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TiO_2 and [TiO_2/β-SiC] microtubes prepared from an original process

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Abstract

Ceramic materials such as oxides and carbides with a controlled design were synthesized using an original pathway called reactive replica process. By this way, micrometric ceramic tubes keeping the morphology of the starting carbon source can be obtained. In our case, carbon fibres were coated by TiO_2 or a [SiO_2–TiO_2] mixed oxide both prepared by a sol–gel process. The [carbon/oxide] material was then further heat-treated at temperatures higher than 1000 °C to form the corresponding interfacial carbide (TiC) or mixed carbide (TiC–SiC). During the carbothermal reaction, a complete conversion of the oxide into the carbide is observed. After removal of the unreacted carbon, TiO_2 and [TiO_2-β-SiC] microtubes are obtained. The formation of the carbides tubes has been followed by several multi-scale characterization techniques (XRD, IR, SEM) as discussed in this paper.

Keywords: Carbides; Oxides; Sol–gel process; TiO_2; SiC

1. Introduction

Carbide ceramics such as SiC and TiC show a great interest for many industrial applications due to their multiple intrinsic properties. Especially, silicon carbide which is a high technology ceramic (density of 3210 kg m^{-3}) is used at high temperatures owing to its properties: high hardness (9 Mohs) and strength, low coefficient of thermal expansion (4×10^{-6}), high heat transfer characteristics and good resistance to oxidation due to the formation of a protective silica layer. Titanium carbide, i.e. TiC, well known for its high melting point (3064.85 °C), low density (4930 kg m^{-3}), high hardness (28–35 GPa), Young's modulus and good resistance to corrosion, is used in numerous industrial fields such as chemistry, mechanics and microelectronics. TiO_2 is widely used due to its stability toward photocorrosion and is low toxicity as a pigment in paints and cosmetics, a support in catalysis and in photocatalysis. For example, it was shown in few papers[1] that the degradation of the methylethylketone can be improved when TiO_2 is combined with a carbide such as SiC; this was attributed to an advantage intergrain coupling. For the main potential applications of ceramic materials, the possibility to prepare materials with a controlled size and shape and which display specific properties is of prime importance.

Among synthetic processes which have been developed to elaborate new types of ceramic materials; the Shape Memory Synthesis (SMS),[2,3] the replicating PU foams[4] and others alternatives routes[5–9] have been investigated.

Vix-Guterl and co-workers[10–13] have developed a new process based on a reactive replica technique to elaborate silicon carbide. Briefly, SiC of tubular morphology was prepared from carbon fibres covered by a silica layer prepared by a sol–gel route. The as-made [C/SiO_2] multimaterial was heated up to 1200 °C under argon flow in order to converse SiO_2 into SiC according to the following reaction:

$$SiO_{2(s)} + 3C_{(s)} \rightarrow SiC_{(s)} + 2CO_{(g)} \quad (1)$$

The idea was then to extent this process to the preparation of other ceramic thin tubes. As presented in this paper, the replica process was applied to prepare TiO_2 or (β-SiC–TiO_2) mixed ceramic tubes starting from a [carbon/oxide] material. The oxide (TiO_2) or mixed oxide (SiO_2–TiO_2) was obtained by a sol–gel process. The preparation of the TiO_2 tubes goes trough an intermediate step corresponding to the formation of titanium carbide according to the following reaction

$$TiO_{2(s)} + 3C_{(s)} \rightarrow TiC_{(s)} + 2CO_{(g)} \quad (2)$$

TiC is then oxidized in TiO_2 during the removal of the unreacted carbon by oxidation. This process allows to prepare thin

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TiO_2 tubes that could not be directly obtained by covering the carbon fibres by the TiO_2 sol.

The resulting tubes were characterized using different techniques such as X-Ray Diffraction (XRD), Scanning Electronic Microscopy (SEM) and Infra-Red spectroscopy (IR).

2. Experimental

2.1. Precursor materials

In this study, the carbon substrate corresponds to polyacrilonitrile-based carbon fibres. Prior to use, the fibres was cleaned of any organic substances by heating at 950 °C under an argon flow during 15 h. Reagent-grade titanium butoxide ($Ti(OBu^n)_4$) was purchased from Aldrich whereas tetraethoxysilane (TEOS), acetylacetone (acacH), ethanol and butanol were purchased from Acros and used without further purification. Hydrochloric acid (Aldrich, 37%) was used as catalyst.

