JOURNAL OF MATERIALS SCIENCE 32 (1997) 6429–6433

Microwave densification of electrophoretically infiltrated silicon carbide composite

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A new method to fabricate SiC composites by microwave heating SiC preforms is described. Preforms were produced by electrophoretically infiltrating SiC fibre (Nicalon) preforms with SiC powder. Samples were heated to 1600 °C in a matter of minutes and held at temperature for 5 min to minimize fibre degradation. To achieve densification, heated preforms required the application of a uniform load. Bulk densities increased from $\sim 0.8\,g\,cm^{-3}$ for the as-infiltrated preforms to over $1.9\,g\,cm^{-3}$ for microwave-heated samples with a small applied load of ~ 13 kPa. Microstructural analysis revealed the presence of some pores and cracks in the matrix; however, large areas of dense SiC matrix material are apparent.

1. Introduction

Silicon carbide composite is a promising high-temperature structural material due to its excellent chemical and physical properties for a wide variety of applications [1–3]. Fabrication methods include hot pressing, reaction bonding or sintering, chemical vapour infiltration, melt infiltration and preceramic polymer processing [4–10]. These methods can yield high-quality composites under a variety of processing conditions. Most of these methods require complex equipment, lengthy processing times and severe processing conditions, resulting in high-cost composites for even simple shapes.

Electrophoretic particle deposition (EPD), though fundamentally different from electroplating, is very similar in practice. A dispersion of charged particles in solution is produced by proper selection of solvent, surfactants, and adjustment of pH (a positive or a negative charge can be effected as desired). A voltage is applied across electrodes immersed in the solution and the charged particles migrate to the electrode surface where they are deposited (a positively charged particle would deposit on the cathode, a negative particle on the anode). With this process, particle deposits several centimetres thick can be produced in a matter of minutes. A process related to EPD, termed electrophoretic particle infiltration (EPI), has been developed to infiltrate fibrous preforms with ceramic particles [11].

This paper describes a fabrication method of silicon carbide composite that involves creating a fibrous preform by EPI followed by microwave densification. Both of these process steps are rapid, of the order of minutes, and use relatively simple equipment. Silicon carbide fibre preforms were electrophoretically infiltrated with silicon carbide powders. These preforms were further processed with microwave energy and an applied load to produce the required densification.

Microwave heating is fundamentally different from the conventional techniques normally used to process materials. The direct coupling of energy to a material with dielectric loss results in extremely rapid heating rates [12]. Typical heating and cooling rates are of the order of hundreds of degrees Celsius per minute. Rapid heating and cooling rates are of great advantage for this system, because the normal densification temperature for silicon carbide exceeds the temperature at which some of the commercially available silicon carbide fibres, such as Nicalon, begin to decompose [13, 14]. Using microwave heating we can take advantage of the relative differences in the rates of the silicon carbide densification and Nicalon fibre decomposition. By heating and cooling rapidly, the silicon carbide powder can be densified before the Nicalon fibre has the opportunity to decompose.

2. Experimental procedure

Preforms were made from two-dimensional, eight-harness satin weave silicon carbide-based fabric. This material is commercially available under the trade name Nicalon, manufactured by Nippon Carbon, Japan. The fabric preform consisted of eight layers of Nicalon HVR. Proper selection of solvent, surfactants, and particle size is critical to form a suspension that will infiltrate the fabric preform. The suspension prepared for these experiments consisted of 1000 ml acetone, 1.5 g cellulose acetate hydrogen phthalate, 100 g SiC powder, and 1.5 ml butylamine.

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The Nicalon was pre-cut to fit within a polyester frame. The back of the frame was covered with silver foil to serve as the deposition electrode. The front of the frame was covered with a polyester screen to contain the fabric. The fabric, once mounted in the frame, was desized in acetone in an ultrasonic cleaner. Although the need for fibre coating is recognized for this material system [15], fibre coatings were generally not applied for these experiments.

The electrophoretic infiltration was performed in a 500 ml Pyrex beaker. The polyester frame with the preform was placed in the vessel with a silver rod about 4 cm from the screen side of the fixture. The silver foil on the back of the fixture served as the anode and the silver rod served as the cathode. A Spellman, Model RHR 30PN30 high-voltage d.c. power source was used to apply 400 V with an initial current of 40 A. Voltage was kept constant and amperage decreased to about 3–4 A over about 50 min, due to increased resistance of the powder deposited at the anode. Voltage and current were continuously measured using a Fluke DMS. Infiltration was continued until the current fell to about 10% of the starting value.

