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Thermal diffusivity of chemically vapour deposited silicon carbide reinforced with silicon carbide or carbon fibres

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The thermal diffusivity of chemically vapour deposited silicon carbide reinforced with either Nicalon SiC yarn or PAN-precursor carbon fibres was measured by the laser-flash method during various time–temperature treatments. The diffusivity was found to depend on the degree of densification, the direction of heat flow with respect to the fibre orientation, and the thermal history. Structural modifications, confirmed by X-ray diffraction, produced large permanent changes in the thermal properties of the SiC–SiC composites when heated above 1200° C, while only minor changes were seen in C–SiC composites heated above 1500° C.

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1. Introduction

Materials intended for use at high temperatures should exhibit high melting points, chemical stability, high strength, and resistance to deformation by creep and failure by thermal shock. Because of the nature of atomic bonding and associated crystal structures encountered in materials for high-temperature service, they tend to be brittle, manifested by low fracture toughness, strength, and impact resistance together with a high susceptibility to catastrophic failure even under conditions of low and moderate thermal shock [1]. This is particularly so for single-phase high-temperature materials with homogeneous composition.

Major improvements in mechanical behaviour of brittle materials have been brought about by the development of composites. Greatly enhanced fracture toughness has been achieved by means of fibre reinforcement of glass and glass-ceramic matrices [2, 3]. Chemically vapour deposited (CVD) silicon carbide reinforced with silicon carbide or carbon fibres represents a special class of such fibre-reinforced materials.

In service, high-temperature materials frequently are subjected to high levels of transient or steady-state heat flow and/or thermal shock. The response of the material to such thermal conditions is a function of the relevant thermophysical properties. For engineering design and interpretation of performance data, these thermophysical properties should be carefully characterized in terms of parameters such as composition, relative density, method of fabrication, and thermal history. It is the purpose of this paper to report such data for the thermal diffusivity of composites consisting of CVD silicon carbide reinforced with silicon carbide or carbon fibres.

2. Experimental details

2.1. Materials

The carbon fibres used for the preparation of the C–SiC composites consisted of a bidirectional satin weave of staple fibres which were obtained

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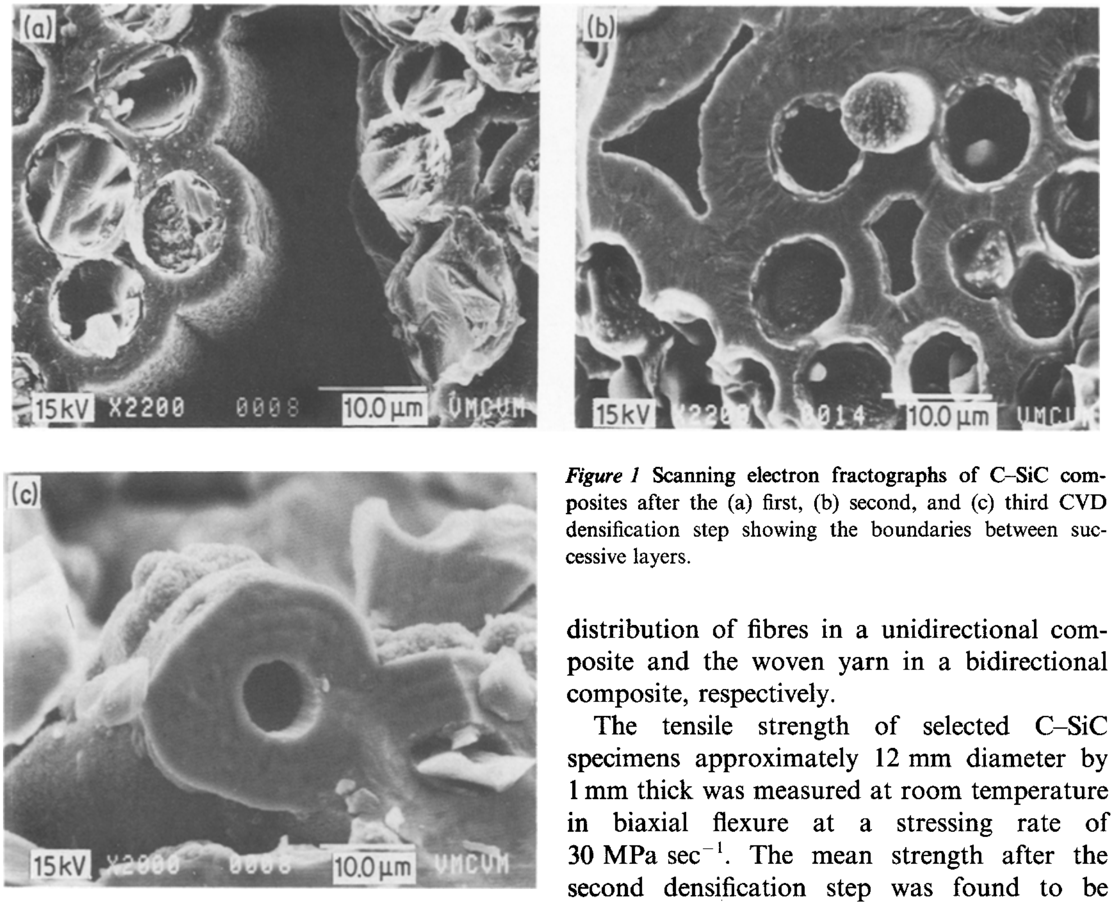

