

Self-propagating combustion synthesis and plasma spraying deposition of TiC–Fe powders

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Abstract

The synthesis of titanium carbide/iron composite from elemental powders by means of self-propagating reactions to be subsequently employed for plasma spray deposition is investigated. The combustion temperature and velocity of propagating front are found to decrease as the amount of iron in the starting mixture increased. In addition, the maximum value of the iron content in the initial mixture allowable for guaranteeing the self-propagating character of the combustion synthesis process is identified. Below this threshold, i.e. 60 wt.%, independently of the iron content, the final products resulted constituted by titanium carbide and iron, being the latter one found as a binder distributed around the carbide grains. In particular, a strong dependence of the grains size of the obtained titanium carbide on the iron content is observed. Once reduced in powder form, the obtained composite, specifically TiC–30 wt.% Fe, is subsequently used for thermal spraying coatings deposition. Adhesion performance, hardness and wear resistance tests results for the obtained coatings by vacuum plasma spraying are also reported.

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1. Introduction

It is well known that plasma spraying represents an attractive technique for the preparation of coatings to be used for wear protection, thermal barriers, electronics, etc. [1,2]. Basically, this technique consists in the injection of powders into the plasma where they first melts and then are accelerated towards the substrate to be coated. Therefore, it is expected that the properties of the obtained coatings are strictly related to the characteristics of the feedstock powders, which depend in turn on their method of synthesis, as well as the operating conditions adopted for plasma spraying deposition.

Plasma sprayed metal-carbides (for instance TiC–Fe) coatings are demonstrated to be potentially very useful for applications where high wear resistance is required [3 and references therein]. A method consisting in the simultaneous synthesis and deposition of TiC–Fe materials by plasma spraying was proposed in the literature [3]. In this latter work, ferro-titanium (FeTi), titanium and carbon were used as reagents to obtain the desired composite material according to the reaction: $\text{FeTi} + \text{Ti} + 2\text{C} \rightarrow 2\text{TiC} + \text{Fe}$. Specifically, the reactants, together with certain amounts of iron for dilution purposes, were first injected as micropellets into the plasma gun and then the resulting product was directly sprayed onto a substrate to form the coating. More recently [4], TiC–Fe composite coatings were obtained by reactive plasma spray synthesis starting from ilmenite (FeTiO_3) ore concentrate as feedstock powders and methane as reactive gas. The process for coating preparation is based on

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the following chemical reaction: $\text{FeTiO}_3 + 4\text{CH}_4 \rightarrow \text{TiC} + \text{Fe} + 3\text{CO} + \text{H}_2$.

Along the lines of some recent studies related to the use of self-propagating high-temperature synthesis (SHS) powders for thermal spray applications, i.e. MoSi_2 and TiC-NiCr [5], $\text{MoSi}_2\text{-Si}_3\text{N}_4$ [6], and FeCr-TiC [7], in this work we investigate the combustion synthesis of TiC-Fe for plasma spray deposition.

SHS, or, more generally, the combustion synthesis technique, is recognized to be an attractive alternative to conventional methods of powders synthesis [8–12]. Briefly, this technique is based on the fact that once the starting mixture is ignited by means of external energy sources for relatively short times, highly exothermic reactions may propagate through the mixture in the form of a self-sustained combustion wave leading to final products progressively without requiring additional energy. SHS is characterized by process simplicity, short reaction time, easy-to-build equipment, low-energy requirements and the possibility of obtaining complex or metastable phases.

To date a wide variety of ceramics, intermetallics and composites have been synthesized by SHS. This technique has been also used to prepare metal-ceramic coating inside cylindrical pipe [13,14].

Due to their importance, the combustion synthesis of TiC-Fe was investigated in the literature by several authors [15–19]. In particular, the influence of iron addition (0–40 wt.%) on TiC combustion synthesis has been studied by Choi and Rhee [15]. It was found that the main role of Fe is binding TiC grains whose size decreased with an increase of the amount of iron added.

The aim of this work is twofold. A systematic study on the effect of iron content on the combustion synthesis parameters, i.e. temperature and velocity, product morphology and composition, is first performed. A wider range of iron amount in the starting mixture, i.e. 0–60 wt.%, as compared to that one reported in the literature, is investigated. Secondly, the results of the deposition of the obtained titanium carbide-iron composites powders by plasma spraying are also reported. It is worth noting that this type of coatings are aimed to protect automotive components, i.e. a synchronizer ring, for extended in-service lifetime. The obtained coatings are then characterized in terms of adhesion performance, hardness tests and wear resistance.