Microwave processing was performed under flowing 95% nitrogen–5% hydrogen using a 2.45 GHz, 6 kW power supply. Samples 72 and 73 were heated overnight to 1000 °C to remove binders and other volatiles before microwave sintering. After this treatment, specimens were encased in yttria-stabilized zirconia fibre insulation board and then placed in a $60\,cm \times 60\,cm \times 60\,cm$ multi-mode cavity. Several samples had magnesia blocks (525 g) placed on top and in some cases below them as well, to aid in densification. The magnesia blocks were dense, monolithic material, whereas the furnace bricks contained large pores and openings which did not provide a smooth surface. In those instances where magnesia blocks were used, they were placed inside the zirconia-based fibre insulation in direct contact with the preform. Temperature was measured using a well-shielded and earthed type-K thermocouple. The thermocouple was inserted through the insulation board casket to make direct contact with the sample.

All samples were encased in epoxy and then sectioned to prevent delamination. The as-sectioned samples were ground and polished to a 0.6 μm finish. Samples were subsequently examined using scanning electron microscopy (SEM). Preform densities were determined by measuring the dimensions of the sample with vernier calipers and weighing on a balance. Composite densities were measured by immersion in isopropyl alcohol. Tensile strengths were measured by individual filaments tests according to ASTM D4018-81.

3. Results and discussion

EPI makes use of the electrophoretic deposition process, but with the inclusion of a ceramic fibre preform such as a two-dimensional lay-up or three-dimensional fibrous preform which is placed in contact with the working electrode (deposition electrode) as shown in Fig. 1. When a voltage is applied, the particles migrate through the porous preform and deposit on to the electrode [11]. Subsequently, more particles deposit on top of this layer and as the process continues, a growth front of material moves from the electrode surface outward into the preform. The growth front then passes through the fibre architecture of the preform filling all of the accessible voids until the preform is entirely impregnated with electro-deposited matrix material. At this point, the applied voltage may be shut off and the electrophoretically particle-infiltrated preform removed for examination and/or further processing. The amount of powder infiltrated can be controlled by the EPI process to tailor the fibre volume fraction in the final composite. Samples prepared for this study are summarized in Table I.

The preforms are friable after infiltration, because the infiltrated powder is contained only by the fabric structure and an organic binder. Preform densities were estimated based on mass and volume, to be $\sim 0.8\,g\,cm^{-3}$.

As-received strengths of Nicalon filaments were measured by single-filament tensile tests to be ~2800 MPa. Nicalon fibres were rapidly heated by microwave energy to 1600 °C for 5 min. Mechanical properties of these treated fibres were measured to be ~2500 MPa, approximately 10% lower than the as-received fibres. Mechanical properties of desized fibres were not determined. The decrease in strength is modest and was deemed acceptable for this study. The cause of the degradation was not investigated further, but it was assumed that the mechanical properties of the fibres would not be degraded further by the presence of matrix material during microwave processing.

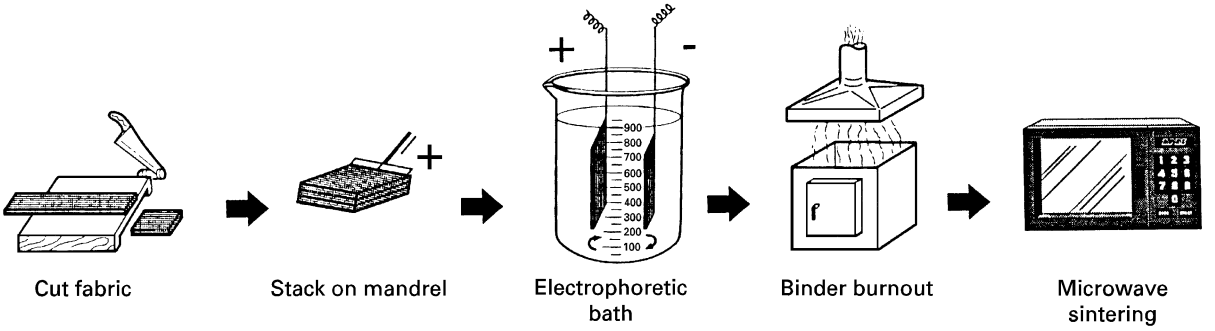

Figure 1 Schematic illustration of the steps for electrophoretic infiltration of ceramic matrix composites.

