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SiC Material Produced by Carbothermal Reduction of a Freeze Gel Silica-carbon Artefact

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Abstract

A carbon–silica artefact was produced by infiltration of phenolic resin into the macroporous texture of a silica sample followed by subsequent carbonisation. The silica material was manufactured using an original sol–gel method. This work reports on the conversion into SiC of the silica–carbon artefact heat-treated up to 1550°C under different gaseous environments. The extent of the carbothermal reduction was followed by thermogravimetric analysis, X-ray diffraction, gas adsorption and scanning electron microscopy. Experiment results demonstrate that a β-SiC artefact with a shape similar to the starting material is obtained by heat treatment of the carbon-silica artefact above 1470°C. Quantitative formation of SiC is observed by lowering the partial pressure of CO in the reactor. Moreover, the as-obtained SiC material exhibits a granular aspect associated with a significant specific surface area. In a more general way, the procedure described in this work to obtain the SiC material may be a promising route for designing ceramic materials with specific properties.

Keywords: SiC, carbon, SiO_2, sol–gel process, carbothermal reduction.

1 Introduction

The production of ceramic bodies is often limited by the processing conditions of conventional methods (e.g. chemical vapour deposition, hot-pressing and sintering processes). As a consequence, alternative procedures which utilize sol–gel technology have been explored in recent years as possible means of producing an array of low cost, net-shape ceramic materials.[1–3] In particular, a modified sol–gel processing technique which will be referred to as freeze gelation or freeze casting has been recently developed.[4,5] The principal advantages of this process are a low sintering temperature, a low level of shrinkage (typically less than 1%) associated with the ability of designing a large variety of shapes for the desired material. Moreover, freeze gelation lends itself to further densification processes due to the inherent porous nature of the material it produces. As an example, the freeze gelation route allows the manufacturing of carbon-silica artefact constituted of porous freeze gel silica pellets infiltrated with carbon.

The manufacturing of silica-carbon artefact is of great interest since it may offer the possibility to prepare SiC materials. In fact, we have shown in previous work that carbon fibres covered with a silica layer produced by a sol–gel method may be a promising route for obtaining fine tubes of SiC after removal of the remaining carbon by gasification.[6] It appears that in a more general way, SiC materials of desired design may be prepared by an appropriate selection of the silica-carbon artefact. Moreover, it would be also of great interest to control the texture of the produced material. Therefore, in the present work a process has been developed whereby a silica–carbon artefact prepared by freeze gelation is expected to be transformed into a SiC body by carbothermal reaction of silica and carbon. The overall reaction between carbon and silica is:[7,8]

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

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In fact reaction (1) proceeds via two stages in which a gaseous intermediate, silicon monoxide (SiO) is formed.[9–13]

The first step consists of a solid–solid or solid–liquid type of reaction between carbon and silica leading to the formation of gaseous silicon monoxide (SiO) and carbon monoxide:

$$SiO_{2(s,l)} + C_{(s)} \leftrightarrow SiO_{(g)} + CO_{(g)} \qquad (2)$$

In a second step, SiO reacts further with carbon according to the following gas–solid reaction:

$$SiO_{(g)} + 2C_{(s)} \leftrightarrow SiC_{(s)} + CO_{(g)} \qquad (3)$$

The equilibrium conditions of reactions (2) and (3) will depend on the temperature and on the partial pressure of SiO, p_{SiO}, and CO, p_{CO}, according to thermodynamic calculations detailed elsewhere.[6] For instance, SiC is formed above 1220 °C for a total pressure ($p_{SiO} + p_{CO}$) equal to 1 kPa. It must be noted that the temperature of formation of SiC decreases as the total pressure is lowered.

The purpose of this work is (i) to demonstrate the possibility of producing a SiC material of desired design starting from porous freeze gel silica pellets infiltrated with carbon and (ii) to study the carbothermal conversion into SiC by heat treatment in argon of the carbon–silica artefact. In particular, the influence of the partial pressure of CO on the yield, the morphology and the structure of the as-obtained SiC is investigated.