2. Experimental set-up and procedure

Titanium, graphite and iron powders, whose properties are listed in Table 1, were mixed according to the stoichiometry of the following reaction:

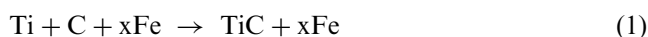


Table 1

Properties of the reactant powders used for the self-propagating combustion synthesis of TiC-xFe

Property	Vendor	Size (μm)	Purity (%)
Titanium	Atlantic Equipment Engineers	20	99.7
Graphite	Aldrich	1–2	
Iron	ALFA AESAR	<10	99.5

where the amount of iron in the starting mixture was varied in the range 0–60 wt.%. Mixing was performed in presence of acetone, as dispersing agents, for about two hours using a centrifugal mill (Tecnatest, Italy). As schematically shown in Fig. 1, two types of configurations were used for combustion synthesis experiments of TiC-xFe . In the first one (cf. Fig. 1a), which was adopted to perform the systematic investigation of the effect of iron addition on combustion temperature, wave velocity and product composition, the initial mixture was uniaxially pressed to form pellets with a diameter of 16 mm and a green density of 50–60% of the theoretical value. On the other hand, the relatively large amount of powders required for plasma spray deposition was obtained by placing the starting mixture inside a steel cylinder (3.6 cm internal diameter and 4 cm high), as schematically illustrated in Fig. 1b. In this case, the relative density of the obtained sample is in the range 47–50% of the theoretical value. Fig. 1 also shows the experimental set-up used in this work. It consisted of a reaction chamber, a power supply (Belotti, Italy; output 0–100 V) which provides the energy required for reaction ignition, a video camera (JVC, TK-1280E) and a video recorder (Panasonic, AG4700 model), and a computer system (Power Macintosh 7200) equipped with a data acquisition board (model PCI-MIO-16XE-50, National Instruments) supported by a software package (LabVIEW, National Instruments). The temperature during reaction evolution as well as the average velocity of the combustion wave were measured using thermocouples (W-Re, 127 μm diameter, Omega Engineering Inc.) embedded in the pellet.

The reaction chamber was first evacuated and then filled with argon (atmospheric pressure). This operation was repeated at least twice in order to ensure an inert environment during reaction evolution. The combustion front was generated at one sample end by using of a heated tungsten coil (R.D. Mathis Company, USA), which was immediately turned off as soon as the reaction was initiated. Then, the reaction self-propagates until reaches the opposite end of the sample.

The obtained products were characterized in terms of chemical composition and microstructure by X-ray diffraction (XRD) analysis (SEIFERT EPM XRD7 diffractometer using CuK_α Ni-filtered radiation), scanning electron microscopy (SEM), and electron dispersive spectroscopy (EDS) microanalysis (HITACHI S 4000

