

Preparation and Analytical Electron Microscopy of a SiC Continuous-Fiber Ceramic Composite

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Continuous-fiber-reinforced SiC/SiC-based matrix composite materials, to be used in the first-wall blanket of a fusion reactor, were prepared by the infiltration of SiC cloth with SiC-based suspensions of various chemical compositions. The compositions were tailored with respect to the calculated activation in a fast-neutron flux. Liquid-phase sintering was used for material densification, using different sintering aids, such as Al_2O_3 , Y_2O_3 , P_2O_5 , AlN, etc. The microstructures of the differently prepared materials were studied with scanning and transmission electron microscopy and microanalysis.

Keywords analytical electron microscopy, first wall, fusion, glass-ceramics, SiC

1. Introduction

Modern materials, developed for use under extreme conditions, e.g., high-temperature aerospace applications or applications in fusion reactors, should have high thermal conductivity, low gas permeability, suitable mechanical properties at elevated temperatures, radiation stability in high fluxes of neutrons, and a high oxidation resistance (Ref 1-3).

Among the few ceramics that approach the required properties are silicon-carbide-based composite materials. Particularly promising is a composite material based on continuous-fiber SiC embedded in a SiC-based matrix with nanometer-sized particles (SiC_f/SiC) (Ref 4).

The high toughness based on the two-dimensional (2D) or three-dimensional (3D) fibrous structure combined with a relatively high chemical resistance, also at temperatures above 1000 °C, enables the use of these materials under special conditions. Because it has the appropriate composition and contains only low-activation elements, it seems that SiC_f/SiC is the most promising candidate material for the first-wall blanket of a future fusion reactor. The current design of the International Thermonuclear Experimental Reactor (ITER, at the same time it means "the way" in Latin) (Cadarache, France) is based on reduced-activation steels (EUROFER steels), which offer good structural integrity, toughness, and physical properties during reduced activation but can only be used up to about 550 °C. This is considered adequate for the experimental purposes of ITER but is totally inadequate for any future reactors, which are expected to produce energy on a commercial basis. The

material for a commercial reactor should be suitable for use at temperatures over 1000 °C, have low activation after neutron irradiation, have good wear resistance under the conditions of service, be sufficiently tough to ensure operational structural reliability, and be resistant to structural or lattice damage from impinging high-energy neutrons, etc. Based on these requirements, SiC_f/SiC -based materials seem to be the proper choice.

The processing of SiC_f/SiC is a complex, multistage process. The fibers are woven in a number of ways into a preform (ideally a 3D preform), which is then infiltrated with SiC, leading to densification. Although many methods have been attempted in the past, the method used currently is chemical vapor infiltration (CVI). In this method a chemical vapor of SiC is allowed to infiltrate the preforms, which are kept at an elevated temperature, and slowly build layers of SiC matrix. The method is used for most commercial products at present but suffers from some processing drawbacks, notably the very long time required for the buildup of sufficient material for the matrix, resulting in the very high cost and the extreme difficulty encountered in eliminating all porosity at the micro as well as macro level. The porosity can present serious problems, such as the low thermal conductivity of the composite, as well as substantially reduced gas impermeability. Fusion applications require maximized thermal conductivity and practically zero porosity and gas permeability (Ref 5).

In this paper, the results are reported on two main topics: an alternative method of infiltration of the SiC fiber preform with a SiC-based matrix material (adapted dip coating and vacuum infiltration with suspensions) and the development of a protective nonpermeable coating on CVI SiC_f/SiC .

