

ENHANCED SiC/SiC COMPOSITES PROCESSED BY REACTIVE MELT INFILTRATION FOR HIGH TEMPERATURE APPLICATIONS

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Abstract

Silicon carbide (SiC) fibers coated with a thin PyC-based interphase and a SiC consolidation in a silicon carbide matrix have shown excellent promises in replacing nickel and cobalt-based alloys for high-temperature applications [1]. The fabrication process of this composite is composed of two main steps. First, a fiber preform is impregnated with a SiC-based slurry, and then it is infiltrated with molten silicon. Reactive chemical species, like carbon, were introduced into the SiC slurry to trap free silicon into SiC. In particular, the process implies well dispersed suspensions. For the stabilization of SiC and SiC-C slurries, the optimized conditions of stability are obtained for the lowest values of zeta-potential and viscosity. The aim of this study is to figure out the influence of carbon on the densification of the material by reactive melt infiltration.

1 Introduction

Decreasing noise and NO_x emissions due to air transport implies to increase the working temperature of engines in regard to common nickel and cobalt-based super alloys uses. To reach this goal, the integration of ceramic matrix composites (CMC) like SiC_f/SiC_m may be done in the hot part of engines. Continuous fiber-reinforced CMCs offer low density, high strength and toughness, and have the potential of delivering increased high-temperature performance with a better environmental stability to handle the harsh combustion environments encountered in the hot part of engines [1]. However, their properties have to be enhanced to resist to mechanical loading at high temperature (T > 1400°C) in an oxidizing moist environment.

To be equivalent to super alloys, their thermal conductivity needs to be at a level as high as these latter. Melt infiltrated (MI) SiC/SiC composites are particularly attractive for high temperature applications (gas turbines) because of their high thermal conductivity, excellent thermal shock resistance, creep resistance, and oxidation resistance compared to other CMCs [2]. In the MI process (or RMI process in case of a reactive infiltration) a porous SiC fiber preform is coated with a thin PyC-based interphase and a SiC consolidation by chemical vapor infiltration. Remaining matrix porosity is filled with SiC particles at room temperature and then infiltrated with molten silicon over 1410°C. Silicon rises by capillary forces in the pore network leading to a SiC+Si matrix characterized by almost no open residual porosity and hence a high thermal conductivity. A major disadvantage of the MI process is the presence of residual free silicon, limiting the working temperature to 1400°C. To reduce free

silicon, reactive chemical species, like carbon, can be introduced into the matrix to trap silicon into SiC. The process implies the stabilization of a SiC-based reference slurry. The introduction of carbon into this latter must not perturb the stability of the new slurry. To avoid the choking-off and optimize the final densification with molten silicon, ratio of carbon introduced into the SiC-slurry has to be limited. Indeed, in presence of carbon, silicon instantly reacts with this latter to form SiC: if the quantity of carbon is too high, a SiC-barrier is formed and diffusion of silicon is blocked. In this context, the objective of the present study was to work on the matrix by tailoring its chemical composition to reduce the fraction of free silicon. Thus, in a first step, the stability of SiC and SiC-C-based slurries was optimized. In a second step, materials based on a SiC-fiber preform were prepared by impregnation with these suspensions and by infiltration with molten silicon.

2 Experimental procedures

2.1 Materials

The adjustment of the process for developing dense composites by RMI was carried out with low cost SiC fibers (Nicalon, Nippon Carbon, Japan).

The silicon carbide used to prepare the aqueous slurry is a commercially available powder (HC Starck, Germany). Figure 1 shows the grain size distribution of SiC powder, and Table 1 shows its physical and chemical characteristics. The addition of Tetramethyl ammonium hydroxide (TMAH) as dispersant ensures a proper dispersability and the fluidity of the suspension [3]. A product 25 wt% watered down was used in this study (Sigma Aldrich, France).

Carbon black powder, manufactured by Lehvoss (Germany) is used to prepare the SiC and C-based slurry, with addition of a dispersant (BYK, Germany) to make these carbon particles hydrophilic. The final densification with molten silicon is carried out using silicon lumps (Sigma Aldrich, France), or silicon powder (HC Starck, Germany).