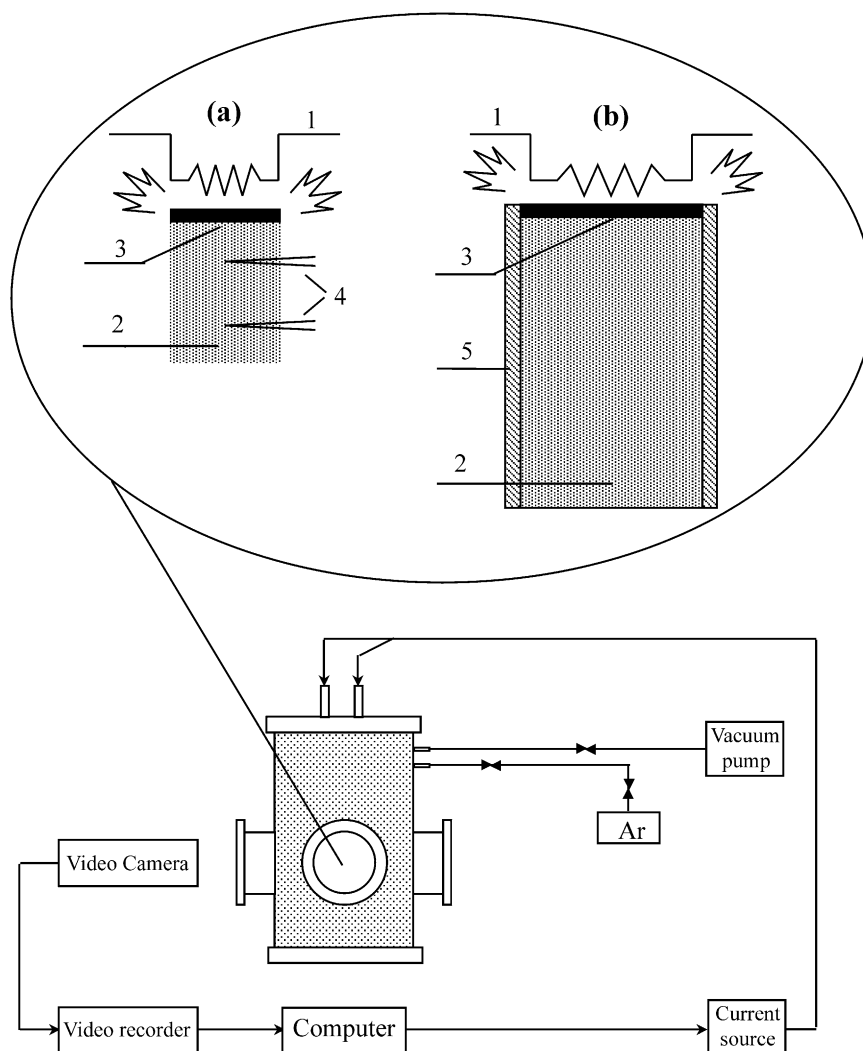


Fig. 1. Schematic representation of the two experimental configurations, i.e. (a) pellet and (b) mixture placed inside a container, used for the self-propagating high-temperature synthesis of TiC-xFe powders: (1) tungsten spiral, (2) initial mixture, (3) combustion front, (4) thermocouples, (5) metal pipe.

Field emission equipped with a KEVEX SIGMA 32 probe at a resolution of 142 eV).

The combustion synthesized TiC-xFe composite products to be used for plasma spraying deposition needed to be further processed. Thus, the porous SHS product was first crushed on a centrifugal mill (TECNOTEST D811), milled on a RETSCH mill (AS 200 BASIC), and, finally sieved mechanically until suitable amounts of plasma spraying feedstock powders, in the size ranges 20–45 and 45–75 μm , were obtained. Particle size distribution of the two powders portions was determined using a laser light scattering (MATERN MASTERSIZER 2000).

Coatings were obtained with a computer controlled vacuum plasma spray facility (Plasma Technik, Switzerland). Either an Ar-N₂ or Ar-H₂ plasma were used with an Ar, N₂ and H₂ flow rate of 40, 3–6 and 4 l/min, respectively. The plasma gun was operated at a voltage of 48 V and a current of 600–700 A with a chamber pressure of 150–220 mbar of Ar, being the spray dis-

tance kept constant at 180 mm from the substrate and the powder feed rate at 25% of the maximum allowed value. Samples were first sand blasted and mounted into the vacuum chamber, where they have been cleaned by sputtering before starting the deposition.

Two type of substrates, i.e. stainless steel and 16Mn-5Cr steel, were used as substrates to be coated. The obtained coatings were characterized in terms of composition and microstructure using SEM, EDS and optical microscopy.

Adhesion by tensile testing (ASTM standard C633) and Vickers hardness were also measured. Specifically, adhesion of the coating to the substrate was measured by performing tensile tests according to the ASTM norm C633. Briefly, two specimens, one coated, the counterpart not-coated, are glued together and mounted into a tensile machine. The stress is increased until the two pieces are separated. This “separation” may occur by a failure of either the coating or the glue.

For the Vickers hardness measurements, each specimen was cut into two equal parts along the axis after deposition. The two surfaces were polished and the hardness values were then determined on the coated layer and the substrates.

Wear resistance tests were conducted using a standard Pin-on-Disk apparatus (CSEM) in air at 25 °C and 35% of relative humidity. The sliding counter body was a steel ball, 6 mm in diameter according to DIN 5401 specification. A normal load of 5 or 10 N was generally applied. Wear cracks were observed and areas were measured by a stylus profilometer.

3. Results and discussion

3.1. Self-propagating combustion synthesis of the TiC–Fe composites

Typical temperature profiles, recorded during the combustion synthesis of TiC–xFe by two thermocouples embedded in the pellet and spaced 1 cm from each other, are reported in Fig. 2. In particular, this figure refers to the case of TiC–40%Fe. It is apparent that the temperature suddenly increases when the wave approaches to the position where the thermocouples are placed, thus reaching its maximum value. Afterwards, it decreases, but with a smaller rate, until reaching room temperature. The maximum temperature resulted to depend on the amount of iron in the starting mixture. In fact, as shown in Fig. 3a where the combustion temperature is reported as a function of the amount of iron, it is seen that the temperature monotonically decreases when increasing the iron content. Correspondingly, as reported in Fig. 3b where the dependence of wave velocity on iron addition is shown, the front speed follows the same behaviour. In addition, it was observed that by

adding more than 60% wt of iron to the starting mixture no self-propagating reaction occurred. Therefore, this value represents the threshold limit for maintaining the self-sustaining character of the process. It is worth noting that slightly different values of temperature and wave velocity were obtained by Choi and Rhee [15], although the general behaviour is the same, as it may be seen from Fig. 3a and b, respectively, where the results of both investigations are reported for sake of comparison. The small discrepancies above may be related to the different powders characteristics used during the two investigations but also to experimental uncertainties. Moreover, as mentioned previously, a wider range of iron content was studied in our case thus identifying its maximum quantity, i.e. 60 wt.%, above which the combustion wave cannot self-propagate upon ignition throughout the entire pellet.

