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Development of titanium-doped carbon–carbon composites

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Abstract The development of titanium-doped carbon matrix–carbon fibre reinforced composites (CCCs) via liquid impregnation of carbon fibre preforms using mesophase pitch is studied. Two different approaches for introducing the dopant into the carbon material are investigated. One consists of doping the matrix precursor followed by the densification of the preform with the doped precursor. The second approach consists of doping the porous preform prior to densification with the undoped mesophase pitch. Titanium-doped CCCs with a very fine distribution of dopant (in the nanometric scale) are obtained by adding TiC nanoparticles to the matrix precursor. Thermal decomposition of titanium butoxide on the carbon preform prior to densification yields doped CCCs with higher titanium content, although with larger dopant size. The combination of these two methods shows the best results in terms of dopant content.

Introduction

Carbon matrix–carbon fibre reinforced composites (CCCs) are the most promising solution for the strike point area of the ITER divertor due to their excellent thermo mechanical properties, thermal shock resistance, high thermal conductivity and absence of melting point in comparison with metals [1]. However, during operation as plasma facing materials in a thermonuclear fusion reactor, CCCs suffer different types of erosion mechanisms [2, 3]. In order to guarantee the lifetime of CCCs, it is necessary to improve significantly the material's chemical erosion and thermal shock resistance. It has been demonstrated that the addition of dispersed metals, such as titanium, to carbon contributes to an increase in thermal conductivity due to the catalytic effect on graphitization [4, 5]. Since thermal conductivity and thermal shock resistance are directly related to each other, the latter can be improved by doping carbon with this element. In addition, this element has a beneficial effect on the chemical erosion, which has been already demonstrated [6].

The development of doped CCCs was yet mainly limited to the use of silicon and/or boron [7, 8]. Nonetheless, the development of doped graphites has been more extensively studied. Direct mixing of metal carbides (e.g. TiC, VC, ZrC and WC) with the carbon powders (coke or self-sintering mesophase) has been widely used to obtain graphites with dispersed dopants in the nano- to micron-scale [9–12]. A homogeneous and fine distribution of the dopants in the carbon material is desirable in order to improve the material properties [13]. However, this is limited by the particle size of the carbides available and by the dispersion achieved during processing. The co-pyrolysis of organometallic compounds (e.g. titanium butoxide or triphenylsilane) with the carbon precursors has also been used to obtain doped graphites with fine and homogeneous dopant dispersion [14, 15]. This method is limited by the availability of organometallic compounds of given metals. Furthermore, the organometallic compound normally decomposes to form the metal oxide and its transformation into carbide during graphitisation may cause deterioration of the carbon material.

Synthetic mesophase pitches from pure aromatic hydrocarbons have been shown as very suitable precursors for the

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development of a broad range of carbon materials with high thermal conductivity, due to their relatively low softening point (SP), very high carbon yield and high graphitizability [16]. Several studies are dedicated to the processing of carbon matrix/carbon fibre reinforced composites using mesophase pitch as matrix precursor [17–21]. In addition to the significantly higher graphitizability of the resultant carbonaceous matrices, the higher carbon yield of the mesophase pitch in comparison to other pitches enables a reduction of the number of densification cycles, with the subsequent reduction in processing time and costs. Liquid densification with mesophase pitch has also advantages in comparison to the chemical vapour infiltration methods frequently used, as these require lengthy fabrication times due to the extremely low reaction rates necessary to maintain a uniform deposition throughout the porous carbon fibre preform. Nonetheless, the processing of mesophase pitch is more complex due to its higher viscosity and the oxidative stabilisation stage required to reduce bloating during carbonisation [18].

This paper studies the development of titanium-doped CCCs via liquid impregnation of a carbon fibre preform using mesophase pitch. Two different approaches for introducing the dopant into the carbon material were investigated. One consists of doping the matrix precursor followed by the densification of the preform with the doped precursor. The second approach consisted of doping the porous preform prior to densification with the undoped mesophase pitch.

Experimental

Raw materials

Naphthalene-derived mesophase pitch (AR) supplied by *Mitsubishi Gas Chemical* was used as matrix precursor to densify 2D PAN-based carbon fibre preforms supplied by *SGL Carbon Group*. Two sources of titanium were used to obtain the doped materials: TiC nanoparticles, 130 nm average size and titanium (IV) butoxide [$Ti(BuO)_4$] (TBO), both supplied by Sigma Aldrich.