2.2. Procedure

The preparation of TiO_2 and [TiO_2–SiO_2] oxides using the sol–gel process was described elsewhere.[14] Briefly, the TiO_2 sol is prepared according to the following procedure: acetylacetone diluted in butanol was added dropwise to a butanolic solution of ($Ti(OBu^n)_4$) under stirring. The stirring was kept for 30 min. The volume ratio is 1:6:2 for acacH:butanol:titanium butoxide, respectively. The homogenisation step was also used to substitute the butoxy groups by acetylacetone groups in order to control the hydrolysis rate of the titanium groups. In a second time, the hydrolysis was performed by adding a solution of HCl (pH = 1, 6) and ethanol (volume ratio 2:3) to the first preparation under magnetic stirring. The final solution was aged 30 min.

Regarding the SiO_2–TiO_2 sol–gel, a TEOS and ethanol (5:20) based solution was prepared and homogenised for half an hour. Then a HCl aqueous solution (pH = 1, 6) was added drop-by-drop to the first one. The resulting solution has been aged for 4 h. Finally an ultimate solution containing $Ti(OBu^n)_4$), butanol and acetylacetone with a controlled volume ratio equal to 1:3:1 was added dropwise to the silica sol under stirring. A mixed sol is obtained with an atomic composition of Si:Ti equal to 0.8:0.2. The sol was aged during 30 min before using. The [SiO_2–TiO_2] reference will be used in the paper to designate this mixed sol.

PAN-based carbon fibres were then covered by a TiO_2 or [SiO_2–TiO_2] layer deposited by using a dip-coating process. Briefly, the carbon fibres wound on a drum are pulled through the sol with a linear rate of 14 cm min^{-1} which corresponds to a residence time of ca. 5 s. After 30 min of drying at room temperature the [carbon/oxide(s)] materials obtained were placed in a quartz boat and treated under argon atmosphere at 950 °C to densify the oxide coatings.

The resulting samples were placed in a alumina crucible (previously carburised to avoid any reaction between crucible and the as-made materials) and introduced in a vertical furnace. The [carbon/oxide(s)] samples were thermal treated, following a heating rate of 2 °C min^{-1}, at 1000 °C (0.5 h) or at 1500 °C (3 h) under Ar with a flow rate equal to 60l h^{-1} and at atmospheric pressure. After reaction the furnace was cooled down to room temperature always under flowing argon. Finally a select treatment such as an oxidation at 700 °C under air is carried out to eliminate the unreacted carbon; tubular ceramics are consequently obtained.

2.3. Characterization

Infrared spectra of studied samples were obtained using a IFS-66 Bruker FT-IR spectrometer equipped with a KBr beam splitter and a DTGS detector. To be analysed, the samples were mixed with KBr and pressed to obtain disks. The spectra were taken in the absorption mode and recorded in the wavenumber range of 4000–400 cm^{-1} by addition of 100 scans and with a resolution of 4 cm^{-1}. Powder X-ray diffraction (XRD) analysis by a Philips X-PERT diffractometer using Cu Kα radiation (wavelength 1.54056 Å) was used to identify the crystal structure of titanium and silicon species. The equipment operated at 40 kV and 20 mA. The scan ranges from 20 to 80° with a step size of 0,05° and a time by step equal to 6 s. The samples were placed on a silicon support for crystallographic analysis. The morphology of the ceramic samples was investigated by scanning electron microscopy (SEM) (Model 525M Philips) equipped with energy dispersive spectrometers (EDS) which allows to determine an elemental mapping of the material. The weight variation of the [C/oxide(s)] during the carbothermal reaction was followed by thermogravimetric analysis (TGA) as a function of time and temperature.

3. Results and discussion

3.1. Characterization of the oxide coatings obtained by a sol–gel process

Characterizations of the oxide coatings were performed by FTIR analysis. The IR spectra of the TiO_2 and [TiO_2–SiO_2] oxides treated at 80 °C and 1000 °C under argon atmosphere are presented in Fig. 1A and B, respectively. At 80 °C, vibration bands relating to alkyls (*), acetyls (△) and diketones (◯) species (Table 1) are observed. These bands disappear completely after heat treatment at 1000 °C whereas only broad bands corresponding to M–O–M, M–O–M′ and M′–O–M′ (with M = Ti and M′ = Si) vibrations are observed. This suggests that TiO_2 and (TiO_2–SiO_2) were completely densified during the heat treatment. The IR spectrum of TiO_2 treated at 1000 °C (Fig. 1A) presents a broad band (□) covering the 550–800 cm^{-1} frequency range which is characteristic of a Ti–O–Ti distortion vibration.[14]