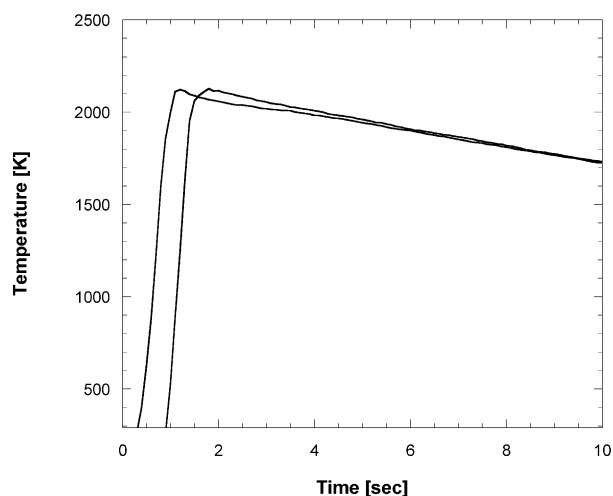


Fig. 2. Temperature profiles recorded during the combustion synthesis of TiC–40%Fe.

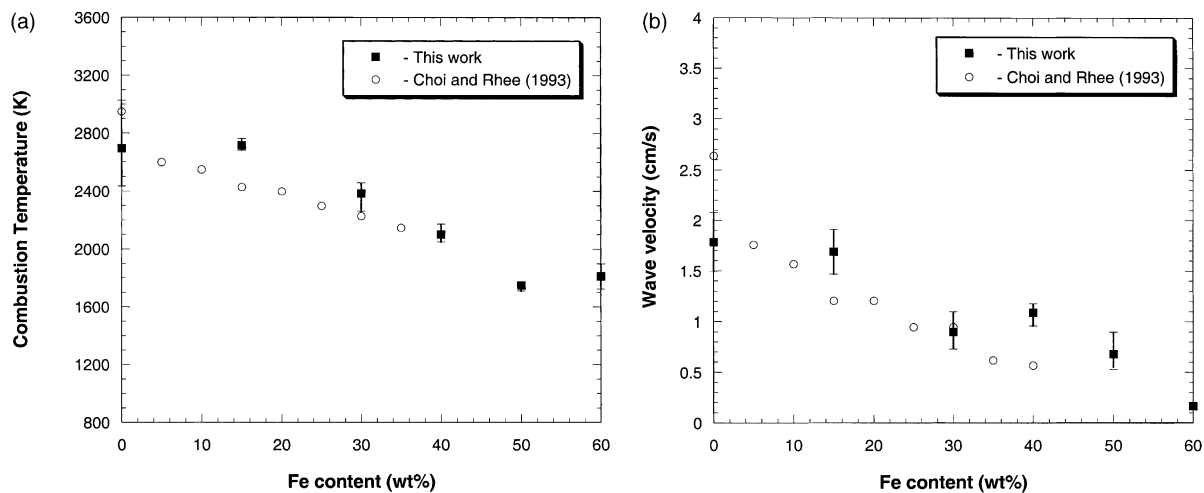


Fig. 3. Effect of iron content in the starting mixture on the maximum combustion temperature (a) and velocity of propagation of the combustion wave (b). Experimental results by Choi and Rhee [15] are also reported for sake of comparison.

As suggested by Choi and Rhee [15], the decrease of combustion temperature and speed of propagation front when augmenting the iron content during combustion synthesis process in the Ti–C–Fe system, may be simply due to the diluent action of this metal in the interaction between Ti and C to form TiC. However, on the basis of

the results obtained by taking advantage of combustion front quenching experiments performed on the TiC–Fe system, Fan et al. [17] proposed that iron also plays an important role in the precipitation of TiC particles, thus influencing the combustion reaction mechanism. In addition, more recently [18], the same authors observed that iron directly interacts with titanium to form FeTi when starting from coarser titanium particles (135–154 μm). In our investigation no secondary phases were observed in the final product. In fact, from the XRD analysis results reported in Fig. 4, it may be seen that, regardless the iron content, the only phases detected during our investigation in the end products are titanium carbide and iron. Of course, as expected, the peak of Fe becomes higher as the amount of this metal added to the starting mixture was increased. On the basis of the result above, the reaction between titanium and carbon seems to be the most favourable than any other possible interaction in the Ti–C–Fe system.