2 Experimental

2.1 Silica–carbon artefact

Silica discs (30 mm in diameter, 3 mm in thickness) were prepared from a 2:1 mixture of colloidal silica (mean particle size equal to 25 nm) and quartz powder (mean particle size equal to 1 μm) using the freeze gel procedure described elsewhere.[4] When a filler is present, the material has a significantly reduced pore volume fraction and a much more rigid structure is formed with the silica acting as a binder to the larger filler particles. Furthermore, the prepared silica sol is rapidly frozen to a subzero temperature during which there is a small volume increase caused by the formation of ice crystals as the water freezes. A gel is then formed in the regions between the ice crystals. On warming back to room temperature and drying off the water, the silica solid exhibits a macroporous structure due to the large regions (e.g. 10 μm in size) previously occupied by ice crystals. At this stage, the volume fraction of pores in the disc is about 0·6. The porous freeze gel silica discs are further infiltrated with a phenolic resin (BP Cellobond J 2027) using a vacuum/pressure infiltration apparatus. The resin impregnated silica discs were then heated overnight at 60 °C to cure the resin. At this stage, about 90% in volume of the pores are filled with the resin. The silica/resin discs were then heated under a flow of argon in an horizontal tube furnace at 850 °C and held for 1 h at the final temperature to carbonise the resin using a heating rate which does not exceed 40 °C h^{-1} to avoid disruption of the material. The average composition of the as-obtained carbon–silica artefact is equal to 27% carbon, 49% colloidal silica and 24% quartz by weight.

2.2 Heat treatment in argon

The as-prepared silica–carbon artefact is then heated in argon at 1550 °C. The used experimental apparatus has been described in detail elsewhere.[14] The starting material (0·20 g) is placed in an alumina crucible and introduced into an alumina tube. The sample holder in alumina was previously carburized in order to avoid any reaction with the carbon contained in the disc. After introducing argon in the system, the sample is then heated at 1550 °C with a linear rate of 600 °C h^{-1} up to 1200 °C and from 1200 to 1550 °C with a rate equal to 300 °C h. The reactor was held 1 h^{-1} at the final temperature. Two types of heat treatment were considered. The first one was carried out in a continuous flow of argon equal to 20 l h^{-1} (dynamic condition). In the second type of treatment, the carbothermal reaction was conducted in a closed system with a starting pressure of argon equal to 70 kPa (static condition). The weight change of the sample during heat treatment was measured gravimetrically using a microbalance (Mettler AE240). The treated samples were recovered and characterized after cooling down in argon.

2.3 Characterization of materials

The amounts of unreacted silica and carbon in the material obtained after heat treatment were determined gravimetrically by selective dissolution in HF solution (40% by vol.) and by gasification in air at 800 °C, respectively. Thereafter, the solid left is analyzed by X-ray diffraction to determine the crystalline phases formed during the heat treatment. The morphological changes of the starting material due to the transformation of the carbon–silica material into SiC are observed by scanning electron microscopy using a Philips SEM 525M apparatus. The samples were pasted on a stub and then metallized with gold. Finally, the specific surface areas are measured on the starting and final materials by krypton adsorption at −196 °C using the B.E.T. equation.