Table 1
Wavenumber of alkyls (*), acetyls (△) and diketones (◯) species

Symbol	Wavenumber (cm^{-1})	Nature
△	1030	$\nu_{(C-O)}$ in (Ti—O—CH_3)
*	1180	ν_{CH_3-CO}
*	1280	ν_{CH_2-CO}
*	1360	$\delta_{(-CH_3-)}$ in (CH_3—CO—)
*	1430	$\delta_{(-CH_2-)}$ in (—CH_2—CO—)
◯	1530–580	$\nu_{(C-C)}$ in β-diketone tied to Ti

On the contrary, three domains of frequencies are observed for the mixed oxide [SiO_2–TiO_2] heat-treated at the same temperature (Fig. 1B): (i) 550–800 cm^{-1} for the Ti–O–Ti vibration[14] (△), (ii) 1000–1200 cm^{-1} relating to the Si–O–Si antisymmetric vibration[12] (●), and (iii) 930 cm^{-1} corresponding to the frequency of the Ti–O–Si mixed link deformation.[14,15] The presence of this last band reflects the good homogeneity of the oxide coating.

3.2. Characterization of the [C/oxide(s)] materials at 1273 K

The XRD patterns of [C/TiO_2] and [C/(TiO_2–SiO_2)] materials heat-treated at 1000 °C during one and half an hour are presented in Fig. 2. Two cristalline species are observed: TiO_2 (symbol (*)) and carbon (symbol (¤)). The titanium oxide is characterized by 11 diffraction peaks which can be indexed according to a tetragonal structure corresponding to the rutile phase of TiO_2. The other principal polymorph of titanium oxide, i.e. anatase, is not observed in your case. For the [C/(TiO_2–SiO_2)] sample, a similar pattern is observed for which it must be noted that no peak characteristic of crystallized silica is detected. This

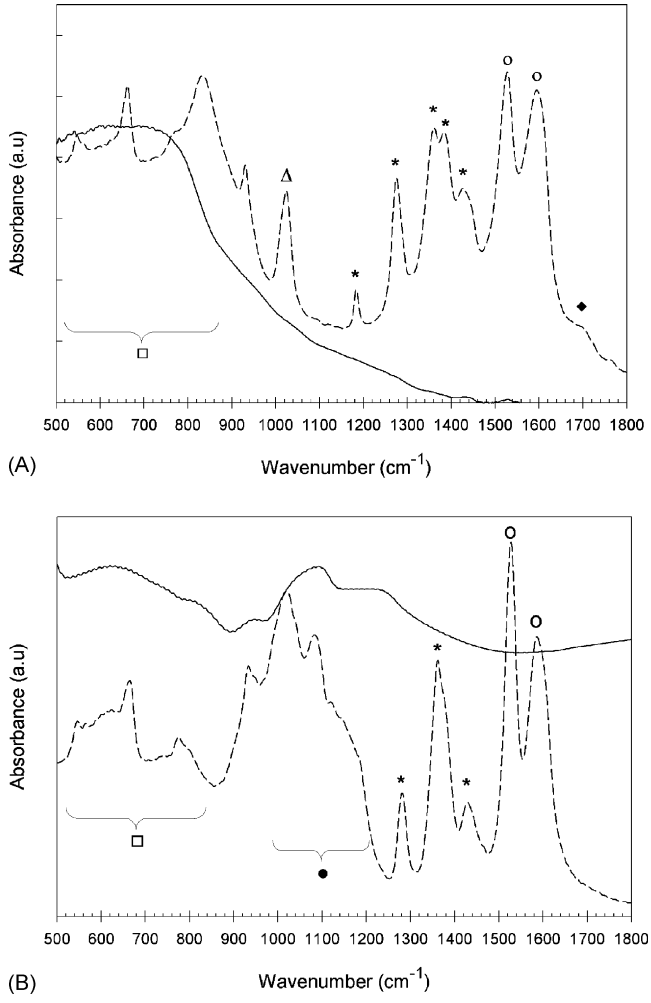

Fig. 1. FTIR spectra of (A) TiO_2 and (B) [TiO_2–SiO_2] oxides prepared by sol–gel process and heated at 80 °C (- - -) and 1000 °C (—).