Figure 1 Scanning electron fractographs of C–SiC composites after the (a) first, (b) second, and (c) third CVD densification step showing the boundaries between successive layers.

from a polyacrylonitrile (PAN) precursor and then heat-treated. The fibre content in these composites was 28 vol %. The silicon carbide fibres in the SiC–SiC composites consisted of Nicalon yarn in either a bidirectional plain weave or a unidirectional orientation with a fibre content of 41 and 45 vol %, respectively.

The fibres were densified by chemical vapour deposition of SiC obtained from mixtures of methyltrichlorosilane and hydrogen at a temperature of about 1000° C. The densification was carried out in a maximum of three successive steps. After each step, the edges of the composite were ground to allow further penetration of the vapour into the interior of the block during the next densification step.

Fig. 1 shows three SEM fractographs of the C–SiC composite following each of the three densification steps. The successive layers of SiC which surround the carbon fibres after the second and third CVD steps are clearly evident. Figs. 2a and 2b are SEM fractographs of SiC–SiC after the second CVD step showing the distribution of fibres in a unidirectional composite and the woven yarn in a bidirectional composite, respectively.

The tensile strength of selected C–SiC specimens approximately 12 mm diameter by 1 mm thick was measured at room temperature in biaxial flexure at a stressing rate of 30 MPa $\sec^{-1}$. The mean strength after the second densification step was found to be 245 MPa, and no significant differences were found for the strength measured in mineral oil, water, or room air.

In order to establish evidence for structural changes due to thermal cycling, selected specimens were analysed by X-ray diffraction using Cu$K\alpha$ radiation. The density and porosity of the specimens used for the measurement of the thermal diffusivity were measured by the Archimedes method using water as the fluid medium.

2.2. Measurement of thermal diffusivity

The flash method [4] was used for measurement of the thermal diffusivity using a glass–neodymium laser as the flash source. The method basically consists of subjecting one face of a specimen in the form of a thin plate to a single laser flash, and then monitoring the transient temperature response of the other face. The specimens for this study ranged from 1 to 3 mm thick and were either square (9 mm × 9 mm) or circular (9 to 12 mm diameter). They were cut from larger blocks using a diamond core drill

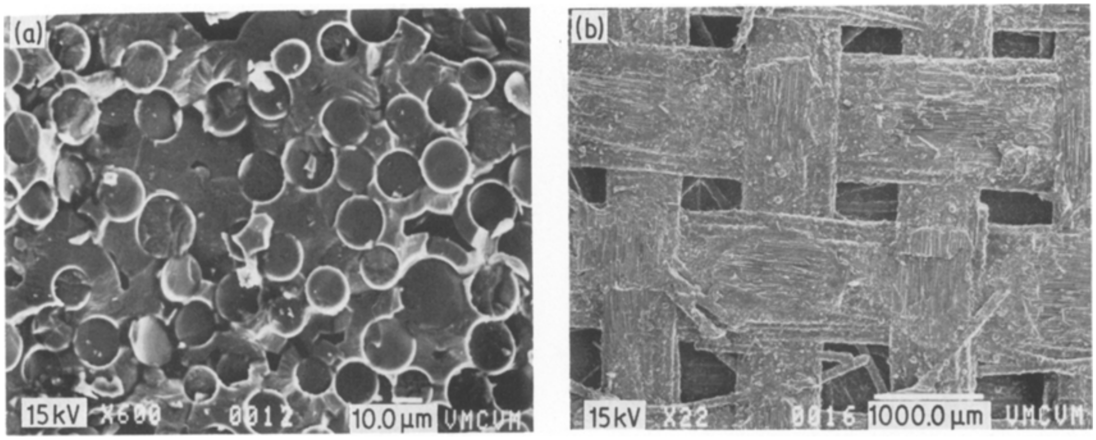

Figure 2 Scanning electron fractographs of SiC–SiC composites after the second densification step with fibres in a (a) unidirectional and (b) bidirectional weave orientation.

and a slow-speed diamond saw. For measurements at elevated temperatures, the specimens were placed in a suitable holder located in the centre of a carbon resistance furnace in which a continuous flow of nitrogen at atmospheric pressure was maintained. For most specimens the heating and cooling rate during temperature cycling averaged about 400° C h^{-1}. Measurements were taken every 100° C with about 10 min allotted for the change of the specimen's ambient temperature and about 5 min allotted for stabilization of the temperature followed by determination of the thermal diffusivity under isothermal conditions. The transient temperature response on the back face of the specimen was monitored with a liquid nitrogen cooled InSb infrared detector from 25 to about 600° C and with a silicon photodiode at higher temperatures.