SiC is a highly covalent compound and therefore its densification without sintering additives is rather difficult. However, it can be achieved by solid-state sintering using boron and carbon, or liquid-phase sintering (LPS) using metal oxides as sintering additives. A eutectic melt in the $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ (Ref 6-8) system is usually used as the sintering aid. In this system, one of the problems is the formation of volatile components (AlO, SiO, CO). The addition of AlN was reported to be more beneficial than Al_2O_3 because the decomposition of added AlN can be effectively suppressed by applying a nitrogen overpressure during sintering (Ref 9). Despite this, the firing temperatures used in solid-state and liquid-phase sintering of SiC are

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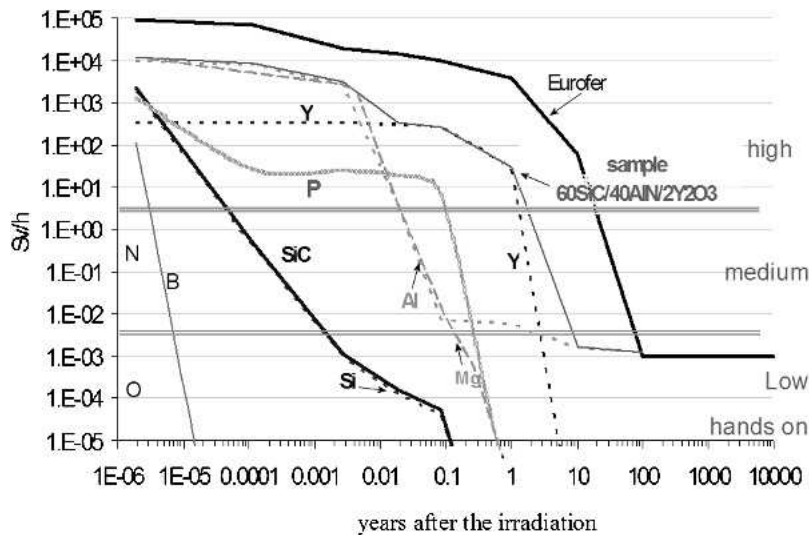


Fig. 1 Calculated contact gamma dose for various materials versus time after the irradiation

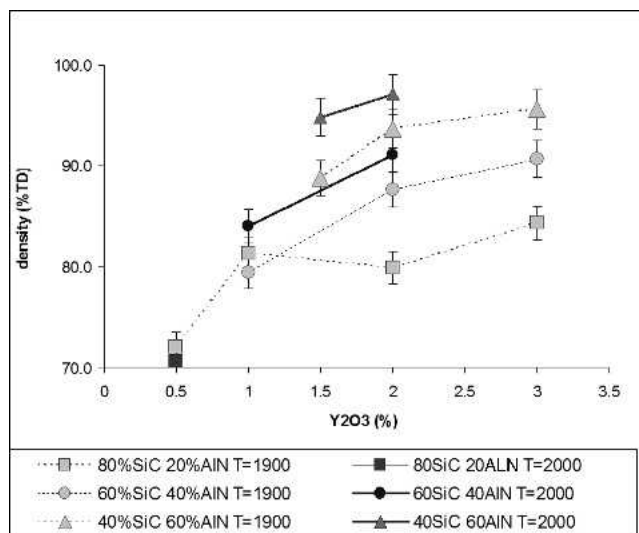


Fig. 2 Density of the SiC-AlN-Y₂O₃ ceramics as a function of composition and sintering temperature

way above 1800 °C, which can have a detrimental effect on the SiC fiber preforms. Also reported are the attempts to prepare dense SiC-based materials with a firing temperature below 1500 °C.

2. Experimental

The starting materials were commercially available SiC (0.5- μ m SiC powder BF-12 (HC Starck, Goslar, Germany) and 50 nm SiC powder (HeFei Kai'er Nano-meter Technology and Development, Ltd., Hefei, China), Y₂O₃ (HC Starck, grade C) and AlN (HC Starck, grade C) powders. The SiC fibers used in this study were uncoated Hi-Nicalon-S (COI Ceramics, San Diego, CA) woven cloth and SiC chemical-vapor-infiltrated SiC cloth (Cerasesp N3 from Snecma, Le Haillan, France). Slurries having up to 70 wt.% solids were prepared by homogenization of the host ceramic powders in distilled water; the pH was adjusted with the addition of tetra-methyl ammonium hydroxide. The uncoated AlN powder was admixed to the slurry in the last 10 min of the homogenization. The slurries were cast