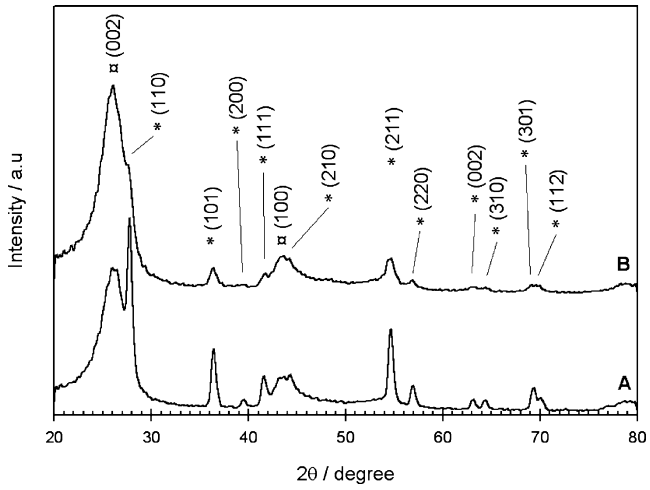

Fig. 2. XRD patterns of (A) [C/TiO_2] and (B) [C/(TiO_2–SiO_2)] materials heat-treated at 1000 °C during 1.5 h.

suggests that SiO_2 is in an amorphous state or that the amount of crystalline silica is lower than 5% by weight. Moreover, the intensities of the TiO_2 peaks are lower for the [C/mixed oxide] sample compared to [C/TiO_2]. The decrease of the peak intensities can be explained by a delay in the oxide titanium crystallisation due to the presence of SiO_2. In fact, SiO_2 forms *metal–oxygen–metal* mixed connections (metal: Si or Ti) which prevent the exclusive formation of TiO_2 and SiO_2 microdomains and consequently delay the crystallization temperature of the two oxides as already mentioned in the literature.[16]

From the XRD characterizations supplemented by thermogravimetric analysis, the composition of the [C/oxides] materials were determined. The following composition were found: 85 wt.% C, 15 wt.% TiO_2 for the [C/TiO_2] sample and 77 wt.% C, 6 wt.% TiO_2, 17 wt.% SiO_2 for the [C/(TiO_2–SiO_2)] material. In regard to reactions (1) and (2), the carbon is present in a large excess and a total conversion of the oxide can then be expected.

SEM images of the [C/TiO_2] and [C/TiO_2–SiO_2]) materials are reported in (Fig. 3A and B), respectively. Both coatings appear as relatively homogeneous as already deduced from the IR experiments. The presence of a longitudinal granular wires (Fig. 3A) suggests that the TiO_2 layer varies in thickness along the fibre axis. A craked layer is voluntarily presented in Fig. 3B in order to show that an oxide layer is actually deposited onto the carbon surface. As shown on this last image, a more homogeneous coating is obtained with the mixed oxide than with the single oxide such as TiO_2 (Fig. 3A).

3.3. High thermal treatment of the [C/oxides] samples

The starting materials, i.e. [C/oxides], were put into a carburised alumina reactor and heat-treated at 1500 °C for 3 h in a furnace under an argon flow at atmospheric pressure. The samples which display a grey-purple colour at the end of the treatment were analysed by XRD as shown in Fig. 4. As expected, TiC and β-SiC were formed during the carbothermal reaction. A low amount of α-SiC (hexagonal polytype of silicon carbide) is also detected as shown by the peak observed at $2\theta = 35°$ (shoul-