After the first densification step, the unidirectionally reinforced SiC–SiC composites were sufficiently porous that measurement of the thermal diffusivity was precluded due to transmission of the laser beam through the total thickness of the specimen. A similar problem was encountered with the bidirectionally reinforced SiC–SiC composites for measurements parallel to one of the weave directions. However, in addition to the direction perpendicular to the fibres, the thermal diffusivity could be measured on specimens for which the direction of heat flow was at a 45° angle to both weave directions. Following the second densification step, the specimens were sufficiently dense that measurements could be made in all directions.

3. Results and discussion

3.1. SiC–SiC

Fig. 3 shows the experimental data for the thermal diffusivity of the SiC–SiC composites at room temperature after the first and second densification steps. The designation "perpendicular" in Fig. 3 denotes measurements with heat flow perpendicular to all the fibres for both the unidirectional and bidirectional composites. The "parallel" direction implies that heat flow was parallel to all the fibres in the unidirectional composites and parallel to the plane of the weave in the bidirectional composites, i.e. parallel to half and perpendicular to half of the fibres. For the data labelled "parallel to 45°", heat flow was in the plane of the bidirectional weave and at an angle of 45° to both weave directions.

The data clearly indicate that for all directions of heat flow, the thermal diffusivity increases with increasing density. Furthermore, the thermal diffusivity parallel to the fibres in the unidirectionally reinforced composites is higher than it is perpendicular to the fibres. The same is true in the bidirectionally reinforced composites for the diffusivity measured in the plane of the fibres compared to the value in the perpendicular direction. For the unidirectional composites, this effect is expected from the theory of the thermal conductivity of composites which requires that heat flow parallel to the fibres yields the maximum value of thermal conductivity [5]. The same effect is expected for the bidirectional composites; however, in this case for heat flow in the plane of the fibres, composite theory predicts that the thermal conductivity

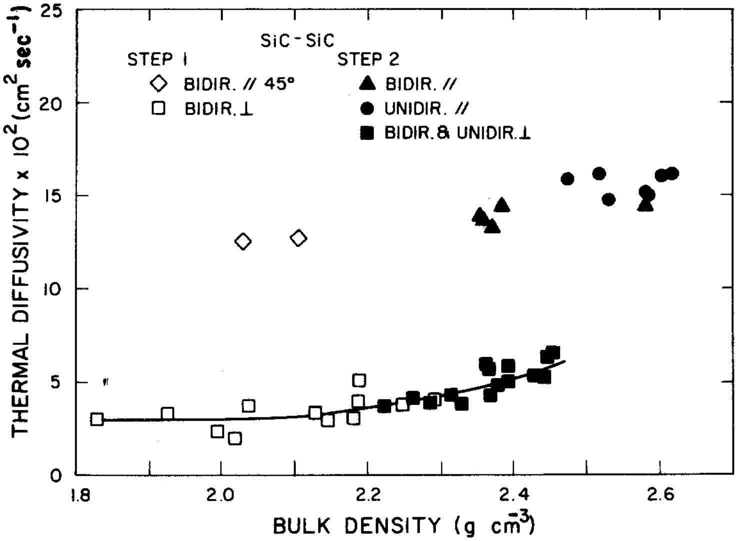

Figure 3 Thermal diffusivity of step 1 bidirectional and step 2 unidirectional and bidirectional SiC–SiC composites at room temperature for various fibre orientations.

should be somewhat less than for heat flow parallel to the fibres in the unidirectional composites. The data in Fig. 3 show that such a difference is relatively small.

The data shown in Fig. 3 indicate that a considerable variation in density exists among the specimens used for measurement of the thermal diffusivity. One major reason for such a range of density is that the densification of the composites is spatially non-uniform. An example of such non-uniformity is illustrated in Figs. 4a and b which show the through-thickness variations of the bulk density, open porosity, and thermal diffusivity perpendicular to the fibres for a bidirectionally reinforced composite that was densified twice. Each specimen about 1 mm thick was cut from a single 9 mm × 9 mm block 9.6 mm thick. The data indicate that regions of the block near the surface exhibit a higher density and corresponding thermal diffusivity than the interior of the block.