3 Results and discussion

Whatever the experimental operating conditions (static or dynamic), SiC of cubic type (β-SiC) is formed during the heat treatment of the silica-carbon artefact as confirmed by XRD analysis. As an example, the XRD pattern of the heat-treated carbon-silica artefact is shown in Fig. 1. The peaks corresponding to silica and silicon carbide can be clearly seen. One additional line at $2\theta = 33{\cdot}82$ ($d = 0{\cdot}265$ nm) is detected near the (111) line of the cubic structure of the silicon carbide at $2\theta = 35{\cdot}64$ ($d_{111} = 0{\cdot}251$ nm) which is characteristic of hexagonal polytypes. The sharp peak at $2\theta = 21.99$ ($d = 0{\cdot}404$ nm) results from the crystallisation of the unreacted amorphous silica into cristobalite. Observations by scanning electron microscopy (SEM) of the carbon-silica artefact and of the as-obtained SiC material after removal of the remaining silica and carbon were made. SEM views of the starting material (Fig. 2) confirm that nearly all macropore voids of the silica pellet are filled by the carbonised resin leading to a well developed carbon-silica interface. Micrographs of the obtained SiC samples reveal that the texture of the starting artefact is preserved during the heat treatment suggesting that their texture originates from carbon located in the macropore voids of the silica disc. In the case of dynamic treatment [Fig. 3(a)], the SiC samples exhibits a granular aspect, the size of the grains varying from some μm to more than 20 μm. Some of the observed cavities result from the removal of the remaining silica after the heat treatment. When the carbothermal reaction is conducted in static operating conditions, the surface of the disc is covered by needle-like whiskers (diameter less than 1 μm in size) which are randomly deposited as shown in Fig. 3(b) whereas almost no whiskers were found in the inner part of the sample. The whiskers consist mainly of SiC as confirmed by electron dispersive spectroscopy (EDS). The origin of the SiC whiskers at the surface of the disc will be discussed in the next section. Measurements of the specific surface area of the investigated materials were made. The specific surface area of the resulting SiC material is close to $35\,\mathrm{m^2\,g^{-1}}$ which is far superior to the value for the silica sample ($0{\cdot}3\,\mathrm{m^2\,g^{-1}}$). In view of the granular aspect of the obtained SiC material, it may be assumed that the measured surface area corresponds to pores and/or microcracks inside the material which are not seen by SEM. Moreover, it appears that the value of the specific surface area does not depend on the pressure of CO in the reactor.

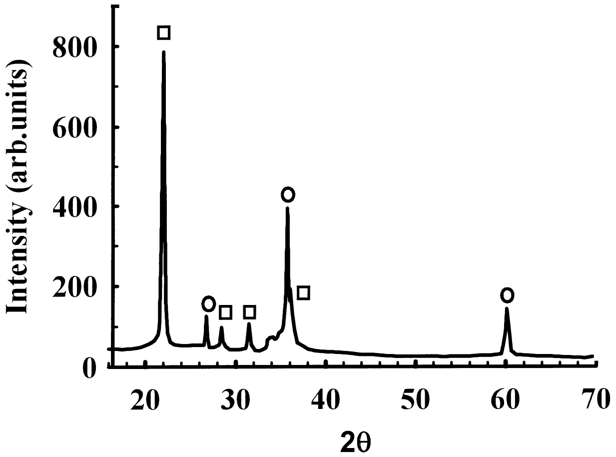

Fig. 1. XRD pattern of the carbon–silica artefact after heat treatment at 1550 °C: (□) SiO_2 peaks; (O) SiC peaks.

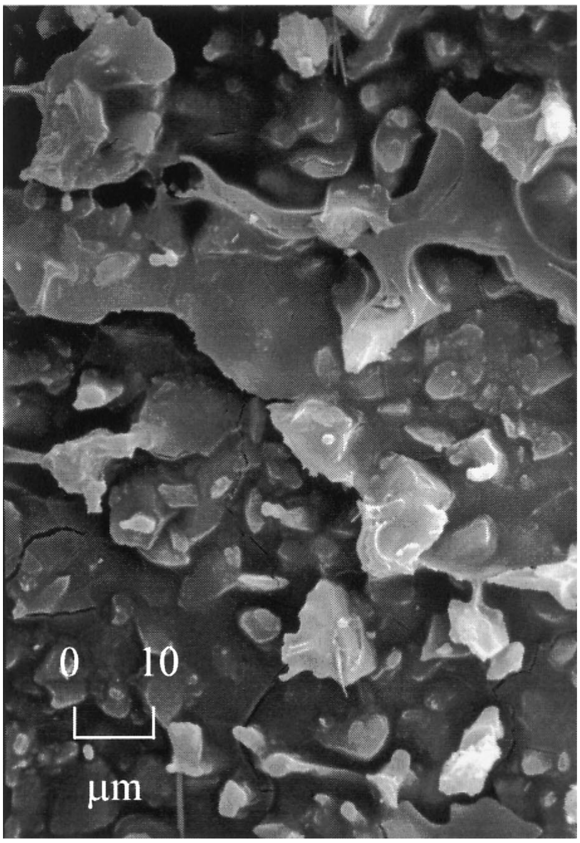

Fig. 2. SEM view of C/SiO_2 material.