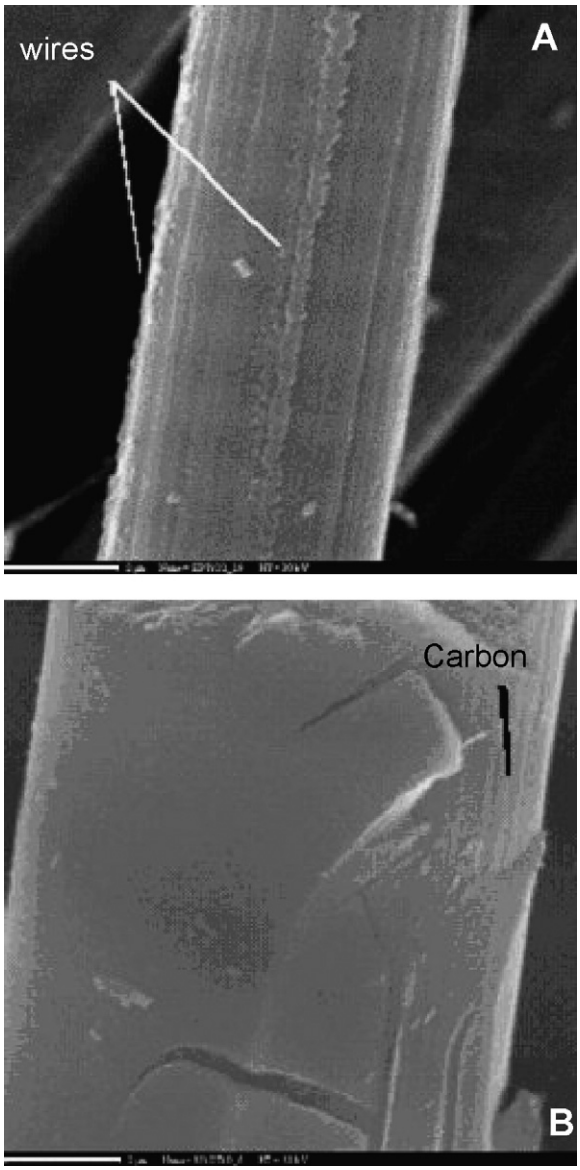

Fig. 3. SEM pictures of (A) [C/TiO_2] and (B) [C/(TiO_2–SiO_2)] materials treated at 1000 °C (1.5 h).

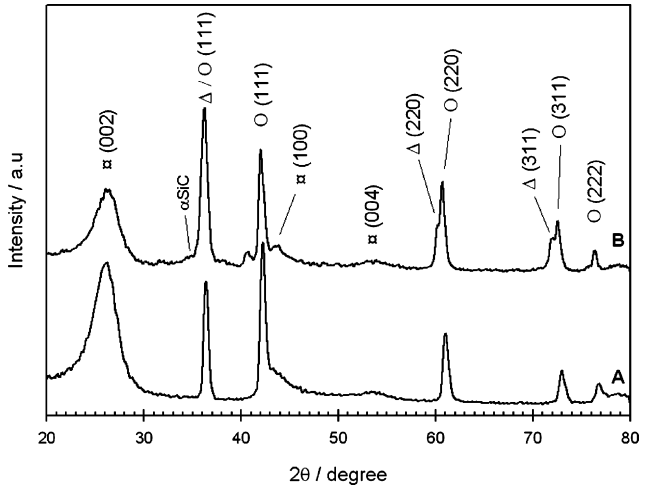

Fig. 4. XRD patterns of (A) [C/TiO_2] and (B) [C/(TiO_2–SiO_2] heated at 1500 °C (3 h). (¤) C; (◯) TiC; (Δ) β-SiC.

Table 2
XRD data of SiC and TiC in the [C/(SiC–TiC)] material

Species	hkl	d_{hkl} (Å)	a (Å)
β-SiC	111	2.51	4.348
	220	1.54	
	311	1.31	
TiC	111	2.48	4.319
	200	2.15	
	220	1.52	
	311	1.29	
	222	1.25	

der of the β-SiC peak). In the case of the mixed carbide in the (C/TiC-β-SiC) material, the approximate lattice parameter values for each carbide, a_{TiC} and a_{SiC}, were determined from Eqs. (3) and (4) (Bragg law) assuming face-centered cubic (fcc) structure as indicated by the JCPDS cards no. 06-0614 and 01-1119, respectively.

$$\frac{1}{d^2} = \frac{1}{a^2}(h^2 + k^2 + l^2) \tag{3}$$

$$\lambda = 2d_{hkl}\sin\theta_{hkl} \tag{4}$$

All the data are reported in Table 2. The lattice parameters calculated for β-SiC and TiC are in good agreement with the literature. Note that no peak characteristic of a mixed carbide such as Ti_xSi_yC was detected on the diffractogramm corresponding of the heat-treatment of [C/(TiO_2/SiO_2)] sample.

According to the XRD analysis, it can be concluded that the heat treatment of the [C/TiO_2] material leads to the formation of TiC according to reaction (2):

$$TiO_{2(s)} + 3C_{(s)} \rightarrow TiC_{(s)} + 2CO_{(g)} \tag{2}$$

whereas the heat treatment of the [C/(TiO_2–SiO_2)] material leads to the formation of a mixed carbide constituted of SiC and TiC. In regard to our experimental results, the following reaction can be proposed (reaction (5)):

$$TiO_{2(s)} + SiO_{2(s)} + 6C_{(s)} \rightarrow TiC_{(s)} + SiC_{(s)} + 4CO_{(g)} \tag{5}$$