In order to study the final products morphology as well as to better characterize them from the chemical composition point of view, SEM and EDS analyses were carried out. Fig. 5a–c show the back-scattered micrographs of the products obtained for the cases of TiC–15%Fe, TiC–30%Fe and TiC–60%Fe, respectively. It may be seen that the obtained products consist of carbide grains, approximately spherical shaped, and

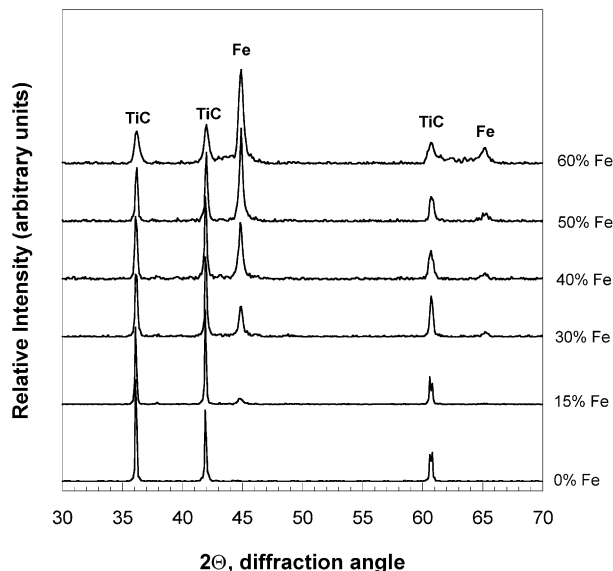


Fig. 4. XRD patterns of reaction products for different values of iron in the starting mixture.

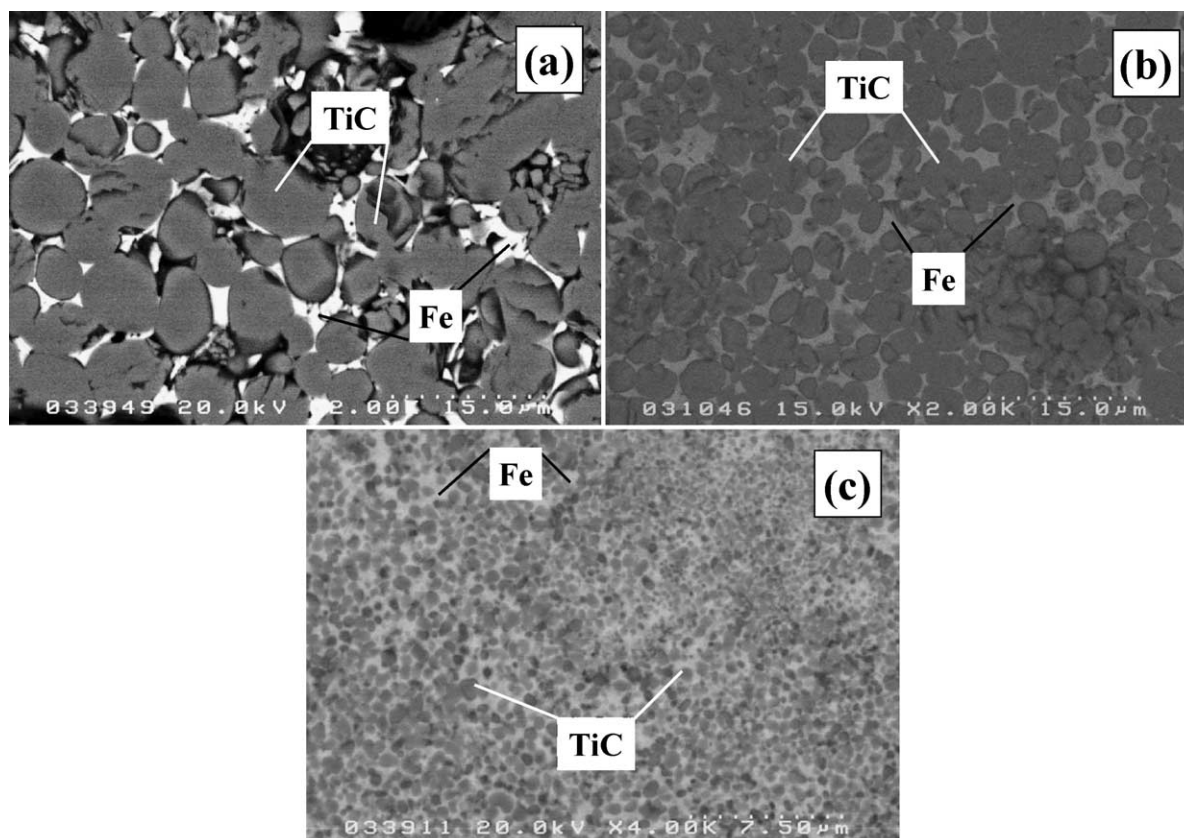


Fig. 5. Microstructures of reaction products corresponding to (a) TiC–15%Fe, (b) TiC–30%Fe, and (c) TiC–60%Fe.

iron, which surrounds TiC particles thus acting as a binder. In addition, EDS microanalysis revealed that the corresponding Ti:C atomic ratio was very close to 1, so that the carbide phase is nearly stoichiometric independently of the addition of iron.

