm.

The total carbon content in plasma-sprayed coatings was measured with a LECO WR112 carbon determinator. The free carbon content was determined by measuring the carbon content in residues after dissolution of the sprayed TiC coatings in an acid solution [18]. Oxygen and nitrogen content was determined with a LECO TC-136 analyzer and Auger analyses were performed with a PHI Model 660 Scanning Auger Microprobe. Samples were sputtered by an argon ion beam for about 4 minutes to obtain constant Auger signals. X-ray diffraction spectra were recorded with a Philips PW1840 diffractometer using the Cu K_{α} line.

3. RESULTS AND DISCUSSION

3.1 Carbon content within sprayed coatings

Table 1 gives the total and free carbon content measured in the starting powder and in coatings sprayed in air and in the inert atmosphere. Substraction of free carbon from total carbon gives the combined carbon content also given in Table 1. Numbers in parentheses correspond to the standard deviation of the analysis results. After spraying the starting TiC powders in air and in the inert atmosphere, the total carbon content is decreased from 19.29 wt.% to 17.5 wt.% and 19.09 wt.%, respectively. In both atmospheres, the total carbon content increases with the carbon coating thickness but this increase is more important with the carbon black coating. Figure 3 shows the combined and the free carbon content within sprayed coatings as a function of the amount of carbon applied on the TiC starting powders. Carbon content within the starting powder is also indicated for comparison. The combined carbon is expressed on the atomic ratio basis (x in TiC_x). In air plasma-sprayed coatings, the combined carbon increases slightly when carbon black is used but it is not changed when graphite is used. Moreover, the free carbon increase is also more important when carbon black-coated particles are used. On the other hand, the combined carbon content in coatings sprayed in the inert atmosphere does not significantly increase with the carbon coating thickness whatever

the carbon crystalline form used. However, in that case, the combined carbon loss is less important than that obtained after air spraying. As observed in coatings sprayed in air, the free carbon content increases with the carbon coating thickness but this increase remains small when graphite is used.

3.2 Carbon coating influence on oxidation

The oxygen content in the starting powder and in coatings sprayed in air and in the inert atmosphere is shown in Figure 4 as a function of the carbon coating thickness. As shown in Fig. 4, the oxygen content increases significantly after spraying in air. However, the oxygen content decreases from 1.13 to 0.85 wt.% when the carbon black coating increases from 0 to 9 wt.% but increases from 1.13 to 1.38 wt.% when a 9 wt.% graphite coating is applied on the TiC powders. This increase is likely related to the larger quantity of binder (PEG) required in that case to insure the adhesion of the total graphite deposited on the core particles during the coating process. On the other hand, in the inert atmosphere, carbon black coatings have no significant effect on the oxygen content after spraying. It is worth mentioning that X-ray diffraction analyses do not reveal the presence of titanium oxide in the plasma-sprayed coatings. This is likely related to the fact that TiO and TiC have a very similar crystalline structure, thus minute quantities of TiO within sprayed TiC coatings may not be revealed by X-ray diffraction analysis [19,20].

3.3 Carbon coating influence on nitridation

In all sprayed coatings, the nitrogen content is increased relatively to the starting powder as shown in Fig. 4. This increase is slightly less important if spraying is done in the inert atmosphere (about 0.5 wt.%) than if it is done in air (about 0.7 wt.%). Moreover, the nitrogen content does not depend on the carbon coating thickness for both the graphite and the carbon black coatings.

3.4 Differences between graphite and carbon black coatings

According to results described above, graphite coatings are less efficient than carbon black coatings to limit the carbon loss and the oxidation within TiC coatings when spraying is carried out in air. Because of its flake form, the graphite powder is likely less adherent to the TiC core particles and could be swept away upon spraying thus reducing the protection of TiC particles against oxidation and decarbonization. Carbon black, because of its small particle size and rounded form (Fig. 2), is less prone to be detached from the core particles. Due to its small particle size, carbon black could also react more efficiently with oxygen. Moreover, it has been reported that the carbon content of a TiC powder in equilibrium with amorphous carbon is larger than in equilibrium with graphite [21]. This has been attributed to the higher activity of the amorphous carbon. Although the carbon black used in this study is not totally amorphous its activity is likely higher than that of graphite favouring the formation of TiC_x with a higher carbon concentration.

3.5 Effect on the spraying efficiency

The spraying efficiency is decreased when carbon coatings are applied on the TiC powders as illustrated in Figure 5. When spraying is done in air, the efficiency is about 40 % for the uncoated starting powder and decreases to 24 % and 28 % for the carbon black- and the graphite-coated powders. A similar decrease is also observed when spraying is carried out in the inert atmosphere but the spraying efficiencies are lower.