TABLE I Electrophoretically infiltrated samples

Sample	Preform	Powder	Initial weight (g)	Final weight (g)	Change(%)
70	Nicalon HVR	SiC	9.21	27.04	193
71	Nicalon HVR	SiC	9.95	31.47	216
72	BN/Nicalon	SiC	11.82	26.80	127
73	BN/Nicalon	SiC + 1%B	11.61	20.77	79

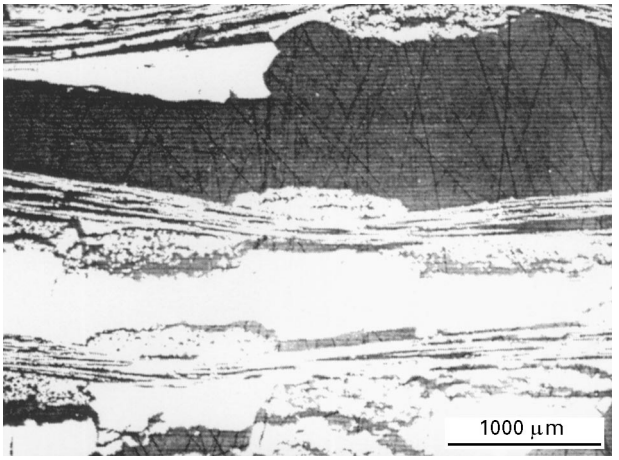

Figure 2 Scanning electron micrograph of sample 70 heated to 1600 °C for 5 min.

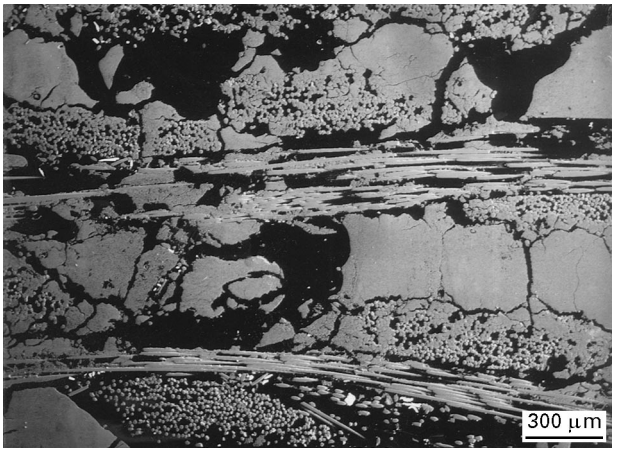

Figure 3 Scanning electron micrograph of sample 71 heated to 1600 °C for 5 min using microwaves.

Initial sintering experiments were performed without applying a load to the sample. Fig. 2 shows a scanning electron micrograph of a polished section of sample 70. The fabric layers appear as longitudinal fibre bundles and sectioned transverse fibre bundles. The matrix material is the large white blocks. The dark regions are mounting material. Much of the matrix material is sintered. Large continuous matrix regions are apparent with small cracks. The outlines of the sintered blocks generally follow the contours of the fabric reinforcement, but it is not in direct contact with it. This is a result of the expansion or swelling of the preform. Bulk density of this sample decreased to $\sim 0.7\,\mathrm{gcm}^{-3}$ due to swelling of the structure. Subsequent experiments were performed with an applied load to minimize this expansion.

Pressure-assisted sintering was performed on samples 71, 72 and 73. Reference to Table I shows that sample 71 is Nicalon HVR with SiC powder, sample 72 is BN coated Nicalon with SiC powder and sample 73 is BN coated Nicalon with SiC and 1% B powder. The composite preforms were placed in zirconia insulation and weight was applied to the top using sintered MgO blocks which applied a constant load of approximately 13 kPa. The composites were heated to 1600 °C and held for 5 min.