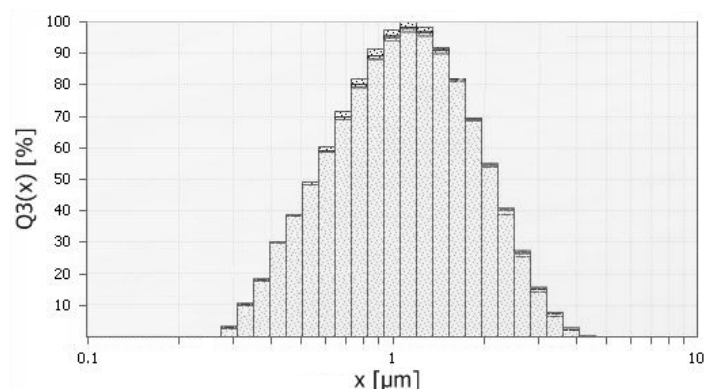


Figure 1. Particle size distribution of SiC powder measured by laser diffraction analysis.

d_{50} (μ)	S_{BET} (m^2/g)	β -SiC (wt%)	Si (wt%)	O (wt%)	Fe (wt%)	Al (wt%)
0.8	11.8	95.7 _{min}	0.1	1.3	0.01	0.02

Table 1. Physical and chemical characteristics of SiC powder.

2.2 Procedure and testing methods

Dispersion of the ceramic powder is the crucial point to form a stable and homogenous aqueous slurry. To reduce values of viscosity and zeta-potential, batches of suspensions containing SiC powders (with or without carbon), deionized water and TMAH were prepared. TMAH is used on one hand as a dispersant, and on the other hand as a base to adjust the pH.

The hydrochloric acid is used to identify the isoelectric point in acidic pH ranges. In the case of SiC-C slurries, both suspensions (SiC and C) are prepared separately, and then mixed together and stirred for 30 minutes. A sonotrode is used to break any agglomerates and provide good particles dispersion (power : 250-300 Watts).

Rheometers suitable for the viscosity measurement of granular suspensions have a cylindrical measurement cell with a fixed cup and a plunger with the same vertical axis and an adjustable rotation speed. Zeta potential measurements were performed on ZetaPROBE (Colloidal Dynamics, USA). It uses the electroacoustic spectral analysis to measure: zeta potential, dynamic mobility, conductivity, pH, temperature and isoelectric point (IEP) of the slurries. A granulometer Analysette 2 (Fritsch, Germany) with laser diffraction analysis (Fraunhofer theory) is used to obtain grain size distribution of SiC and C particles.

After the SiC and SiC-C slurries stabilization, SiC-fiber preforms are impregnated under vacuum with these latter. Figure 2 shows the installation used for the slurry impregnation. The suspension is poured above the preform. The bottom of the cell is set under vacuum forcing the slurry to pass through the preform. A filter placed under the preform traps particles whereas the aqueous solvent passes through. Particles form a layer on the filter that grows into the pores of the preform. If the vacuum is insufficient, a 30 bars maximum pressure may be applied on the upper part to ensure an optimum filling of the porosity.

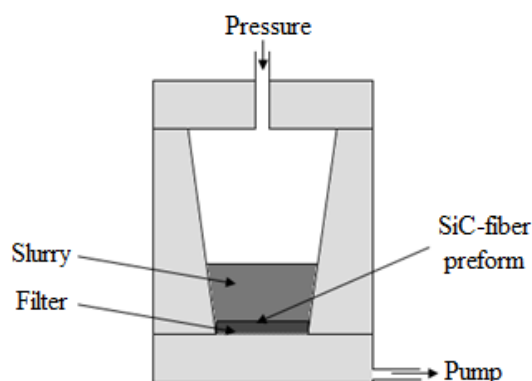


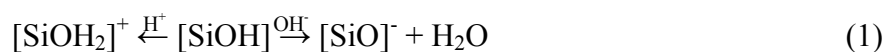
Figure 2. Vacuum impregnation installation used to introduce powders within the porosity of a fiber preform.

The process of infiltration by molten silicon requires a particular installation combining high temperature and reduced pressure. This treatment is carried out in an inductive furnace at a higher temperature than the melting point of silicon, namely $T > 1410^{\circ}\text{C}$.