3.6 Effect on the coating microstructure

Microstructural observations show that the porosity of coatings sprayed in the inert atmosphere is slightly higher when carbon-coated particles are used . Figure 6 shows electron micrographs of TiC coatings obtained with the uncoated starting particles and with the 9% carbon black-coated particles. However, coatings obtained with the other carbon-coated particles present a less important porosity increase. Coatings sprayed in

air are more porous and the porosity does not change significantly when carbon-coated TiC particles are used.

Previous investigations have shown that some TiC particles are partially melted during plasma spraying producing a coating microstructure containing both small and large grains [9,10]. Small grains result from the solidification of a melted layer around the TiC particles during spraying and contain less carbon than larger grains. Figure 7 presents an example of such a partially-melted TiC particle sprayed in air on a grit-blasted steel substrate. Auger analyses reveal that a very severe carbon loss and oxidation occur upon spraying in the melted region of partially-melted TiC particles. The relative peak-to-peak C/Ti and O/Ti Auger signals measured in the melted zone and in the starting powder are given in Table 2. The carbon signal decreases by a factor 7 and the oxygen signal increases by a factor 6 after spraying showing that the resulting material contains approximately comparable oxygen and carbon concentrations. The formation of such highly-degraded zones in coatings sprayed in air is likely a factor responsible for the lower thermal shock performance of these coatings compared to coatings sprayed in an inert atmosphere [6,8].

4. CONCLUSION

In order to limit the carbon loss of TiC powders during plasma spraying in air or in an inert atmosphere and to decrease the oxidation occurring when spraying is carried out in air, different carbon coatings were applied on the TiC powders by an agglutination coating technique. Carbon black coatings are found to provide a better protection against the material degradation. A higher free carbon content is found in coatings obtained with the carbon-coated particles. Such a free carbon increase may be advantageous when TiC coatings are used in thermal shock applications. It could allow a partial re-carbonization of the substoichiometric-sprayed TiC_x material during high temperature cycling. Auger analyses have revealed the formation of severely degraded zones within air-sprayed

coatings that could be responsible for the lower thermal shock performance of these coatings compared to coatings sprayed in an inert atmosphere.

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TABLE 1: Carbon content of the TiC starting powder and of TiC plasma-sprayed coatings.

Samples	Spray atmosphere	Total carbon (wt.%)	Free carbon (wt.%)	Combined carbon (wt.%)
Starting powder	--	19.29 (0.04)*	0.11 (0.02)	19.18 (0.04)
uncoated	air	17.50 (0.00)	0.38 (0.05)	17.12 (0.05)
1 % graphite	air	17.61 (0.02)	0.16 (0.05)	17.45 (0.06)
3 % graphite	air	17.56 (0.01)	0.39 (0.04)	17.18 (0.05)
9 % graphite	air	17.53 (0.03)	0.48 (0.01)	17.05 (0.04)
1 % carbon black	air	18.02 (0.00)	0.47 (0.07)	17.56 (0.07)
3 % carbon black	air	18.12 (0.03)	0.56 (0.08)	17.56 (0.09)
9 % carbon black	air	18.59 (0.02)	0.89 (0.01)	17.70 (0.02)
uncoated	inert	19.09 (0.13)	0.91 (0.08)	18.18 (0.15)
1 % graphite	inert	19.42 (0.01)	1.00 (0.09)	18.43 (0.10)
3 % graphite	inert	19.45 (0.03)	0.88 (0.00)	18.57 (0.03)
9 % graphite	inert	19.71 (0.08)	1.39 (0.09)	18.32 (0.12)
1 % carbon black	inert	19.72 (0.03)	1.32 (0.04)	18.40 (0.05)
3 % carbon black	inert	20.15 (0.01)	1.90 (0.19)	18.25 (0.19)
9 % carbon black	inert	21.01 (0.02)	2.78 (0.02)	18.23 (0.03)

* Number in parentheses are standard deviations of measured values.

TABLE 2: Relative peak-to-peak Auger signals measured in the starting TiC powder and in the resolidified zone of particles partially melted during spraying in air.

Sample	C/Ti	O/Ti
starting powder	4.5	0.12
solidified zone	0.65	0.70

FIGURE CAPTIONS

- Fig. 1: Particle size distribution of the starting TiC powders.
- Fig. 2: TiC particles coated a) with carbon black (1 wt.%) and b) with graphite (1 wt.%).
- Fig. 3: Combined and free carbon content in plasma-sprayed TiC coatings as a function of the carbon coating thickness. Composition of the TiC starting powder is also given for comparison.
- Fig. 4: Oxygen and nitrogen content in plasma-sprayed TiC coatings as a function of the carbon coating thickness. Composition of the TiC starting powder is also given for comparison.
- Fig. 5: Variation of the deposition efficiency with the carbon coating thickness in air and in the inert atmosphere.
- Fig. 6: Electron micrographs of coatings sprayed in the inert atmosphere a) with uncoated TiC powders and b) with 9 wt.% carbon black-coated powders.
- Fig. 7: Example of a particle partially melted during plasma spraying in air.