3.1 Reactivity of the carbon–silica artefact

3.1.1 Heat treatment in static conditions

The amount of produced SiC is estimated gravimetrically after removal of the remaining silica and carbon. Since the amount of carbon in the disc is far smaller that the amount of silica, the formation of SiC will be determined in respect to the consumption of carbon. It has been observed that in the static condition where the partial pressure of CO is estimated to reach 1 kPa, the fraction of unreacted carbon, *f*, after heat treatment at 1550 °C followed by an isothermal plateau is equal to 0·37 (see Table 1). This value indicates that only

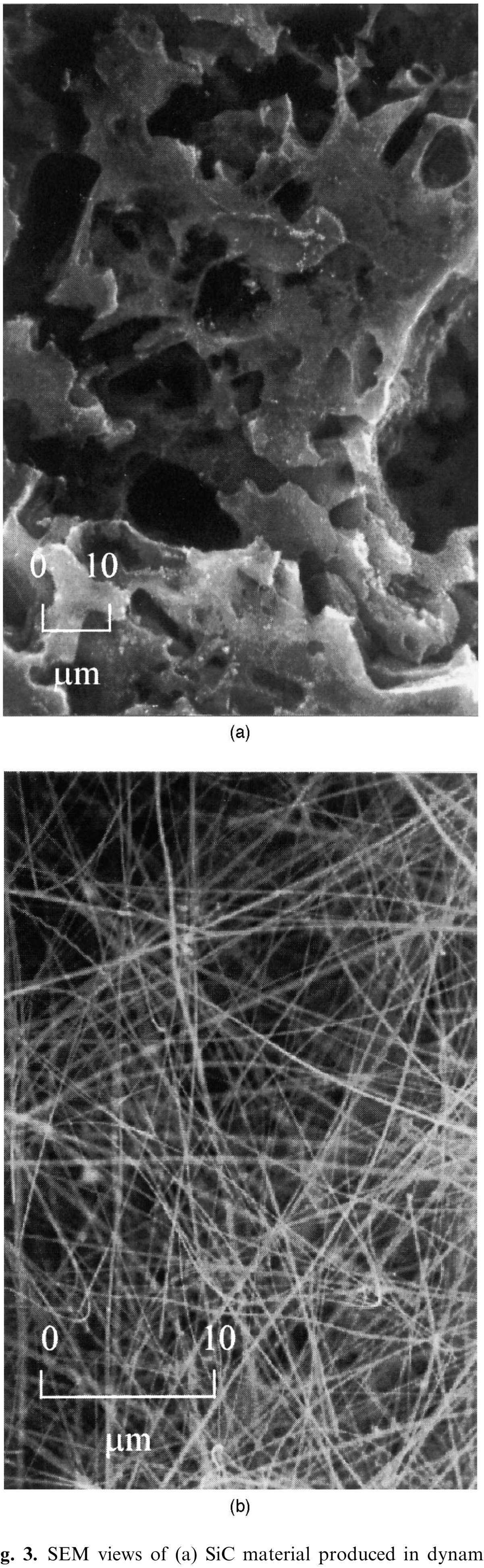

Fig. 3. SEM views of (a) SiC material produced in dynamic conditions; (b) SiC material produced in static conditions.

a little more than half of the carbon has reacted with silica. This fact may be attributed to the accumulation of CO formed in reactions (2) and (3) which would hinder the formation of gaseous species in reaction (2) and consequently the rate of formation of SiC will be drastically reduced. Furthermore, the yield of SiC, τ, defined as the ratio of the amount of C converted into SiC according to reaction (1) to the total amount of consumed carbon is also computed. In static condition, τ is equal to 0·80 (see Table 1) suggesting that about 20% of the initial amount of carbon is consumed without giving SiC. However, it appears from the mass balance that the carbon which has reacted without SiC formation has lead to consumption of an equivalent fraction of silica, consistent with the stoichiometry shown in reaction (2). Hence, a fraction of SiO resulting from reaction (2) does not react further with carbon (reaction 3) but probably escapes from the sample macropores. Moreover, a transient accumulation of SiO and CO in the reactor explain the presence of the SiC whiskers at the surface of the sample as already mentioned in the literature.[6,8,13,15] Indeed, SiO may further react with CO at the external surface of the samples according to the following reaction:

$$\mathrm{SiO_{(g)} + 3CO_{(g)} \leftrightarrow SiC_{(s)} + 2CO_{2(g)}} \qquad (4)$$