3 Results and discussion

3.1 Stabilization of the SiC and SiC-C slurries

In colloidal processing, the key step to form a stable and homogenous aqueous suspension is the dispersion of ceramic powder. The suspension stability is achieved via the generation of repulsive forces between particles. It is generally considered that the SiC powder surface consists in an oxide film [4] and the major functional group on the surface is the silanol group (SiOH) [5]. The surface charge of SiC powder in water is attributed to the dissociation of the silanol group according to the following reaction:



The addition of a strong organic base, as TMAH, can promote the dissociation of the silanol group, inducing more negative charge to SiC surface [3]. The low molecular weight of the

dispersant would result in negligible steric effect on the stabilization of the suspension, suggesting that electrostatic forces should be the dominant factor in the stabilization in the present situation. Thereby, TMAH can efficiently improve the dispersability of SiC powder and the fluidity of the slurry. Li *et al.* [3] observed that the optimum dispersion is achieved for a pH value of 10. This condition corresponds to a minimum in viscosity and the maximum in zeta potential for a SiC-based aqueous suspension. Figure 3 shows a pH sweep for the SiC suspension and confirms a minimum of viscosity at pH 10. The zeta potential for its part, continues to decrease with basic pH because of the increase of negative charges on the surface.

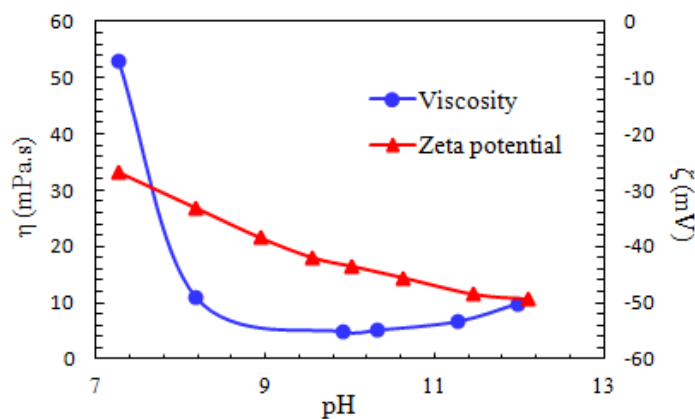


Figure 3. Evolution of zeta potential and viscosity with the pH of a SiC-based aqueous suspension.

Given that the method for preparing the C-based suspension is supplied, no stabilization work has been made on this latter. The SiC-C slurry is prepared by mixing the two suspensions together. However, before mixing SiC-based and C-based slurries, their compatibility has been checked in terms of surface charges of the particles to prevent their agglomeration. Table 2 reports the negative zeta potential of the C-based particles. It appears that the surface charge of these both particles is negative. Thus, the repulsion of particles is promoted instead of their agglomeration. Once the mixture done, after stirring and ultrasonic breaking of aggregates, zeta potential and viscosity were measured. The characteristics of the SiC-C suspension are also reported in Table 2. The slurry remains fluid: the mixture will not affect the impregnation of fiber preforms with the SiC-C suspension. A value of zeta potential around -30 mV indicates a good electrostatic repulsion between particles. To ensure that the particles do not agglomerate, a particle size analysis was performed. The results shown in Figure 4 indicate a good dispersion of SiC and C particles into the aqueous slurry (similar distribution to that in Figure 1).

	SiC-based slurry	C-based slurry	Mixture of SiC and C slurries
pH	10,2	7,75	9,67
Zeta potential (mV)	$-63,9 \pm 0,2$	$-57,9 \pm 0,2$	$-28,24 \pm 0,12$
Viscosity (mPa.s)	$6,8 \pm 0,25$	$12,6 \pm 0,1$	$4,6 \pm 0,07$
d50 (μm)	0,9	0,7	0,8

Table 2. Main characteristics of the aqueous suspensions: a) SiC-based, b) C-based, c) SiC-C-based.