By following the weight variation of the sample during the heat treatment by thermogravimetric analysis, the degree of conversion (α and α') of the oxide into the carbide can be computed. α is the degree of conversion of TiO_2 into TiC according reaction (2) whereas α' corresponds to the degree of conversion of the mixed oxide into the mixed carbide according to reaction (5). α and α'can be estimated according to the following equation:

$$\alpha, \alpha' = \frac{\Delta m_{\text{exp.}}}{\Delta m_{th.}} \tag{6}$$

where $\Delta m_{\text{exp.}}$ represents the experimental weight loss of the sample measured by TGA during the heat treatment and $\Delta m_{\text{th.}}$ is the theoretical weight loss assuming that the overall reaction occurs according reactions (2) (α) or (5) (α').[17] The values of α and/or α' lie between 0 (no conversion) and 1 (total conversion). In our experimental conditions, the α and α' values are equal to 0.94 and 0.97 for [C/TiO_2] and [C/(TiO_2–SiO_2)], respectively

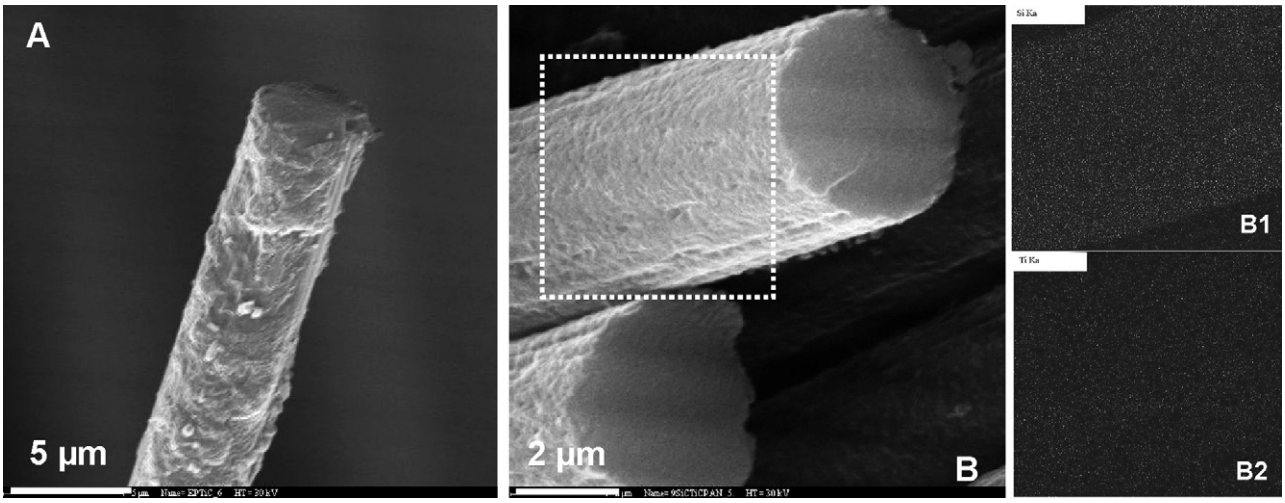

Fig. 5. SEM micrographs of (A) [C/TiC] ($\alpha = 0.94$) and (B) [C/(TiC-β-SiC)] ($\alpha' = 0.97$).

indicating that an almost complete conversion of the oxide into the carbide takes place.

SEM views of the carbide coatings obtained are shown in Fig. 5(A) and (B). The TiC coating (Fig. 5A), seems to be rougher than the [TiC-β-SiC] mixed carbides coating (Fig. 5B). The elemental mapping performed on the TiC coating (not presented here) indicates that the titanium is homogeneously distributed in the coating arounding the carbon fibre. As for the starting TiO_2 layer (see Fig. 3), the resulting carbide coating varies in thickness along the carbon fibre axis. On the contrary, the [TiC-β-SiC] coating (Fig. 5B) displays an homogeneous appearance with few disparities and presents a 'cauliflower' morphology close to the one observed with a SiC-based coating as shown in previous works.[11–13] This is not surprising since the mixed carbide is constituted of ∼60 wt.% of SiC. The composition by weight of the mixed carbide was determined by computation from the initial composition of the oxide layer and knowing that the degree of conversion (α') is close to 1.

Electron dispersive spectroscopy (EDX) and elemental mapping analysis (Figs. 5B1 and B2 issued from Picture 5B: dot lined zone) underline that the Si and Ti elements are intimately mixed in the TiC-β-SiC coating; no isolated TiC and/or β-SiC microdomains were detected. This suggests that both β-SiC and TiC carbides are formed in the same grain.