However, the situation dramatically changes from the microstructure point of view as the amount of iron is augmented. In fact, Fig. 5a–c shows that an increase of iron amount corresponds to a significant decrease of the size of the carbide grains formed. Specifically, the average size of the obtained carbide grains was about 7, 3, and less than 1 μm , when using 15, 30 and 60% of iron, respectively. These results are consistent to those found by Choi and Rhee [15], although the minimum TiC grains size obtained during their investigation was 1.5 μm for the case of TiC–40%Fe, while in our investigation for the case TiC–60%Fe (cf. Fig. 5c) was mainly less than 1 μm . It was suggested [15] that the decrease of TiC grains size as the amount of iron increases is related to the fact that liquid iron surrounding the carbide grains reduce the driving force for TiC grain growth and prevent the occurrence of sintering phenomena between the obtained grains to form larger ones.

3.2. Plasma Spray Deposition of the TiC–Fe powders

Before considering in detail the preparation of TiC–Fe coatings by plasma spray process, let us first examine the results of the characterization of SHS powders to be used as starting material.

Size distribution of the synthesized TiC–30%Fe powder, as obtained following the procedure described in the experimental section, are illustrated in Fig. 6a and b. Here, the gaussian and the cumulative curves corresponding to the two powder fractions resulting after sieving are reported. It may be seen that both of the TiC–30%Fe powder portions exhibit a narrow size dis-

tribution around the mean value of about 38 and 65 μm , respectively. However, “tails” of the gaussian distribution of these powders towards the low sizes are present. A similar behaviour was found for the NiCr–TiC powders produced by SHS and then used for thermal spray deposition by Bartuli et al. [5].

Fig. 7a and b shows two SEM back-scattered micrographs of the SHS powders used as feedstock for plasma spraying, for the case of 20–45 μm particle size range and TiC–30%Fe composition. Specifically, while Fig. 7a shows a general view of the powders after synthesis by SHS, crushing and sieving, the corresponding detailed microstructure may be observed in Fig. 7b. According to what already seen in Fig. 5, each powders particle appear to be constituted by carbide phase grains dispersed into an iron matrix which serves as a binder.

Due to the large number of parameters involved in the plasma spraying process, three of them, namely plasma gas mixture, flow rate and energy input, were varied when preparing the coatings.

The cross section of the coating obtained using Ar–N₂ as plasma gas as well as the SHS TiC–30%Fe powders with particles size in the range of 20–45 μm is shown in Fig. 8. Three different zones can be identified when examining the microstructure of the deposited coating. In particular, SEM and EDS investigations revealed that titanium carbide grains (“grey” areas) display spherical shape and resulted to be embedded in a iron matrix (“white” areas). In addition, “black” areas rich of carbon and oxygen, being the former one the dominant element, are also found in the coating. This finding may be a consequence of a reaction occurring between titanium carbide with the nitrogen present in the plasma gas, thus resulting in the formation of free C. It is worth noting that, the latter one, once incorporated into the coating, easily breaks during grinding/polishing of the samples, thus giving rise to extended irregularities of the polished surfaces.