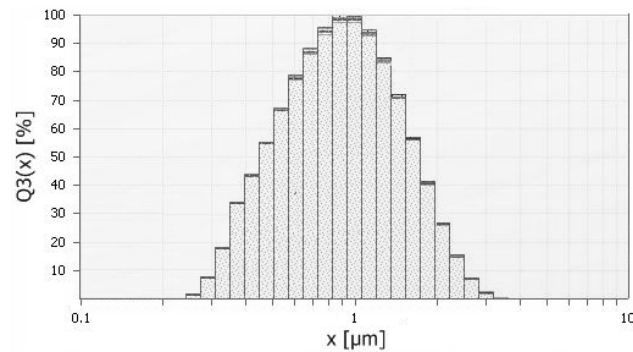


Figure 4. Particle size distribution of the mixture of SiC and C particles.

3.2 Introduction of ceramic powders into the porous network of a fiber preform

After the under-vacuum slurry impregnation step, the inter-tows porosity of the preform is homogeneously filled by the particles, as shown in Figure 5. The SiC and C powders are present inside the inter-tows matrix but not in the intra-tow pores, because of a too narrow pore size entrance for the powders.

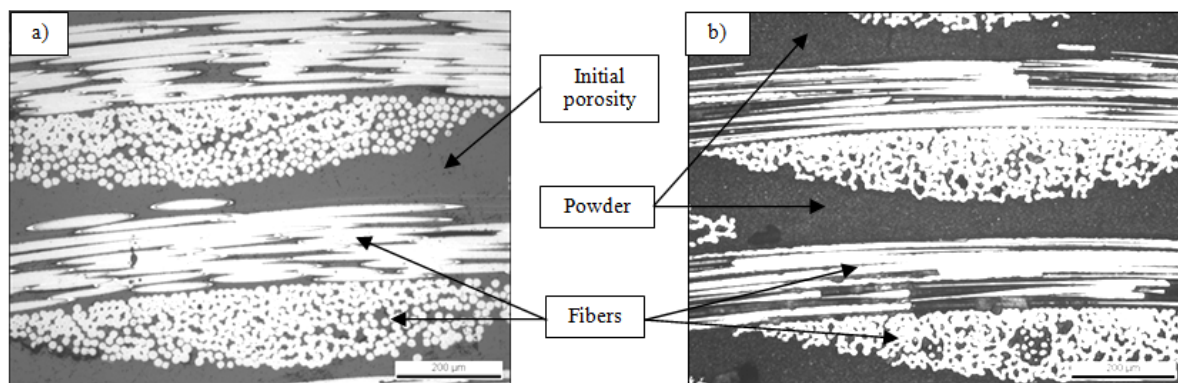


Figure 5. Micrographs of fiber preforms (a) before impregnation with the ceramic powders, (b) after impregnation.

The powder is homogeneously distributed into the material with limited residual macro pores. About 50% of the pore volume is filled with SiC and C particles after impregnation (estimation from mass gain and initial knowledge of the pore volume by gas pycnometer).

3.3 Fiber-preforms densification by silicon melt infiltration

On one hand, introduction of a carbon powder into the preform leads to reduce the fraction of free-silicon by trapping this latter into SiC. On the other hand, it helps the wetting by the molten silicon thanks to the carboreduction of silica (equation 2) and by increasing locally the temperature due to exothermal reaction [6].



Figure 6 shows micrographs of the composite after silicon melt infiltration. With the detection of secondary electrons (Figure 6.a) a picture of the surface topography is obtained. The presence of only a few residual open pores in the matrix reflects a proper densification. However, the picture taken with the detection of backscattered electrons (Figure 6.b), shows matrix cracks near the fiber tows created by the RMI treatment. These cracks are not well filled with silicon in the central area of the sample. This phenomenon is attributed to the poor thermal stability of Nicalon fibers. Indeed, the non-stoichiometry of this latter and the oxygen

content (about 12%wt) lead to an important degassing of the fibers at temperatures above 1000°C.