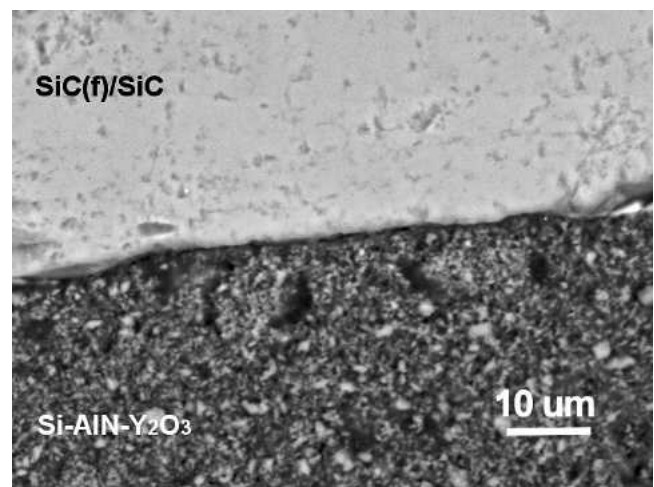


Fig. 3 SEM micrograph of the CVI SiC_f/matrix interface with the composition of 60SiC/40AlN + 2Y₂O₃, prepared at 2000 °C

and closed into nonporous polymer molds and heated at 50 °C. After 2 h, the solid green parts were removed from the molds and dried at room temperature in the open air for 24 h. The sintering was conducted at temperatures up to 1950 °C in a nitrogen atmosphere in a furnace with graphite heating elements.

The suspensions for another set of experiments were prepared by homogenization of the ceramic powders by ball milling. The slip-infiltration method was used to infiltrate the SiC fiber preforms. Infiltration was carried out in vacuum by dipping the treated preform in the slip and stirring continuously, without mixing in any air. The infiltrated preforms were then dried in air and dipped for a second time to enhance the coating. Sintering was carried out in a nitrogen atmosphere at 1900-2000 °C. In a third set of experiments, SiC-based slurries with the addition of a phosphorous-containing compound were prepared and infiltrated in SiC preforms. The samples were sintered at 1400 °C in argon or nitrogen. After sintering, the materials were examined by x-ray diffraction, optical microscopy, scanning and transmission electron microscopy (SEM, TEM), and microanalysis.

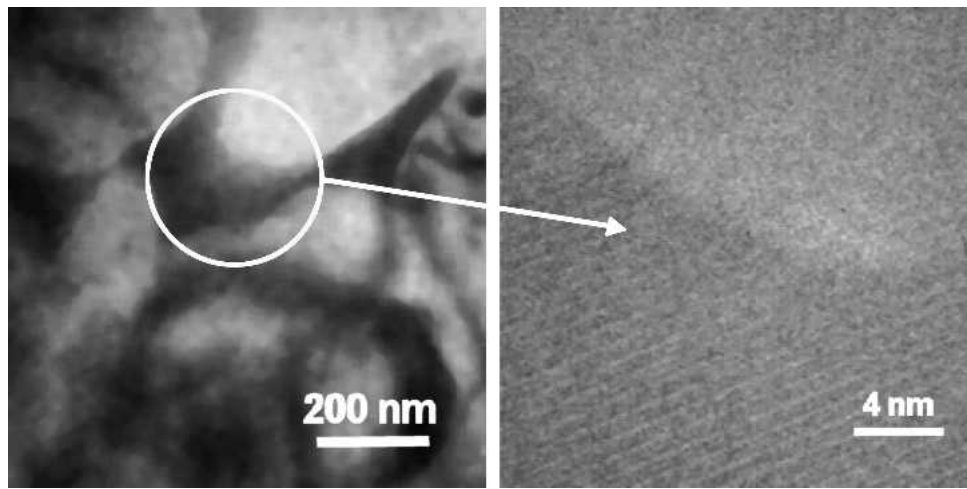


Fig. 4 TEM micrograph of the sample 60SiC/40AlN + 2Y₂O₃ and enlarged area of the SiC grain/secondary phase interface

3. Results and Discussion

To prepare a composite material with low activation in a fast-neutron flux and with defined mechanical and thermal properties, the matrix composition had to be tailored. The activation (contact gamma dose) as a function of the chemical composition was first calculated, assuming a fast-neutron spectrum similar to that expected in a fusion reactor (Ref 10).