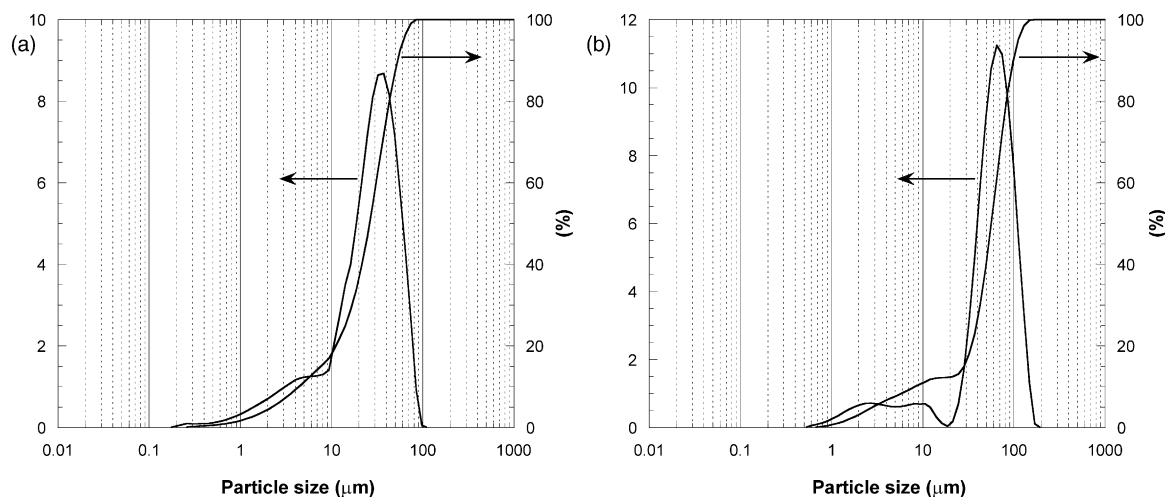


Fig. 6. Size distribution (Gaussian and cumulative curve) of the SHS TiC–30%Fe powders as obtained by a laser light scattering MATERN MASTERSIZER 2000: (a) 20–45 μm , (b) 45–75 μm .

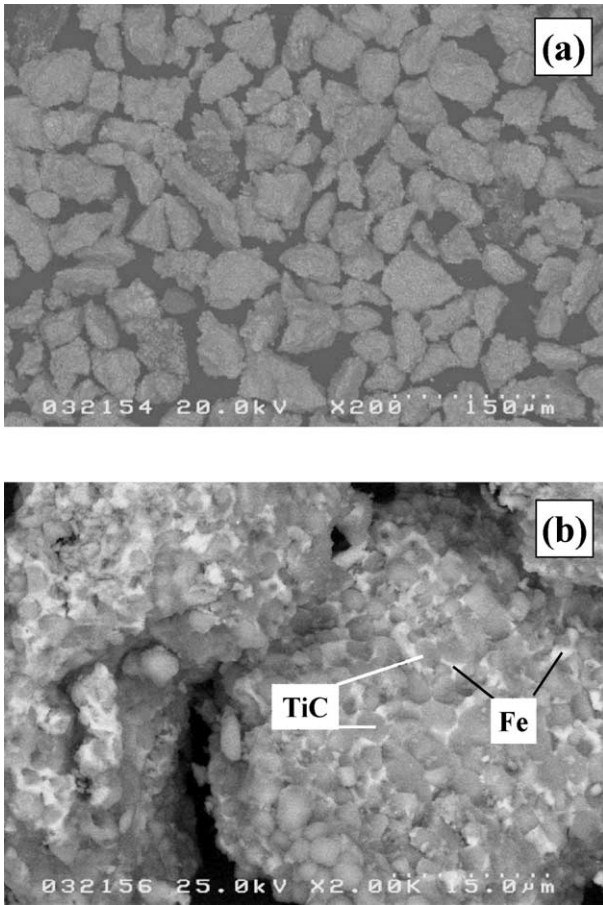


Fig. 7. SEM back-scattered micrographs of SHS TiC–30%Fe powders (20–45 μm) used as feedstock for plasma spraying: general (a) and detailed (b) views.

On the other hand, the obtained coating resulted improved when the deposition was performed by changing the plasma gas mixture to Ar–H₂. The corresponding cross section as well as a detailed view of the coating obtained under the latter experimental conditions are shown in Fig. 9a and b, respectively. It is possible to observe that the extension of the “black” areas are strongly reduced as compared to the previous case, i.e.

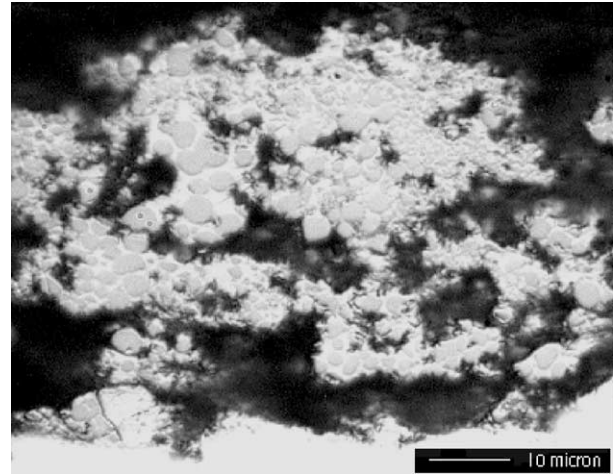


Fig. 8. Cross section of a TiC–30%Fe plasma spraying coating obtained using Ar–N₂ as plasma gas.

when adopting Ar–N₂ as plasma gas mixture, and the coating obtained resulted to be much more regular.