3.4. Formation of the tubular ceramic materials

To obtain the ceramic tubes, the [C/TiC] and [C/β-SiC–TiC] samples were oxidized in an air flow at 700 °C during 2 h in order to remove the unreacted carbon. After oxidation, the solid recovered was analysed by XRD. The patterns obtained are presented in Fig. 6A and B. The peaks in Fig. 6A correspond to the TiO_2 rutile phase; no TiO_2 anatase phase was detected. The peaks in Fig. 6B are attributed to TiO_2 (*) and β-SiC (Δ). It must be noted that the peaks related to TiC disappeared after the treatment in air due to the oxidation of TiC into TiO_2 that occurs at a lower temperature than the carbon oxidation.[18] It was experimentally verified that TiC oxidises at temperatures as low as 350 °C. TiC is oxidized into TiO_2 according to the following reaction:

$$TiC_{(s)} + 3/2O_{2(g)} \rightarrow TiO_{2(s)} + CO_{(g)} \quad (8)$$

On the contrary, the oxidation of SiC into SiO_2 is negligible in our experimental conditions as shown in previous papers.[11,13]

Therefore, TiO_2 and [TiO_2-β-SiC] tubes are obtained from the [C/TiC] and [C/TiC-β-SiC] materials after the removal of the unreacted carbon.

SEM views of the TiO_2 and [TiO_2-β-SiC] tubes are shown in Fig. 7. Tubular micrometrics tubes were obtained which keep the morphology of the starting carbon source. The fact that the morphology of the initial carbon can be transposed to the final ceramic material confirm that the oxide(s) coating was uniformly deposited at the onset of the carbothermal reaction. Some morphology characteristics of the tubes obtained are given in Table 3.

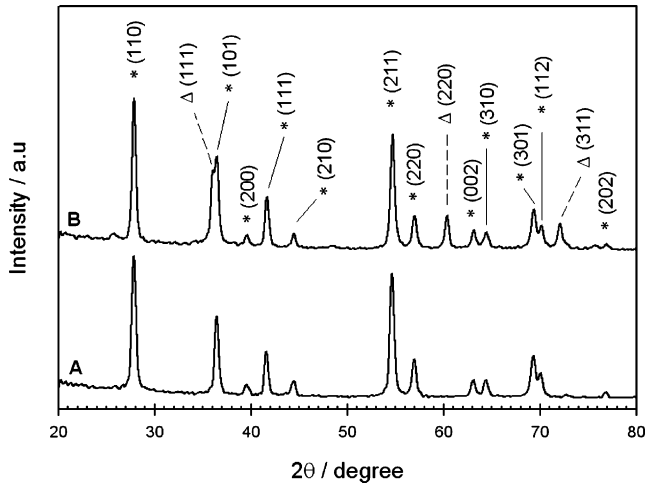

Fig. 6. XRD patterns of (A) [C/TiC] and (B) [C/(TiC-β-SiC] heated at 700 °C under air. (*) TiO_2 and (Δ) β-SiC.