Methods for introducing titanium

Doping the matrix precursor using titanium butoxide

Titanium butoxide was selected as dopant precursor due to its relatively low price and availability in comparison to other titanium organometallic compounds. The mesophase pitch was mixed with TBO (3 and 15 wt% Ti) at 325 °C in a 1L stainless steel stirred reactor (100 rpm) for 1 h. A nitrogen pressure of 0.2 MPa was used to avoid volatiles release and the evaporation of the organometallic compound. The final cool down to room temperature was performed under pressure. The resultant precursors were labelled AR–TBO-3 and AR–TBO-15, respectively.

Doping the matrix precursor by adding TiC nanoparticles

The mesophase pitch was mixed with 5, 10 and 15 wt% nanoparticles. For this purpose, the same reactor and the same conditions were used as described above, except an operating temperature of 350 °C. The resultant precursors were labelled AR–TiC-5, AR–TiC-10 and AR–TiC-15, respectively.

Doping the carbon fibre preform by thermal decomposition of titanium butoxide

The carbon fibre preform was placed in a stainless steel reactor covered by a solution of TBO in toluene (ratio 1:2, equivalent to 2% TiO_2). The reactor was then heated under nitrogen atmosphere to 400 °C, a temperature high enough for the thermal decomposition of the organometallic compound into TiO_2. These conditions were maintained for 1 h.

Doping the carbon fibre preform by decomposition of titanium butoxide through a sol–gel process

The method used is similar to the sol–gel route described in the literature [22]. The carbon fibre preform was covered by titanium butoxide and placed in a sonic bath. An ice-cooled solution of 15% H_2O_2 was added to induce the formation of a non-stable complex of Ti–H_2O_2. This rapidly undergoes a highly exothermic reaction with formation of H_2O, O_2, butanol and a yellow gel corresponding to poly-peroxotitanic acid, which is then dried at 150 °C for 5 h to induce its decomposition into titanium oxide.

Characterisation of matrix precursors

The suitability of the doped precursors obtained for the densification of the carbon fibre preforms was evaluated by determining their softening temperature and scanning electron microscopy (SEM). The results obtained were compared to those corresponding to the raw mesophase pitch (AR).

Mettler SP of the different matrix precursors was measured using a Mettler Toledo FP90 following the ASTM D3104 standard procedure. Measurements were preformed inside an inert atmosphere chamber to avoid oxidation of the sample during the experiment. A small cup (with pierced bottom) was filled with approximately 0.5 g of precursor. The cup was placed in the Mettler furnace and preheated to 20 °C below the expected SP. Subsequently, the oven temperature (maximum 350 °C) was increased at a rate of 2 °C min^{-1} until a drop of pitch flowed through the hole, which characterised the softening temperature of the pitch.

The dispersion of the dopant in the matrix precursor was studied by SEM, using a Zeiss DSM 942 microscope and a backscattered electrons detector. The analysis of the chemical composition on specific areas of the sample was performed using an X-ray energy dispersive analyser (EDX).

Preparation of carbon–carbon composites

Carbon–carbon composites were obtained using a liquid impregnation process. The carbon fibre preforms were densified by liquid impregnation with the matrix precursor, i.e. either the mesophase pitch (AR) or the doped precursors described above. The conditions were optimised taking the softening temperature of the precursors and the temperature of decomposition of the mesophase pitch into account (volatile release is significant at temperatures above 350 °C).

The carbon fibre preform was introduced in an autoclave and covered with the matrix precursor. The autoclave was heated under vacuum up to 350 °C, temperature that ensures the melting of the precursor. Then, a nitrogen pressure of 0.5 MPa was applied in order to force the precursor into the preform. After 3 h, cooling to room temperature was performed under pressure.