Fig. 3 shows the microstructure of the sample 71. Dense areas of SiC are present in the area between the fibres and there is no evidence of delamination. Fig. 4 shows sample 73, which was first preheated to 1000 °C to remove any residual solvent. This sample also densified, but the micrograph shows that the microstructure of this sample contains more void volume. This is consistent with the bulk densities, which are $\sim 1.2\,\mathrm{gcm}^{-3}$ for sample 71 and $\sim 1.3\,\mathrm{gcm}^{-3}$ for sample 73.

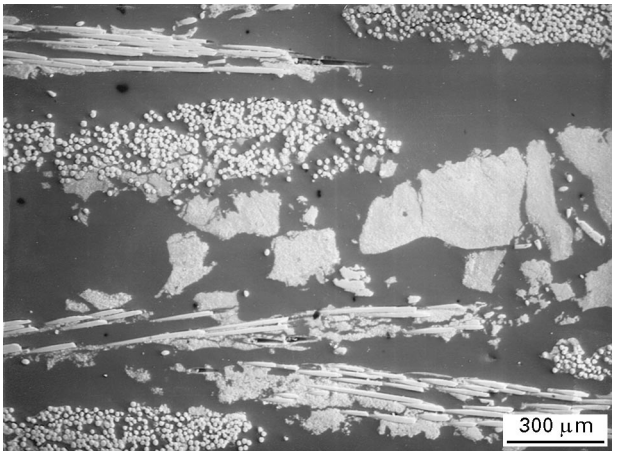

Figure 4 Sample 73 heated to 1600 °C for 5 min using microwaves. This sample was first preheated to 1000 °C to remove any residual solvent.

The difference in apparent densification is probably not due to the preheat procedure, because sample 73, which underwent the preheat to 1000 °C to remove residual solvent, would be expected to be of higher density. The difference in densification is probably due to the different compositions of infiltrated matrix powder. Sample 71 is Nicalon HVR infiltrated with SiC powder while sample 73 is BN-coated Nicalon infiltrated with SiC powder and 1% B powder, added as a sintering aid [16]. Rather than providing a glassy

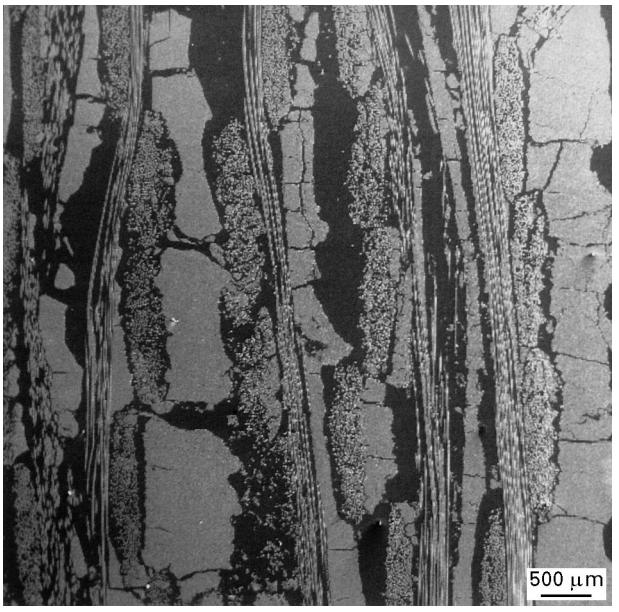

Figure 5 Sample 72A heated to 1600 °C for 5 min. Pressure applied with MgO setter on top.

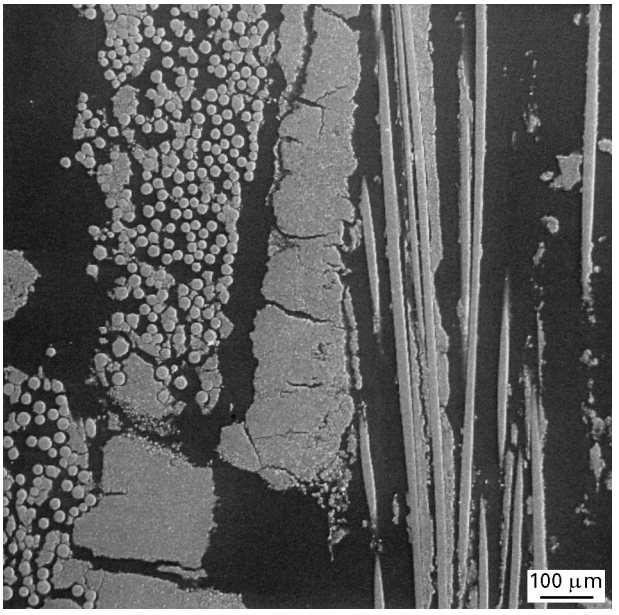

Figure 6 Sample 72A heated to 1600 °C for 5 min. Pressure applied with MgO setter on top.