The diagram in Fig. 1 shows the contact gamma dose as a function of the time after the irradiation for the materials and elements used in this study and a comparison with the Eurofer steel (used in current designs of fusion reactors). The results suggest that the gamma dose for the composition of the sample SiC-AlN-Y₂O₃ is significantly higher than for the pure SiC but still lower than for the EUROFER composition. The contact gamma dose for the particular elements implies that yttria makes the main contribution to the high dose, but it drops after approximately one year, whereas later aluminum does not allow a further decrease of the dose. This suggests that both these elements should be minimized or completely avoided to achieve the minimum possible dose.

The double horizontal lines in Fig. 1 represent the dose boundaries between high-radioactive, medium-radioactive and low-radioactive waste. The “hands on” dose is the dose of radioactive material permitted to be handled with bare hands (skin contact).

To minimize the activation of the SiC-based materials, a set of experiments was performed in which the influence of the amount of sintering additives on the density of the fired samples was studied.

In these experiments, the composition of the matrix material was varied in terms of yttria (0.5-3 wt.%) and AlN content (20-60 wt.%), considering the potentially beneficial effect of the AlN as a highly thermal-conductive material. The sintering temperatures were 1900 and 2000 °C, with an adapted heating regimen. As the diagram in Fig. 2 shows, the density increases with increasing AlN and Y₂O₃ content and with increasing temperature. The highest final density, i.e., 98% theoretical density, was achieved with a composition containing 40% SiC, 60% AlN, and 2% Y₂O₃ at 2000 °C.

The microstructure of the sintered material was analyzed by SEM and TEM. Figure 3(a) shows the Si-AlN-Y₂O₃ layer on

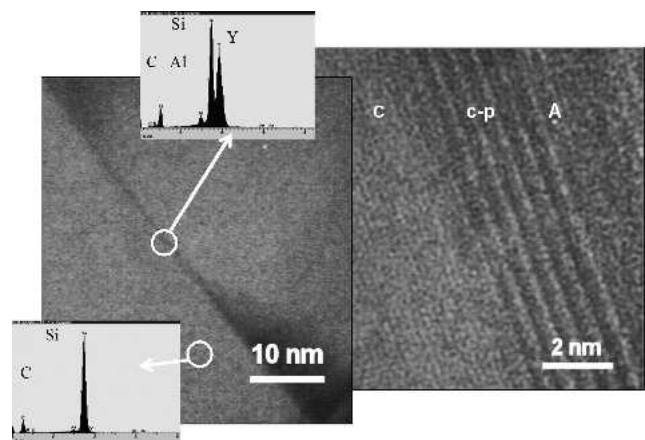


Fig. 5 TEM micrograph of a grain boundary (between two SiC grains) and EDXS spectra of SiC grain (bottom inset) and grain-boundary secondary phase (top inset). The right micrograph is a high-resolution TEM image of SiC/secondary phase interface. c, cubic SiC phase; c-p, polytypes of SiC; A, amorphous intergranular phase

the SiC_f/SiC. The interface reveals relatively satisfactory adhesion, even though some parts of the layer were not fully adhered to the substrate. The most probable reason for this was the large shrinkage during sintering.

Figure 4 shows TEM micrographs of the sample 60SiC/40AlN + 2Y₂O₃. Besides 100-200 nm sized SiC grains, an yttrium-rich secondary phase (darker contrast on micrograph) was observed. Using high-resolution TEM, it was found that this secondary phase, located at 3-grain junctions, was crystalline, which might have a beneficial influence on the high-temperature mechanical properties.

Figure 5 shows TEM micrographs of a grain boundary between two adjacent SiC grains. Using energy dispersive x-ray spectroscopy (EDXS) it was found that the grain-boundary region is enriched in Y and Al content (inset at the top). High-resolution TEM of the grain-boundary region the presence of an amorphous secondary phase revealed the presence of various polytypes inside the SiC grains.