Fig. 5 shows the temperature dependence of twice-densified unidirectional SiC–SiC composites subjected to various heat treatments. The data in Figs. 5a and b were obtained by heating to 1200 and 1800° C, respectively, without a holding period at the peak temperature. In contrast, the data in Fig. 5c were obtained by heating to 1800° C in about 30 min, holding at this temperature for 3 h, and then cooling at the regular rate. As shown in Fig. 5a the data obtained during heating and cooling coincide, suggesting that heating to 1200° C over the time period involved produces no permanent structural or compositional changes in the composite. However, heating to 1800° C results in a significant increase in thermal diffusivity, terminating in a value at room temperature which is over two times greater. The time dependence of this change is exemplified by Fig. 5c which shows an even larger increase upon cooling, with the final room temperature value being over three times the initial value.

These permanent increases in thermal diffusivity were accompanied by mass losses and changes in the X-ray diffraction pattern as summarized in Table I for the data shown in Fig. 5 as well as for other heat treatment schedules. The mass losses are thought to be associated with compositional changes in the SiC fibres, most likely in the form of the loss of CO, as observed in Mah *et al.* [6]. This arises because the Nicalon SiC fibres actually contain about 25% silica and 10% carbon in addition to the SiC [7]. Mah *et al.* also noted a sharpening of the (1 1 1) diffraction peak of β-SiC, in agreement with the present findings. Such a sharpening of the diffraction peak indicates a change in the fibres from nearly amorphous to a more crystalline form which, due to a corresponding increase in the phonon mean-free-path, explains the observed increases in the thermal diffusivity. It can thus be concluded that the thermal diffusivity of these SiC–SiC composites is a function of thermal history above a temperature of 1200° C.

Fig. 6a shows the temperature dependence of the thermal diffusivity for two specimens of bidirectionally reinforced, twice-densified SiC–

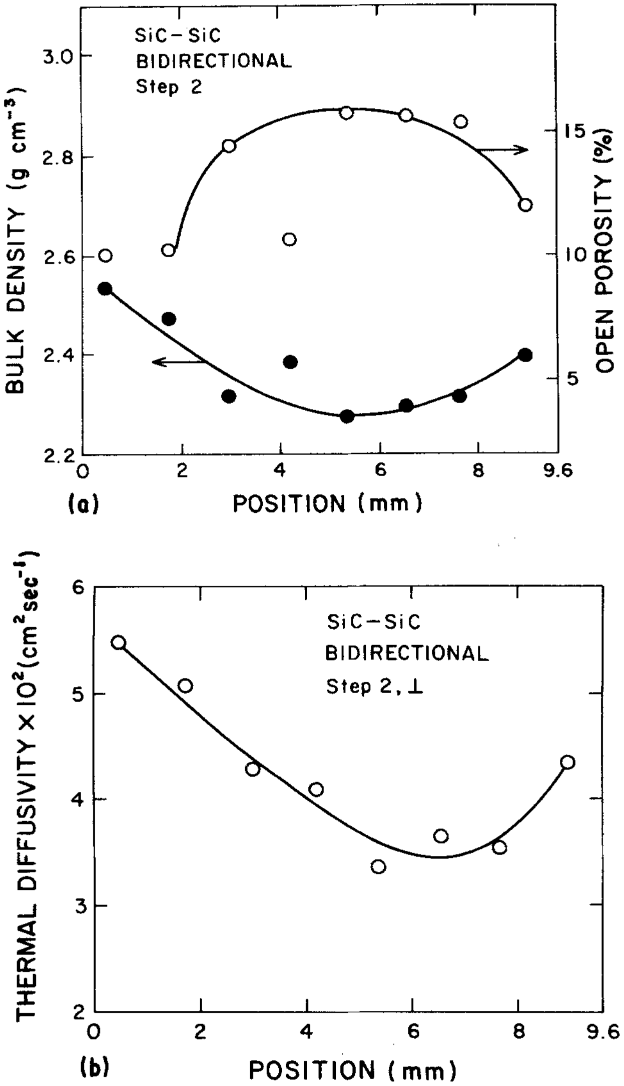

Figure 4 Variation of (a) bulk density and open porosity and (b) thermal diffusivity through the plate thickness of a step 2 bidirectional SiC–SiC composite.

SiC composites cycled to 1800° C. The diffusivity was measured perpendicular to the reinforcement (perpendicular to all fibres) and parallel to the reinforcement (parallel to half and perpendicular to half of the fibres). The values in the parallel direction are consistently higher than those in the perpendicular direction, and both show increases similar to Fig. 5. A comparable situation is shown in Fig. 6b for unidirectional composites cycled to 1400° C.