The densified preforms were submitted to a stabilisation process prior to carbonisation, in order to reduce the fluidity of the precursor and therefore avoid exudation from the preform. Stabilisation was carried out in air (20 L/min) at 170 °C for 24 h followed by 12 h at 200 °C. Once stabilised, the composites were carbonised at 1,000 °C in a furnace using a heating rate of 1 °C/min and a nitrogen flow of 80 L/h. The final temperature was maintained for 30 min after which the sample was left to cool down to room temperature. The resultant composites were labelled CC–AR (undoped composite); CC–TiC-5, CC–TiC-10 and CC–TiC-15 (doped composites obtained by doping the mesophase pitch with TiC nanoparticles); CC–TD (doped composite obtained by thermal decomposition of TBO on the preform followed by densification with AR); CC–H_2O_2 (composite obtained by decomposition of TBO using H_2O_2 followed by densification with AR).

Characterisation of carbon/carbon composites

The titanium content of the composites was determined from their ash content, which was obtained from the residue resulting from burning the composite at 800 °C until constant weight, following the UNE 32004 standard. The bulk density was calculated by measuring the dimensions and the weight of the samples. Open porosity was determined by water immersion, according to the ASTM C20 standard. The dispersion of the dopant in the composites was studied by SEM as described in 'Characterisation of matrix precursors' section.

Results and discussion

CCCs obtained by doping matrix precursors

The main challenge of this study is to obtain matrix precursors with dispersed dopant without increasing excessively the softening temperature of the doped precursor, as this would cause problems for densification of the carbon fibre preforms. Therefore, the softening temperature of the resultant-doped precursors is a key parameter to evaluate the potential of the studied methods.

Using titanium butoxide

During the mixing of the mesophase pitch with titanium butoxide, the organometallic compound decomposes into TiO_2. The softening temperature of the doped precursors increased from 290 °C (AR) to 305 °C and >350 °C for the mixtures using 3 and 15 wt% titanium, respectively (Table 1). Furthermore, no real softening of the second precursor was observed. Therefore, the doped precursor AR–TBO-15 was directly discharged, as its high softening temperature accompanied by the low fluidity would make the densification of the carbon fibre preform impossible. Moreover, while the dispersion of titanium in the AR–TBO-3 sample was homogeneous, with TiO_2 particles in the submicron scale, the sample with higher amount of titanium showed large agglomerates of TiO_2 (Fig. 1).

Densification of the carbon fibre preform with AR–TBO-3 was carried out, as its softening temperature seems reasonable for this process. In spite of this, the process was not successful, as the precursor was not able to impregnate the centre of the preform (only a depth of ~1 mm was

Table 1 Softening temperatures of matrix precursors

Matrix precursor	Softening temperature (°C)
AR	290
AR–TBO-3	305
AR–TBO-15	>350
AR–TiC-5	290
AR–TiC-10	294
AR–TiC-15	297

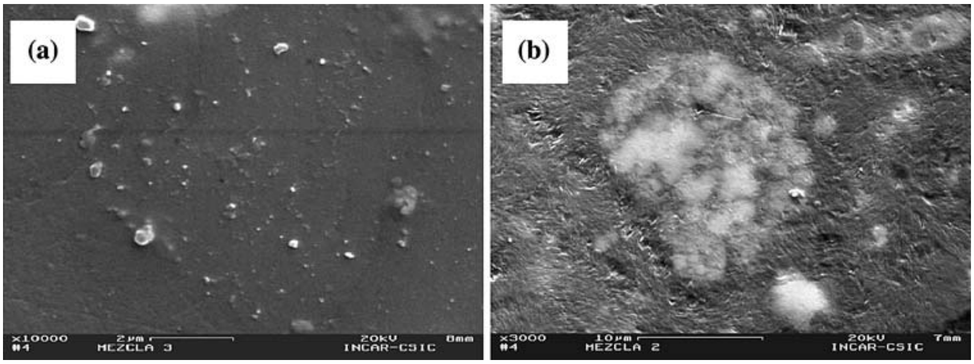

Fig. 1 SEM micrographs of doped precursors: **a** AR–TBO-3 and **b** AR–TBO-15

densified). In order to understand the reasons that impede the penetration of the pitch, the SP of the precursor remaining outside the preform after densification was measured. The values obtained were higher than 350 °C. This evidences that the doped precursor undergoes chemical reactions (polymerisation/condensation) at the conditions used for densification, which cause the softening temperature to significantly increase, thus impeding a successful densification of the preform.