Obviously, to achieve a high final density, a substantial amount of yttria is needed (Fig. 2). Such an amount of added

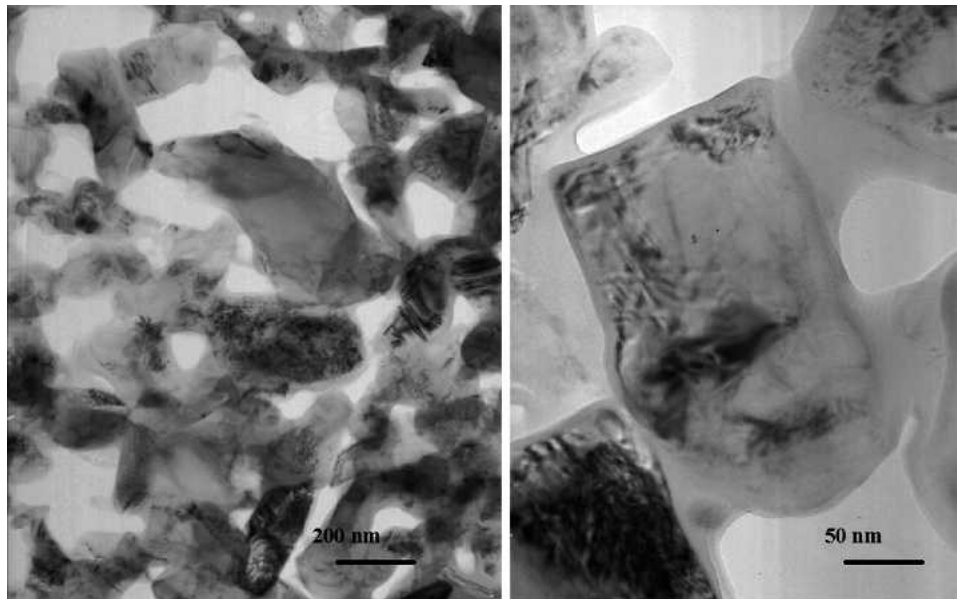


Fig. 6 TEM micrographs of the SiC-SiO₂ glass-ceramic composite. The pores are etching artifacts and were formed as a result of preferential etching of secondary phase during the TEM specimen preparation.

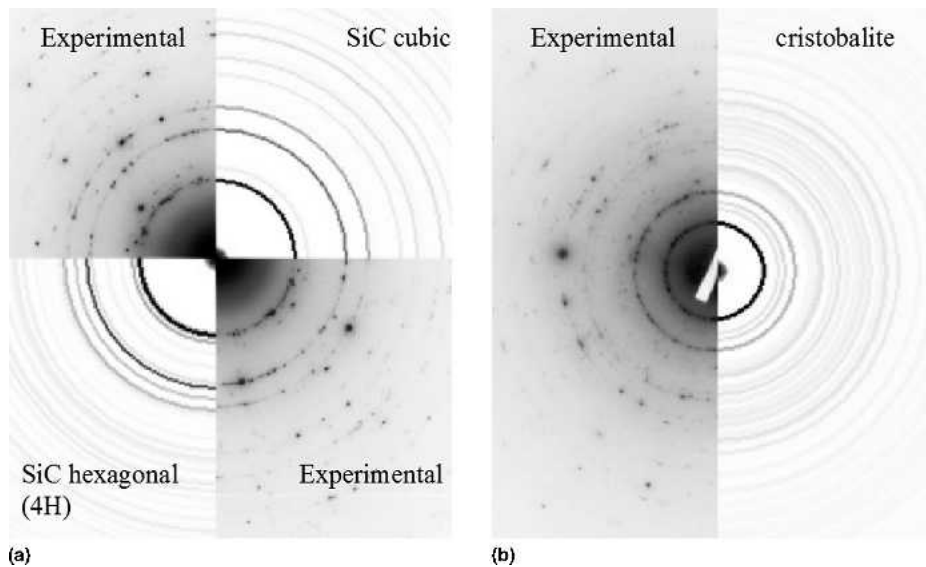


Fig. 7 (a) Experimental and simulated SAED patterns of samples with a large amount of cubic SiC grains; (b) experimental and simulated SAED patterns of sample with crystalline SiO₂ (cristobalite alpha, low) in secondary phase

yttrium gives rise to a high activation of the material in the neutron flux (Fig. 1).