Analogous considerations can be made on the basis of the results obtained when using powders in the particle size range 45–75 μm while keeping the composition the same, i.e. TiC–30%Fe, being the resulting coatings characterized by similar microstructures to those shown in Figs. 8 and 9, for the cases of Ar–N₂ and Ar–H₂, respectively.

Let us now consider the results obtained from adhesion performance, hardness and wear resistance tests.

On the basis of the tensile tests performed to evaluate the adhesion of the coating following the procedure described in the experimental section, it was found that for both types of substrates stainless steel and 16 Mn–5Cr steel, the glue failed at a stress of 60–70 MPa indicating that adhesion of the coatings is satisfactory.

The hardness tests conducted as described in the experimental section reveals that the Vickers hardness in the substrate is about 800 in the hardened zone, i.e. close to the coating–substrate interface, and drops to about 300 in the matrix. On the other hand, the hardness of the coating varied between the extremely high values of the TiC particles, i.e. up to 1750, and

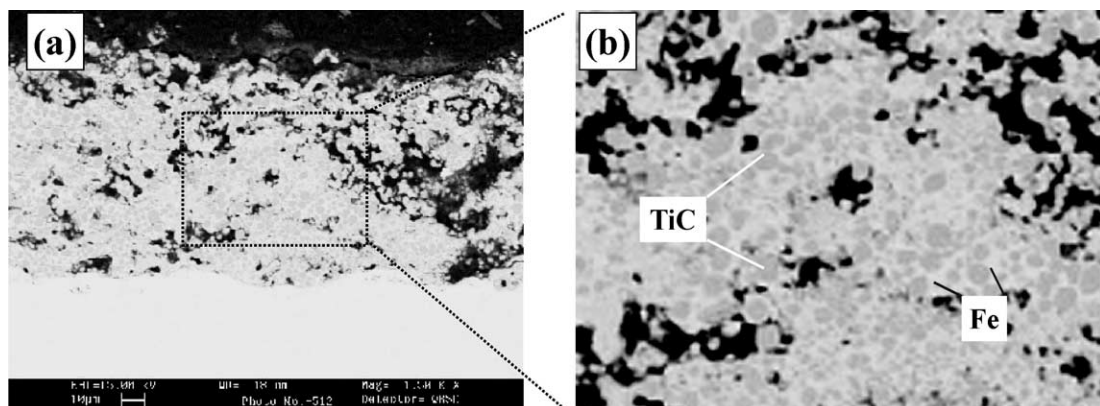


Fig. 9. Cross section of a TiC–30%Fe plasma spraying coating obtained using Ar–H₂ as plasma gas: general (a) and detailed (b) views.

Table 2
Weight loss after pin-on-disk testing under dry conditions

	Distance (m)	Load (N)	Sample, weight loss ($\text{kg} \times 10^{-4}$)	Sphere, weight loss ($\text{kg} \times 10^{-4}$)
Coated side	500	5	1	10.5
	500	10	1.5	17.4
Uncoated side	500	5	16.0	3.7
	500	10	21.0	1.5

the much lower values into the Fe–matrix, i.e. about 350.

Wear resistance tests were conducted as also described in the experimental section. The samples were tested on both sides, i.e. the case hardened side and the coated side. The data shown in Table 2 indicate that, under the spraying conditions adopted, the wear resistance of the coated side of the sample is significantly increased in comparison to the uncoated side which is only case hardened.

4. Concluding remarks

The preparation of TiC–Fe coatings by plasma spraying deposition using a two step process was investigated in this work.

Specifically, the first step consisted in the synthesis of the titanium carbide/iron composite from elemental powders through self-propagating reactions. In particular, the influence of iron content on the combustion synthesis process as well as on the characteristics of the obtained product was systematically studied. It was seen that the combustion temperature and wave propagation decreased as the amount of iron in the starting mixture was augmented. Moreover, it was demonstrated that the reaction maintained the self-propagating character if the iron content was equal or less than 60 wt.%. The only phases detected in the end products were iron and nearly stoichiometric titanium carbide, being the first one distributed as a binder around the carbide grains. In addition, a strong influence of the presence of iron in the grain size of the TiC formed was observed. In particular, grains size of the carbide phase obtained for the case of 60 wt.% of iron was less than 1 μm .

After crushing and sieving of the SHS product, the obtained powders were used as feedstock for plasma spray deposition, which represent the second step of the proposed process. Specifically, the TiC–30%Fe composite powders were deposited on stainless steel and 16 Mn–5Cr steel samples case hardened. It was found that the use of Ar–H₂ plasma gas is preferred as compared to Ar–N₂. Adhesion performance, hardness and wear resistance tests revealed that the obtained coating exhibits satisfactory results for potential practical applications of such a metal-matrix composite as thermal spray feed stock powder.

Acknowledgements

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