Despite that doping carbon precursors using organometallic compounds is described in the literature as a successful method to develop doped graphites [15], this method is not useful to develop doped carbon–carbon composites.

Using TiC nanoparticles

Doping the matrix precursor directly with TiC nanoparticles was studied as an alternative to the method discussed above. The softening temperature of the doped precursors obtained was found to be suitable for the densification process, as it was not modified after adding 5 wt% TiC and only increased to 297 °C after the addition of 15 wt% to the mesophase pitch (Table 1). SEM studies of the doped precursors showed a homogeneous dispersion of the carbide. The particle size was at the nanometric scale, accompanied by some agglomerates with maximum size of 2 μm in the precursors with higher concentration of dopant.

Based on these results, densification of the carbon fibre preforms was carried out with the three doped precursors obtained. After densification, the initial porosity of the preform (40 vol.%) was reduced to 7%, the same value as that obtained for the undoped mesophase pitch (AR). This indicates that the doped precursors are suitable for densification. The resultant densified preforms were stabilised and then carbonised. The characteristics of the carbonised composites are summarised in Table 2. The porosity of the doped composites (~20–21 vol.%) is similar to that obtained with the undoped mesophase pitch, indicating again the suitability of these doped precursors for densification. The bulk density increases slightly with increasing the titanium content in the composite, influenced by the higher density of the carbide. As the carbide is only introduced in the matrix, the titanium content in whole composite is rather low, even for the composite CC–TiC-15 (3.4 wt% Ti, 0.85 at.% Ti). However, the amount of carbide introduced in the matrix precursor is limited by its softening temperature, and cannot be further increased.

The carbonised composites were examined by SEM in order to study the distribution of the dopant in the material (Fig. 2). In general, titanium carbide is homogeneously distributed in the composite, as shown in Fig. 2d, with particles mainly in nanometric scale. In the composite with the lowest carbide content, CC–TiC-5, the carbide is hardly observed in the matrix (Fig. 2a), although it can be detected throughout the material by EDX. Only in some regions small agglomerates (<1 μm) can be observed (Fig. 2b). Despite the good distribution of the dopant in this composite, higher contents would be required in order to contribute to a significant improvement of the material

Table 2 Characteristics of carbonised composites

Sample	Ti (wt%)	Ti (at.%)	Open porosity (vol.%)	Bulk density (g/cm^3)
CC–AR	–	–	21	1.42
CC–TiC-5	1.13	0.28	21	1.42
CC–TiC-10	2.29	0.57	20	1.44
CC–TiC-15	3.40	0.85	21	1.46
CC–TD	3.98	1.00	21	1.48
CC–H_2O_2	2.90	0.73	22	1.44