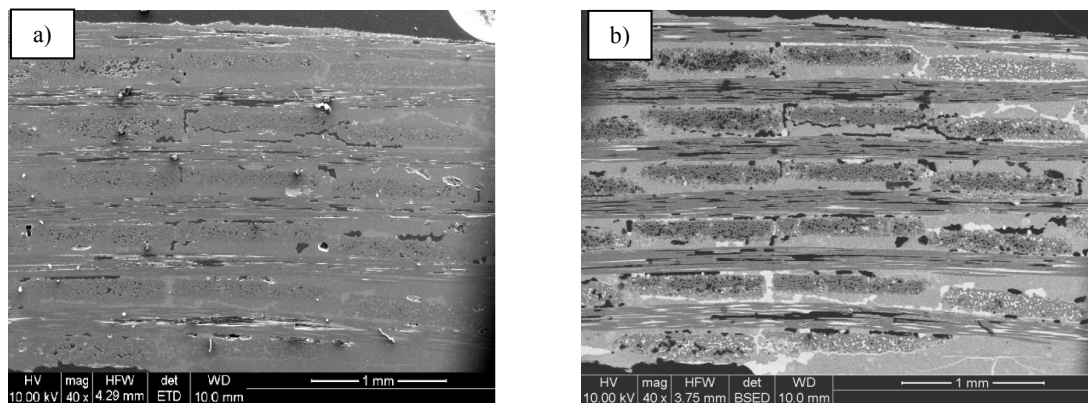


Figure 6. SEM micrographs of fiber preforms impregnated with a SiC-C slurry and infiltrated with molten silicon (a) secondary electrons, (b) backscattered electrons.

A structural analysis of the material was made by X-ray diffraction. Figure 7 presents the diffractogram of the composite after silicon melt infiltration, with and without prior introduction of carbon into the matrix. The intensity of the feature diffraction peaks of silicon is significantly decreased when a SiC-C based slurry is used.

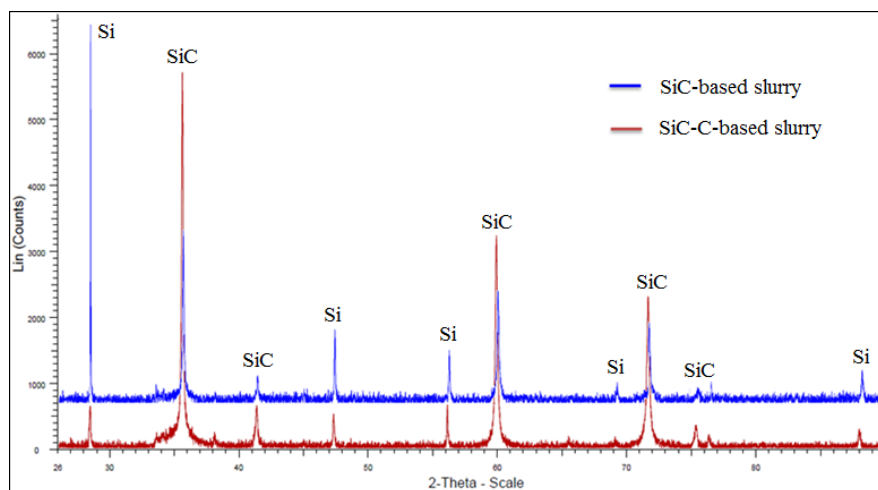


Figure 7. Comparative X-ray diffraction diagrams after silicon infiltration of preforms impregnated with a slurry containing carbon or not.

4 Conclusion

Ceramic matrix composites were processed by a low cost and a short-time process based on the reactive melt infiltration of silicon into a fiber preform containing silicon carbide and carbon powders. A first step consisted in stabilizing a SiC-based slurry in order to introduce carbon particles into. Carbon particles are used to fix free residual silicon. An under-vacuum SiC-C slurry impregnation step was optimized to introduce a maximum of particles into the porous network of the fiber preform. Using Nicalon SiC fibers is relevant to reduce the cost for adjusting the process, mainly the slurry impregnation step. However, these fibers are significantly degraded above 1000°C. Despite using a prior degassing step for the desoxidation of SiC particles, Nicalon fibers continuously degas during the RMI process and their use is a drawback to a good densification of the material by silicon melt infiltration. One

way would be the use more thermally stable SiC fibers as Hi-Nicalon type S fibers (Nippon Carbon, Japan), to overcome the trouble caused by degassing fibers.

Acknowledgements

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