In further experiments, dense SiC-based material without any yttria addition were prepared. From Fig. 1, it appears that there are several light elements (P, Si, O) suitable in terms of neutron activation.

A glass-ceramic composite was prepared where SiC grains (particles) were densely packed in a glassy phase. Such a material would, however, not have a high thermal conductivity, nor would it have good high-temperature mechanical properties, but if the amount and the composition of the glassy phase are optimized, it could be used as a coating material deposited on a CVI SiC_r/SiC composite, improving the gas-impermeability. Such coatings should have good adhesion with the base material.

Using nano-sized SiC powders and a controlled oxidative

atmosphere during the firing process at 1400 °C a SiC-SiO₂-based material was prepared. In Fig. 6, the TEM micrograph of a SiC grain surrounded with a secondary, SiO₂-rich phase is shown.

Using selected-area electron diffraction it was found that SiC grains were predominantly in the cubic and 4H hexagonal forms. Besides the glassy SiO₂ phase, also nanometer-sized crystallites of cristobalite were found. In Fig. 7, the comparison of the experimental and calculated (simulated) selected area diffraction (SAED) patterns for SiC (Fig. 7a) and SiO₂ (Fig. 7b) is displayed.

The SiC-SiO₂ material used for the infiltration of the SiC_r preforms did not result in a dense and pore-free composite. Many cracks, voids, and other defects were observed, as shown in Fig. 8, where the SEM image of the fiber/matrix interface is shown. A large amount of shrinkage during the firing and poor

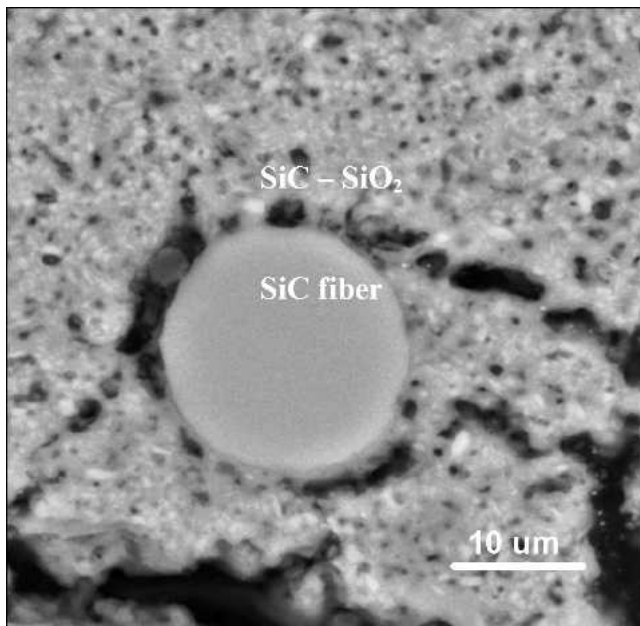


Fig. 8 SEM micrograph of the SiC_f/SiC-SiO₂ interface

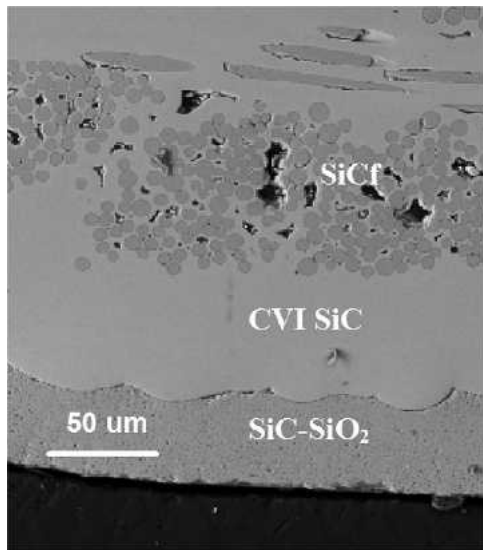


Fig. 9 SEM micrograph of the cross section of the SiC_f/SiC (CVI) coated with a layer of SiC-SiO₂-based material

adhesion were assumed to be the main reasons for the formation of the defects.