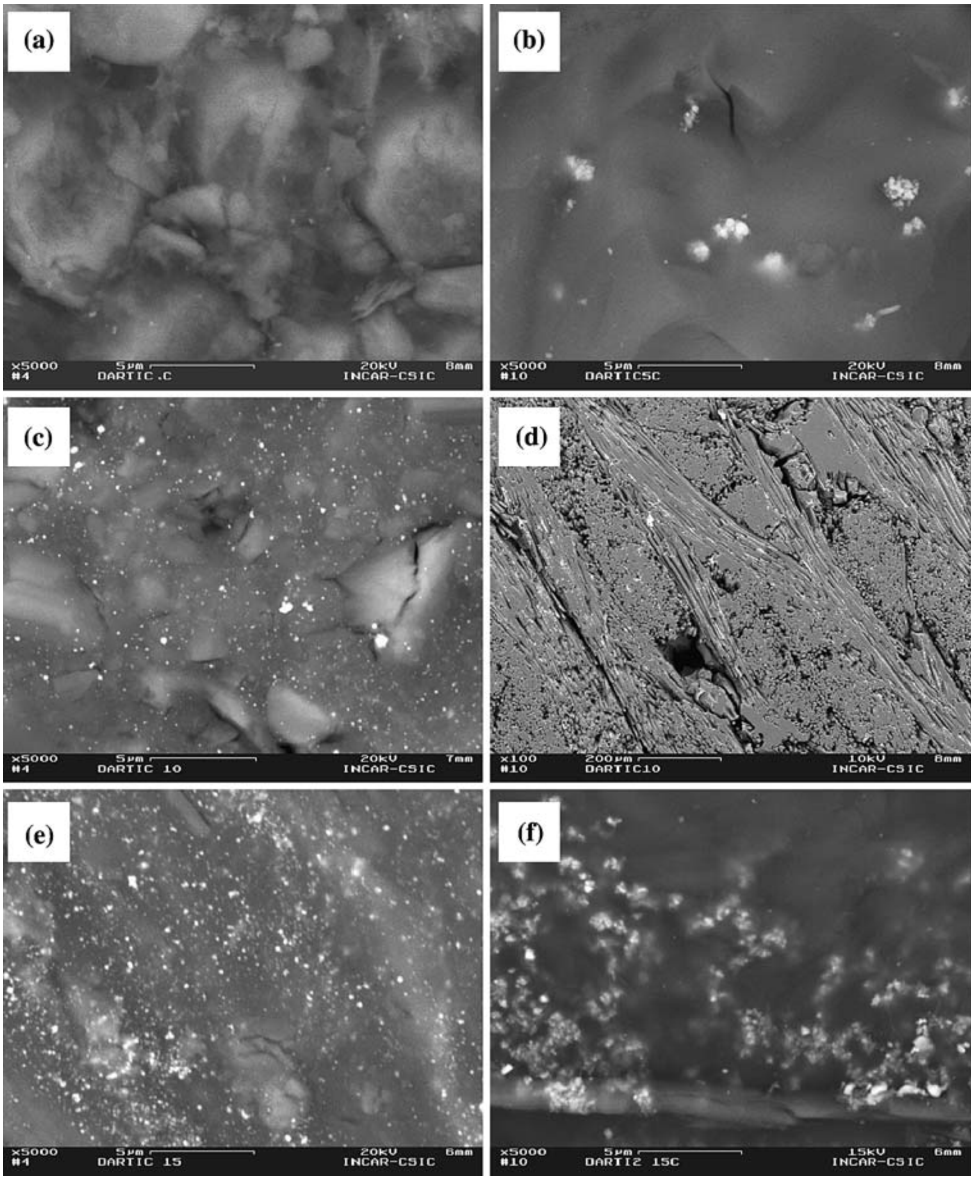

Fig. 2 SEM micrographs of composites doped with TiC nanoparticles: **a**, **b** CC–TiC-5; **c**, **d** CC–TiC-10 and **e**, **f** CC–TiC-15

properties [5]. The carbide particles are clearly observed in the composite CC–TiC-10 (Fig. 2c and d) homogeneously throughout the whole composite and with particle sizes mainly in the nanometric scale. A fairly good distribution of dopant is still observed in the composite with the highest carbide content, CC–TiC-15 (Fig. 2e), although there are regions, especially closer to the surface of the material, with agglomerates of larger size (<2 μm) formed of nanoparticles (Fig. 2f). This evidences a gradient formation in the distribution of the dopant in the composite.

The results obtained indicate that doping the matrix precursor with titanium carbide nanoparticles is a suitable method to develop titanium-doped carbon–carbon composites, as it yields a rather homogeneous distribution of dopant in the material. The optimum carbide content to be introduced in the matrix precursor seems to be 10 wt%, as higher contents yield a higher presence of agglomerates in the composite and a slightly less homogeneous distribution of the dopant. Furthermore, the dopant is already forming the carbide, which is a significant advantage in comparison to other methods that introduce the dopant in the form of oxide.

CCCs obtained by doping carbon fibre peforms

Thermal decomposition of titanium butoxide

The doped preform obtained by decomposition of titanium butoxide into TiO_2 at 400 °C was studied by SEM in order to observe the dispersion of the dopant and, therefore, evaluate the potential of this method. The image in Fig. 3b shows that the dispersion of the oxide is