phase to promote sintering the boron probably oxidized to B_2O_3 during the preheat and volatilized during the microwave processing. B_2O_3 has a vapour pressure of about 500 Pa at 1600 °C.

Sample 72 was sectioned in half. Part of the sample was densified using only an MgO setter on the top (sample 72A) and the other half was densified using MgO setters on top and bottom (sample 72B). Sample 72A is shown in Figs 5 and 6. Sample 72B is shown in Fig. 7. The sample for which the setters were used top and bottom appears to have a denser microstructure than the sample for which an MgO setter was only used on the top. Measured densities confirm this observation. Sample 72A with an MgO setter on top only has a density of $\sim 1.4\,g\,cm^{-3}$, while sample 72B has a density of $\sim 1.9\,g\,cm^{-3}$. Sample 72A contacted

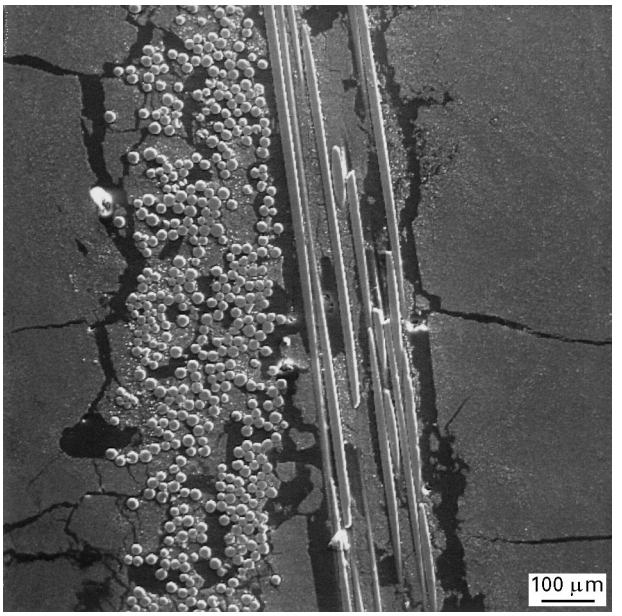

Figure 7 Sample 72B heated to 1600 °C for 5 min. Pressure applied with MgO setters on top and bottom.

the furnace brick on the bottom side. The brick is porous with large openings, which applies non-uniform pressure on the sample. The MgO setters are dense blocks which apply uniform pressure.

4. Conclusion

Nicalon preforms can be electrophoretically infiltrated with SiC powder and co-infiltrated with additional powders, such as sintering aids, in predetermined quantities. The volume fraction of fibre in the final composite can be controlled by the amount of powder infiltrated in the EPI process and the applied load during microwave heating.

Infiltrated matrix powder can be sintered to high density by microwave heating. An applied load is necessary to achieve good consolidation. The microstructure of the densified samples in this study is relatively open and the samples are not sufficiently dense for structural silicon carbide composite material due to the small applied load. Under the conditions of these experiments, bulk densities of $\sim 1.9\,g\,cm^{-3}$ were achieved. The application of higher loads is probably required to achieve complete densification. These experiments were designed to demonstrate feasibility for fabricating silicon carbide composites by EPI followed by microwave heating. Regions of dense SiC were achieved by microwave heating within the powdered preforms. Additional experiments are required to optimize infiltration conditions, microwave heating conditions, and determine mechanical properties.

From a practical viewpoint, this fabrication method has the potential to produce good-quality SiC composite rapidly, in a matter of minutes, and economically, due to the simple equipment requirements and rapid processing times.

Acknowledgements

The authors thank the US Department of Energy for support under the CRADA PTS LA95P10043-003

with the National Center for Manufacturing Sciences, and Ann Marie Kelly for preparation of SEM samples.

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Received 2 April
and accepted 14 July 1997