Coating of SiC_f/SiC composite with SiC-SiO₂-based material again confirmed the poor adhesion of the coating with the base material (Fig. 9).

To minimize the content of glassy phase and to improve the adhesion of the glass-ceramic composite to the SiC base material, compositions from the SiC-P₂O₅-Al₂O₃ system were prepared. Phosphorus pentoxide forms with alumina and silica (always present at the surface of SiC) as low-melting-point eutectics (around 1200 °C). After firing, compositions in argon or nitrogen dense material were obtained with a relatively small amount of glass. The secondary phase contains a low concentration of phosphorous, which evaporated during the firing at elevated temperatures. The adhesion of this material to the SiC fibers or SiC_f/SiC composite was surprisingly good. In Fig. 10,

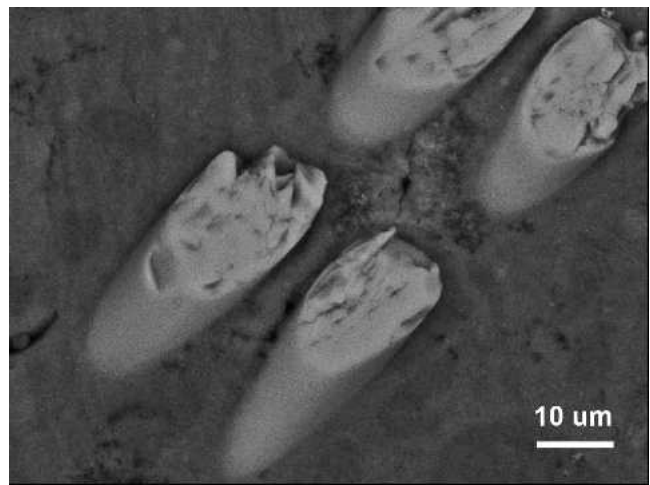


Fig. 10 SEM micrograph of the SiC fibers in SiC-P-Al-O based matrix material

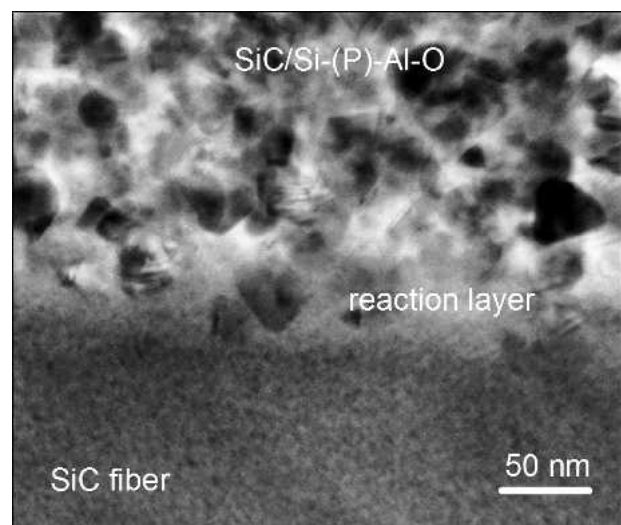


Fig. 11 TEM micrograph of the SiC_f/SiC-P-Al-O based matrix interface

the SEM image of the SiC fibers embedded in the SiC-P-Al-O matrix is shown. No large defects were observed around the fibers. In Fig. 11, the TEM micrographs of the interface between the matrix layer and the SiC fiber is displayed. The matrix is composed of fine SiC particles bonded with the phosphorous-containing secondary phase. The matrix phase reacts with the SiC fiber forming a glassy reaction layer.

4. Conclusions

The infiltration of SiC-fiber preforms with a SiC-based ceramic slurry could be accomplished using adapted dip coating or vacuum infiltration. Using low neutron-activation compounds, such as SiC, SiO₂, and P₂O₅, and a moderate sintering temperature (1400 °C), dense matrix material with good adhesion to the original SiC fibers could be attained. This ceramic-glass composite could be used as a coating for the base SiC_f/SiC material, produced with chemical vapor deposition, which could benefit the gas permeability.

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