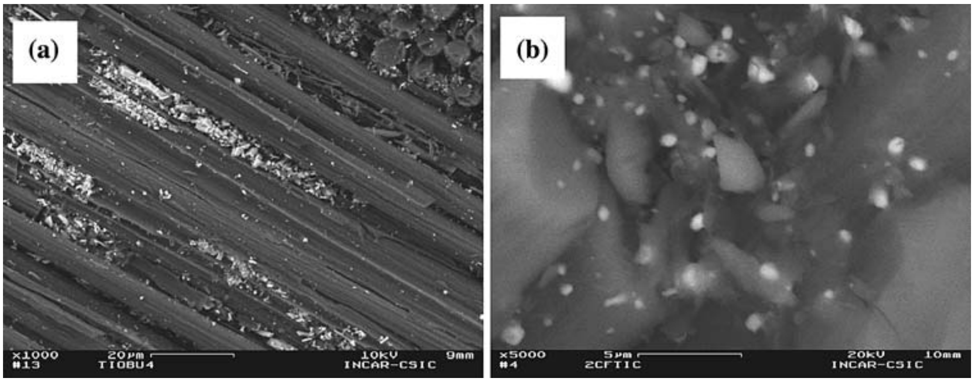

Fig. 3 SEM micrographs of carbon fibre preform after thermal decomposition of TBO

rather good, with particle sizes of 1–2 µm but also Ti is detected by EDX in areas where it is not visible due to the nanometric size of the TiO_2 particles. However, there are some areas of the doped preform where large agglomerates (up to 100 µm) are observed (Fig. 3a). These results indicate that this method could be suitable to obtain doped carbon–carbon composites, although the dopant size is generally larger.

The doped preform was densified with mesophase pitch AR to obtain the titanium-doped composite (CC–TD). Densification was successfully accomplished, with 7 vol.% porosity before carbonisation and 21 vol.% in the carbonised composite (Table 2), similar to the other composites developed. The titanium content in the composite was 3.98 wt%, the highest of the composites developed in this study. The dispersion of dopant does not change significantly in the carbonised composite.

Based on the obtained results, this method is suitable to developed titanium-doped carbon–carbon composites, as it allows introducing a higher concentration of dopant in the composite, although it is in the form of TiO_2 particles of larger size.

Decomposition of titanium butoxide through a sol–gel process

The doped preform obtained using a sol–gel process for the impregnation and decomposition of titanium butoxide shows a significant content of agglomerates with sizes between 10 and 20 µm (Fig. 4a). Different to the samples

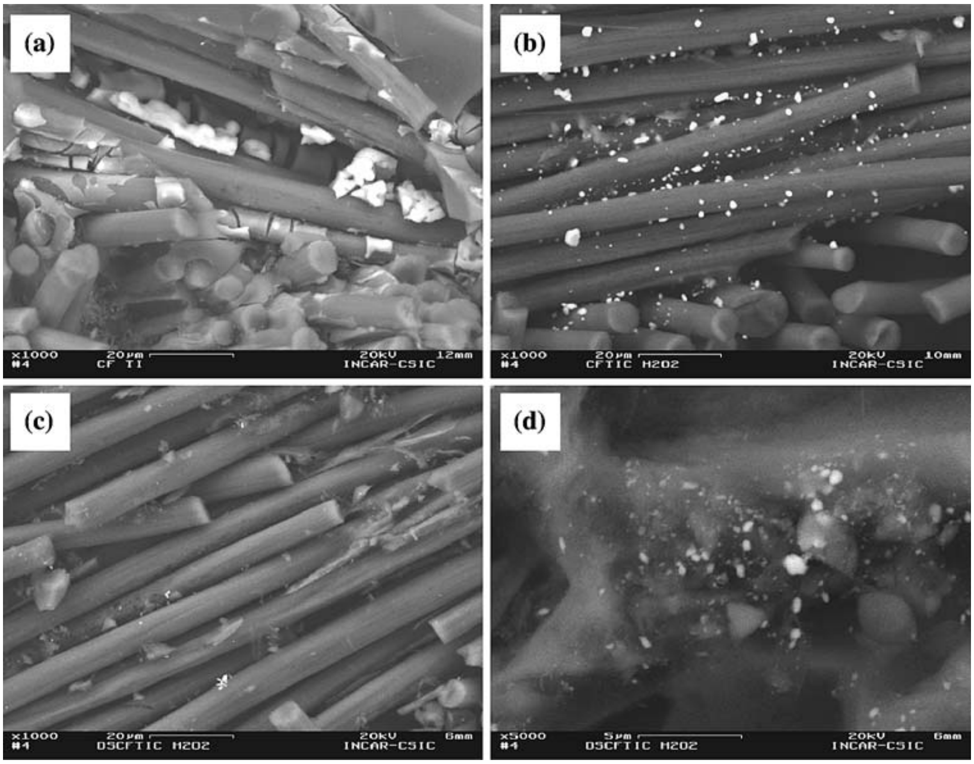

Fig. 4 SEM micrographs of: **a** carbon fibre preform after decomposition of TBO with H_2O_2; **b** doped preform after treatment at 1,000 °C and **c**, **d** carbonised composite