TABLE I Mass loss, room temperature thermal diffusivity, and change in the X-ray diffraction peak height of β-SiC for SiC–SiC specimens cycled to various temperatures

Temperature (° C)	Mass loss (%)	Thermal diffusivity (cm^2 sec^{-1})		Relative (1 1 1) peak height
		Initial	Final	
As-received	–	0.052	0.052	1.00
1200	1.4	0.057	0.057	1.00
1400	1.5	0.049	0.053	1.07
1600	2.3	0.056	0.071	1.58
1600/3 h	7.7	0.052	0.070	–
1800	7.9	0.065	0.140	1.80
1800/3 h	8.7	0.063	0.204	–

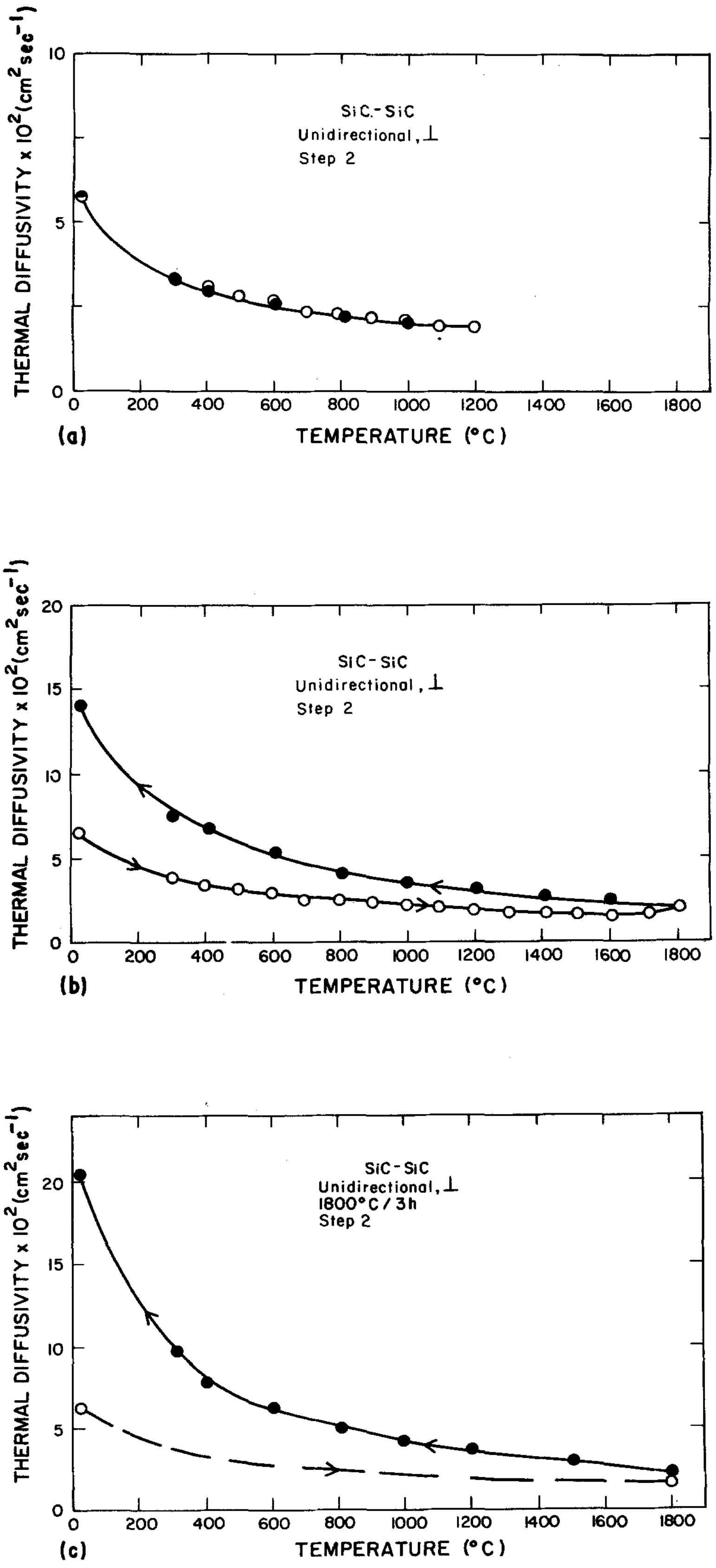

Figure 5 Temperature dependence of the thermal diffusivity perpendicular to the fibres in a step 2 unidirectional SiC–SiC composite (a) cycled to 1200° C, (b) cycled to 1800° C, and (c) heated rapidly to 1800° C, held for 3 h, and then cooled at the normal rate. The densities of the specimens were 2.39, 2.47, 2.45 g cm^{-3}, respectively. Open (closed) symbols indicate data taken during heating (cooling).