Reaction (4) favours the growth of SiC whiskers which are similar to those obtained by chemical vapour deposition with SiO and CO as the primary reactants.[16] Since an significant amount of carbon remains in the material, the produced CO_2 may be scavenged by the Boudouard reaction:

$$\mathrm{CO_2 + C \rightarrow 2CO} \qquad (5)$$

However, it must be noted that the amount of whiskers is quite small in comparison to the amount of bulk SiC as confirmed by SEM. This observation is consistent with a value of τ lower than 1.

3.1.2 Heat treatment in dynamic conditions

As an example, the weight changes in dynamic conditions of the silica-carbon artefact and of the carbon resin as a function of treatment time are shown in Fig. 4 along with the corresponding

Table 1. Fraction of unreacted carbon, *f*, and yield of SiC, τ, as a function of the operating conditions

Operating condition of furnace	*Fraction of unreacted carbon* (f)	*Yield of SiC* (τ)
Dynamic	0.12	0.93
Static	0.37	0.80

temperature profile (heating and isothermal plateau). In dynamic conditions, the partial pressure of CO is lower than 0·1 kPa. It can be seen that the carbothermal reaction becomes significant at about 1370 °C whereas the weight loss measured below this temperature may be mainly attributed to the fraction of carbon in the disc being pyrolysed without reaction with silica. It must be noted that the pyrolysis of the carbon resin is completed at the onset of the carbothermal reaction and that the carbon weight loss due to devolatilization does not exceed 4% of the initial amount of carbon contained in the starting material. At the end of the experiment, (*f*) and (*t*) are estimated gravimetrically. The obtained values are 0·12 and 0·93, respectively, indicating that nearly all carbon of the starting carbon–silica artefact has been converted into SiC according to (1). In this case, the amount of produced SiC and consequently the degree of conversion into SiC (ξ) may be deduced from the weight loss curve of the artefact as reported in Fig. 5 as a function of treatment time. Comparison of Figs 4 and 5 shows that the rate of the carbothermal reaction reaches a maximum about 15 min after the onset of the isothermal plateau at 1550 °C. At that stage, ξ is equal to 0·55 suggesting that slightly more than half of the total amount of SiC has already been formed when reaching this point. After 1 h of isothermal treatment, ξ is equal to 0·86 which corresponds to a value of *f* close to 0·14. Hence, it can be seen that this value obtained by continuous measurement is in reasonable agreement with the one estimated gravimetrically ($f = 0{\cdot}12$) indicating that the weight loss observed during heat treatment actually corresponds to the formation of SiC. Further experiments were carried out with increasing time of isothermal treatment at 1550 °C. The amount of formed SiC associated with the degree of conversion (ξ) are shown in Table 2. It can be seen that the operating conditions exert a quite significant effect since the amount of formed SiC increases with the time of the isothermal treatment. A degree of conversion close to 1 is reached for a treatment time of 3 h indicating that the amount of SiC is then close to the stoichiometric value. For a longer time of isothermal treatment at 1550 °C, a slight decrease of the amount of silicon carbide is found which may be due to its reaction with the remaining oxide since nearly all the carbon has been consumed:

$$\mathrm{SiC} + 2\mathrm{SiO_2} \leftrightarrow 3\mathrm{SiO} + \mathrm{CO} \qquad (6)$$

It must be also noted that for treatment time higher than 3 h, the presence of a few SiC whiskers on the surface of the disc was revealed by SEM examination resulting from the reaction between SiO and CO as already mentioned in the previous section. However, it can be seen in Table 2 that the specific surface of the final SiC material is not significantly affected by the isothermal treatment time suggesting that the reaction of SiC with the remaining SiO_2 does not modify the texture of the as-obtained sample.