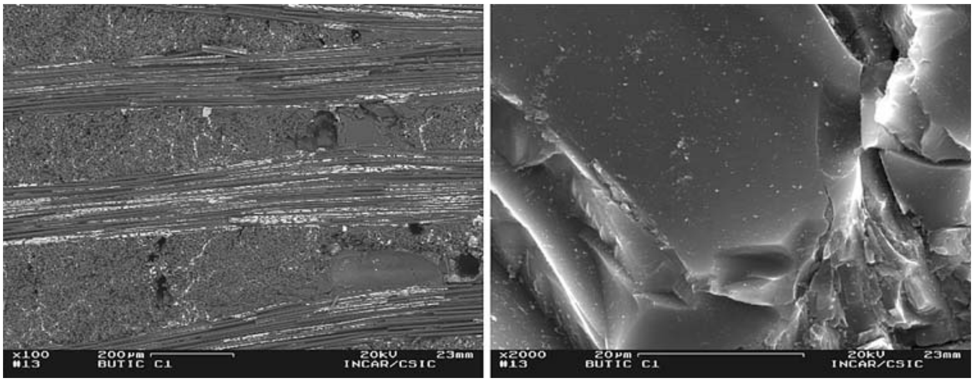

Fig. 5 SEM micrographs of Ti-doped composite obtained by combination of doping methods

obtained using the other doping methods, this one shows films that contain TiO_2 coating the fibres. The doped preform was treated at 1,000 °C in order to investigate whether the films were stable or not. The films were not evident after this treatment (Fig. 4b), indicating that they consisted of an instable compound of titanium. It is interesting to note that after the thermal treatment, the titanium oxide particles are significantly smaller and better dispersed in the preform.

The doped preform was densified with mesophase pitch AR to obtain the doped composite (CC–H_2O_2). As in the previous case, densification was successfully accomplished and the carbonised composite has similar porosity (Table 2). The titanium content is 2.90 wt%. The dispersion of the TiO_2 particles in the carbonised composite is rather good, particles being mainly in the nanometric scale range, although some larger particles, maximum size 1–2 μm are observed. Therefore, although this method seems to be efficient to develop titanium doped carbon–carbon composites, the thermal decomposition of titanium butoxide is preferred, as it is easier and allows a higher concentration of dopant in the composite.

Combination of doping methods

In order to increase the titanium content in the CCCs, two of the methods described above were combined. First, the preform was doped by thermal decomposition of TBO (as described in 'Doping the carbon fibre preform by thermal decomposition of titanium butoxide' section). Then, the doped preform was densified with mesophase pitch doped with 10% TiC nanoparticles (see 'Doping the matrix precursor by adding TiC nanoparticles' section). As could be expected the resultant composites have a higher dopant content than that obtained using a single doping method (6.3 wt% Ti vs. 3.98 wt% obtained in CC–TD). The high titanium content of these materials is evident in the SEM micrographs shown in Fig. 5, where the dopant is well distributed in the whole composite. Although some larger agglomerates around fibre bundles are observed, the dopant is overall finely dispersed in the material (nanometric scale).

Conclusions

Densification of carbon fibre preforms with mesophase pitch doped with TiC nanoparticles proved to be a very successful method to manufacture Ti-doped CCCs with homogeneously and finely dispersed dopant.

Thermal decomposition of titanium butoxide on the carbon fibre preform followed by densification with undoped mesophase pitch was also found to be an easy and efficient method to developed Ti-doped CCCs. Although the dopant size is larger than in the previous method, it is possible to introduce higher amounts of dopant.

The combination of these two doping methods, first thermal decomposition of TBO on the preform followed by densification with TiC-doped mesophase, enabled to obtain doped CCCs with a higher concentration of dopant, up to 6.3 wt% Ti.

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