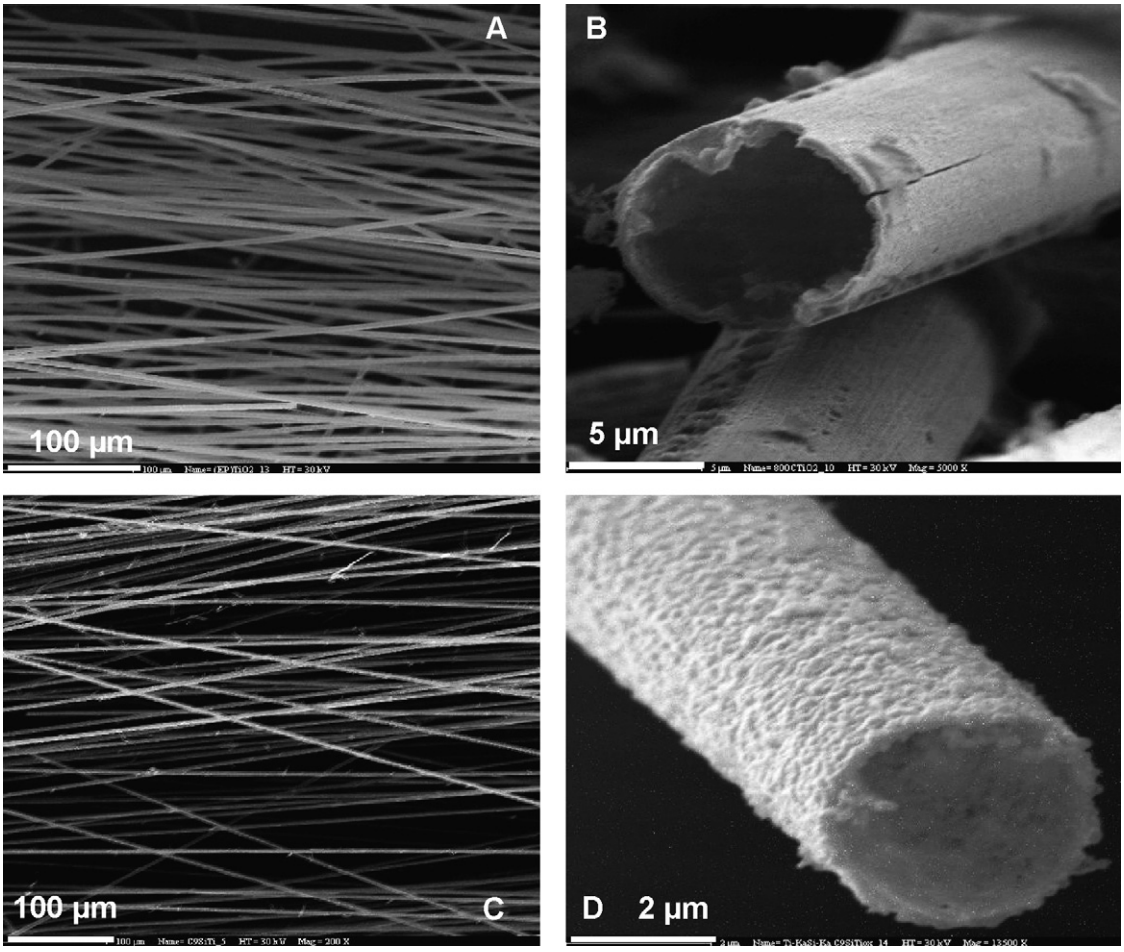

Fig. 7. SEM micrographs of tubular (A and B) TiO_2 and (C and D) [TiO_2-β-SiC] materials.

Table 3
Dimensional parameters of TiO_2 and [TiO_2-β-SiC] tubes

	L (μm)	Ø (μm)	e (μm)
TiO_2	500	6–8	0.15 ± 0.05
[TiO_2/β-SiC]	700	4–5	0.15 ± 0.02

L: length, Ø: internal diameter, and e: thick.

4. Conclusion

Tubular ceramic tubes can be prepared from carbon fibres by a non-conventional pathway based on a reactive replica technique. By this way, thin tubes of TiO_2 or [TiO_2-β-SiC] which keep the morphology of the carbon source can be obtained. This synthesis pathway requires three steps: (a) the deposit on the carbon fibre of an oxide layer (TiO_2 or a mixed oxide SiO_2–TiO_2) prepared by a sol–gel process, (b) the heat treatment above 1000 °C under an argon flow at atmospheric pressure to form the carbide or the mixed carbide by reaction between the carbon and the oxide, and (c) the removal of the unreacted carbon by oxidation.

The heat treatment of the [C/SiO_2–TiO_2] leads to the formation of a mixed carbide coating in which β-SiC and TiC are intimately mixed rather than to the formation of a mixed carbide such as Ti_xSi_yC. In view of the characterization results, the reaction proposed to explain the formation of the mixed carbide is the following (5):

$$TiO_{2(s)} + SiO_{2(s)} + 6C_{(s)} \rightarrow TiC_{(s)} + SiC_{(s)} + 4CO_{(g)} \quad (5)$$

TiO_2 is then selectively forms during the carbon removal due to the inertness of the β-SiC during the oxidation. At the final, TiO_2 and [TiO_2-β-SiC] tubes of micrometric dimension are obtained. It must be noted that similar TiO_2 tubes could not be obtained by a simple deposit of a TiO_2 sol on the carbon surface. In view of the results obtained, we can expected to prepare TiC tubes if the stoechiometry of the initial precursors can be controlled, i.e. if the ratio between the carbon and the oxide(s) (TiO_2 or TiO_2–SiO_2) can be adjusted so that the totality of the carbon is consumed during the carbothermal reaction. That supposes also that the thickness of the oxide deposited must be strictly controlled. The reactive replica process allows to prepare ceramic materials with a tailored shape and based on one type of carbide or a mixture of carbides. This leads to materials which can be potentially interesting in various fields of applications (anti-oxidation coating, photocatalytic and catalytic applications . . .).

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