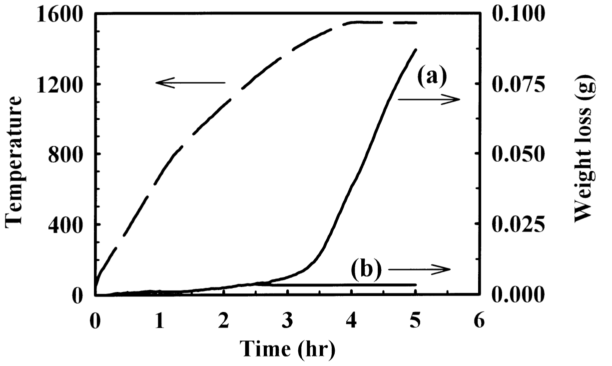

Fig. 4. (—) weight losses as a function of treatment time under dynamic conditions of (a) carbon-silica sample and (b) carbon resin; (- - -) temperature profile of the reactor.

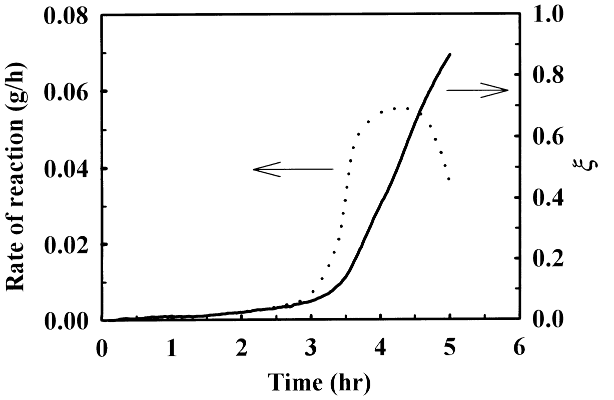

Fig. 5. (...) Rate of carbothermal reduction and (-) degree of conversion as a function of treatment time under dynamic conditions.

Table 2. Amount of SiC, degree of conversion and specific surface area of SiC as a function of the isothermal treatment time under dynamic conditions

Isothermal treatment time (h)	*SiC (mg)/(100 mg starting material)*	*Degree of conversion* (ξ)	*Specific surface area* ($m^2 g^{-1}$)
0	18	0·53	—
1	29	0·86	32
3	34	1	28
6	29	0·85	28

4 Conclusion

This work demonstrates the possibility of obtaining macroporous net-shape silicon carbide material by carbothermal reduction of a carbon–silica artefact prepared by an original sol-gel process. Infiltration of phenolic resin into the macroporous voids of a freeze gel silica disc followed by subsequent carbonization produces the starting carbon–silica artefact. Experimental results establish that the kinetics of the carbothermal reaction of the artefact and the morphology of the as-obtained material are governed by the experimental conditions and in particular the partial pressure of CO. The carbothermal reduction of the starting material which is a complex multistep reaction involving the formation of volatile suboxide, SiO, leads to a quantitative formation of SiC provided there is a rather low partial pressure of CO during the heat treatment. It has been shown that the conversion of carbon into SiC is more effective in dynamic conditions ($p_{CO} < 0{\cdot}1\ kPa$) than in static conditions ($p_{CO} = 0{\cdot}1\ kPa$) for which a significant fraction of carbon remains unreacted at the end of the experiment. This fact is linked to too a high pressure of CO in the reactor which tends to suppress reaction (2) and consequently also affects the yield of SiC by inhibiting the reaction of SiO with C (reaction 3). As a consequence, SiC whiskers may be formed at the surface of the sample due to reaction of SiO diffusing outside of the porosity of the material with CO (reaction 4). Interestingly, SEM views clearly show that the artefact does not lose its morphology during the carbothermal reaction. Moreover, the as-obtained silicon carbide has a significant specific surface area. This property may be very interesting in various fields of application.

The fabrication of this new material on the basis of solid precursors may permits the design of advanced ceramic material with specific properties.

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