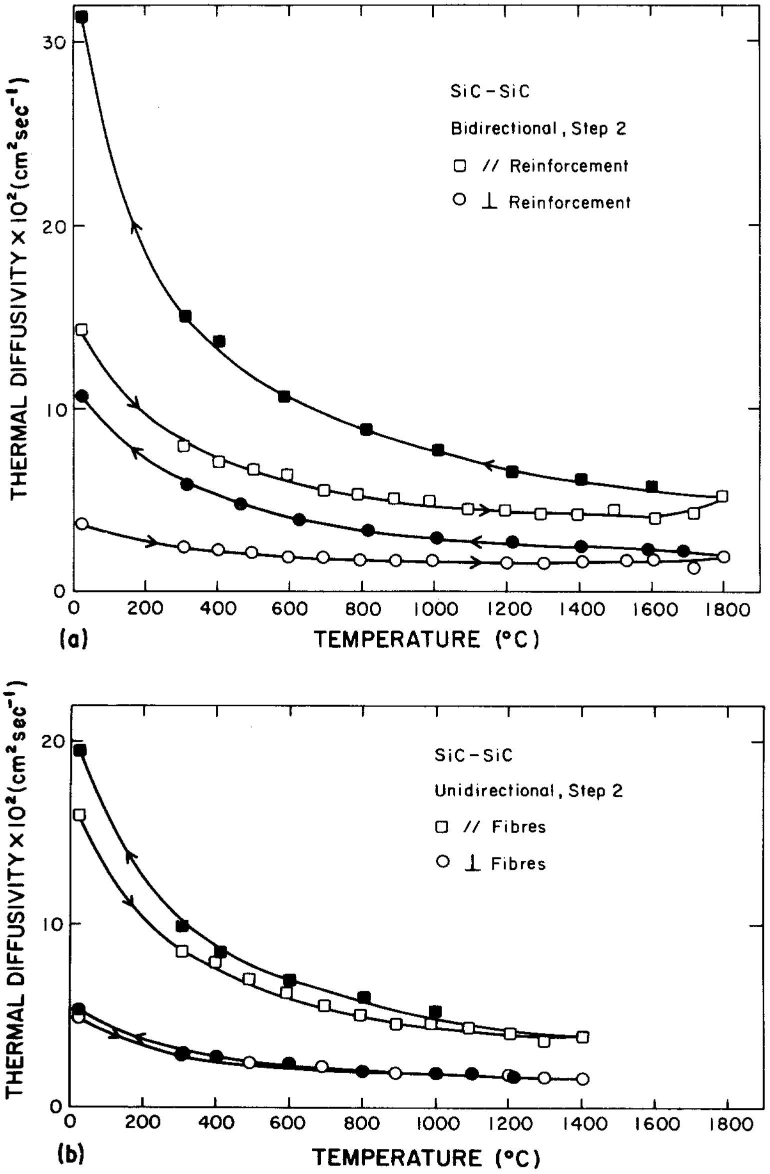

Figure 6 Temperature dependence of the thermal diffusivity parallel and perpendicular to the reinforcement in a step 2 SiC–SiC composite with (a) bidirectionally woven fibres, cycled to 1800° C, density of 2.58 and 2.33 g cm^{-3}, and (b) unidirectional fibres, cycled to 1400° C, density of 2.60 and 2.39 g cm^{-3}. Open (closed) symbols indicate data taken during heating (cooling).

The thermal diffusivity of the specimen of Fig. 6b measured parallel to the fibres was converted to thermal conductivity using the measured bulk density and the known specific heat of crystalline SiC [8] and the Nicalon fibres [7]. The resulting conductivity is given in Fig. 7 along with the thermal conductivity of the Nicalon fibres. Only values up to 1000° C are indicated since no hysteresis due to crystallization occurs below this temperature. Using the conductivity of the composite and of the fibres, the conductivity of the CVD SiC matrix was calculated by means of the theory for the thermal conductivity of mixtures for a uniaxial composite in which heat flow is parallel to cylindrical fibres [5]. The porosity in the composite was also assumed to be oriented along the fibre axis – a reasonable assumption judging by the microstructure. The resulting conductivity of the matrix material, which is also given in Fig. 7, shows a strong negative temperature dependence indicative of a crystalline material in which phonons are the primary mechanism of heat transfer. The values are considerably higher than those given by McMurtry *et al.* [9] for CVD SiC with an average crystallite size of 38.5 nm; however, they are considerably lower than values for other CVD SiC specimens measured in the

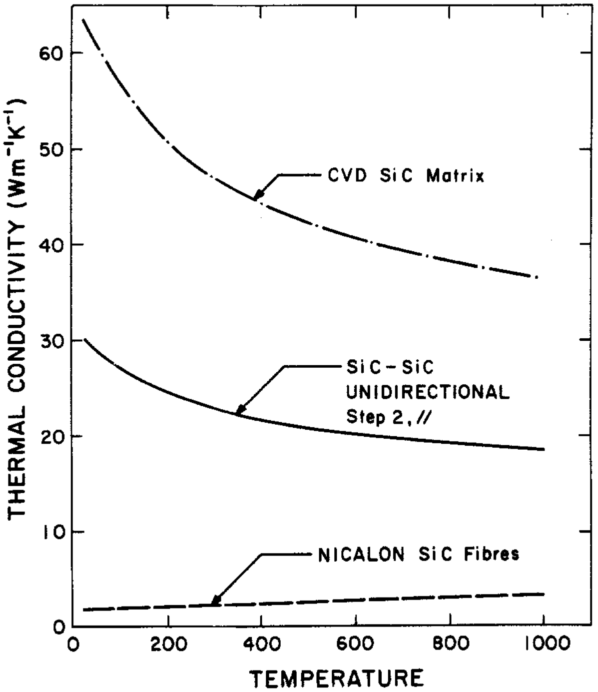

Figure 7 Thermal conductivity of the CVD SiC matrix determined from composite theory [5] using the conductivity of Nicalon SiC fibres [7] and the data from Fig. 6b where the diffusivity was measured parallel to the fibres.

authors' laboratory. This reflects the complex microstructure that results from various conditions used for CVD.

3.2. C–SiC

Fig. 8 shows the experimental data for the thermal diffusivity of the C–SiC composites at room temperature after each of the three densification steps. As for the SiC–SiC composites shown in Fig. 3, the thermal diffusivity of the C–SiC composites increases with increasing density and is higher when measured parallel to one of the fibre directions than it is perpendicular to all the fibres. Again, this is a result of the fibre geometry and does not imply that the diffusivity of the carbon fibres exceeds that of the CVD SiC matrix. However, comparison of the diffusivity data for the two types of composites shown in Figs. 3 and 8 reveals that at a given density, the diffusivity of the C–SiC exceeds that of the

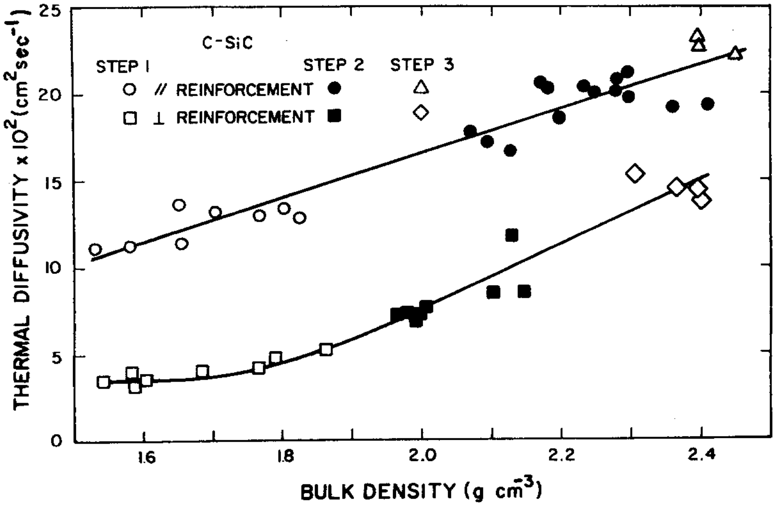

Figure 8 Thermal diffusivity parallel and perpendicular to the bidirectionally woven carbon reinforcement in step 1, 2 and 3 C–SiC specimens at room temperature.

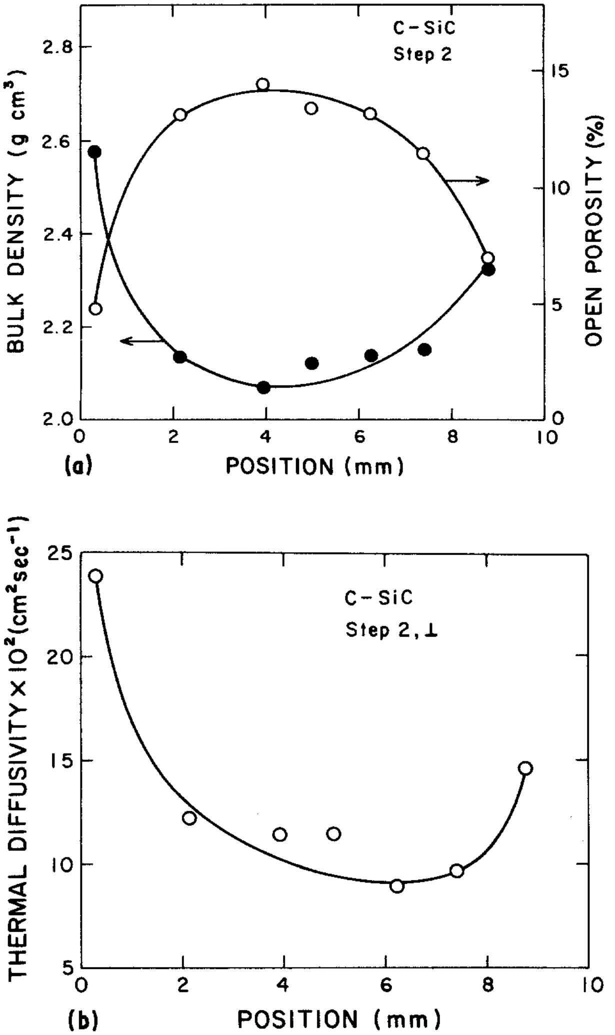

Figure 9 Variation of (a) bulk density and open porosity and (b) thermal diffusivity through the plate thickness of a step 2 C–SiC composite.

SiC–SiC composites. This can be attributed partly to the higher volume content of the denser, higher diffusivity CVD SiC phase in the C–SiC composites, and partly to the higher thermal conductivity of the carbon fibres compared to the SiC fibres [7, 10]. The complex pore structures in these materials prevent an accurate analysis of the differences in the thermal diffusivity between the two composite systems.

Figs. 9a and b show the spatial dependence of the bulk density, open porosity, and thermal diffusivity in a twice-densified block with a total thickness of 10 mm. These data are also similar to those of the SiC–SiC and indicate that the maximum densification in the CVD process occurs near the surface.

Fig. 10 shows the temperature dependence of the thermal diffusivity up to 1500° C of four C–SiC composites, two low density step 1 specimens and two intermediate density step 2 specimens. On return to room temperature, the thermal diffusivity for all specimens cycled to this temperature was essentially unchanged, being within the range of experimental accuracy of about 5%. This indicates that over the time period of the measurement, heating to 1500° C does not produce a permanent structural or compositional change in the composite. However, note that at the higher temperatures, the thermal diffusivity of the low density specimens is almost independent of temperature, whereas the higher density specimens of the second densification step show a more negative temperature dependence. This difference can be attributed to a larger contribution to the heat flow by radiation across the pores in the low density specimens [11].

Fig. 11 gives the temperature dependence of

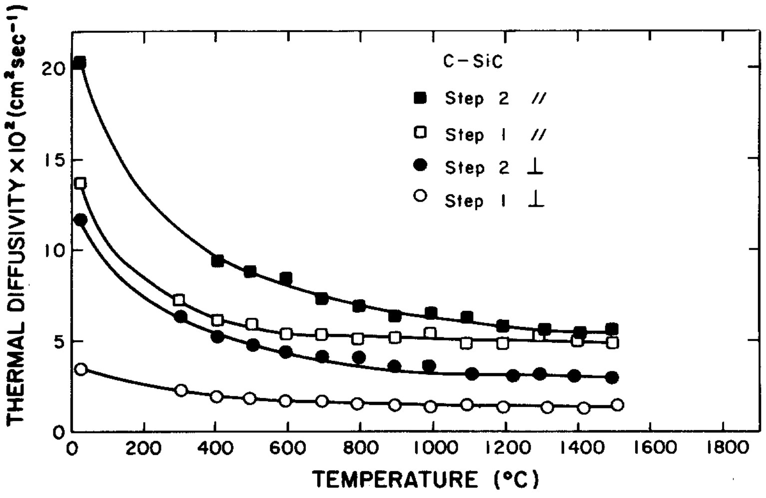

Figure 10 Temperature dependence of the thermal diffusivity to 1500° C parallel and perpendicular to the reinforcement in both low density step 1 (1.66 and 1.54 g cm^{-3}) and intermediate density step 2 (2.33 and 2.13 g cm^{-3}) C–SiC specimens.

the thermal diffusivity measured up to 1800° C parallel and perpendicular to the reinforcement on twice-densified specimens of intermediate density, 2.23 and 2.13 g cm^{-3}, respectively. The data taken during cooling are higher than those during heating, but the relative increase is much less than that observed in the SiC–SiC composites cycled to the same temperature as shown in Fig. 5b. X-ray diffraction analysis revealed that the carbon fibres were unaffected and that the increase in diffusivity could be attributed to a slight change in the CVD SiC matrix, possibly an annealing of defects and slight grain growth.

Fig. 12 shows the temperature dependence of the thermal diffusivity parallel and perpendicular to the reinforcement for two step 3 specimens with densities of 2.40 and 2.37 g cm^{-3}, respectively. These densities are among the highest values measured for twice-densified C–SiC and are significantly higher than those of the specimens of Fig. 11. These specimens also show a permanent increase in the thermal diffusivity following heating to 1800° C, but only at temperatures above about 300° C. Further cooling produces an apparent discontinuity such that the diffusivity falls below the data obtained during heating. This effect was also observed for specimens heated rapidly to 1800° C and held for 3 h before cooling. A similar crossover was also observed for heavily microcracked polycrystalline aluminium titanate [12], which was attributed to the generation of a higher density of microcracks following heating to the higher temperatures. A similar effect related to the density may be operating in the step 3 C–SiC composites which contain the maximum amount of CVD SiC. In support of this, Fig. 13 shows a scanning electron fracto-

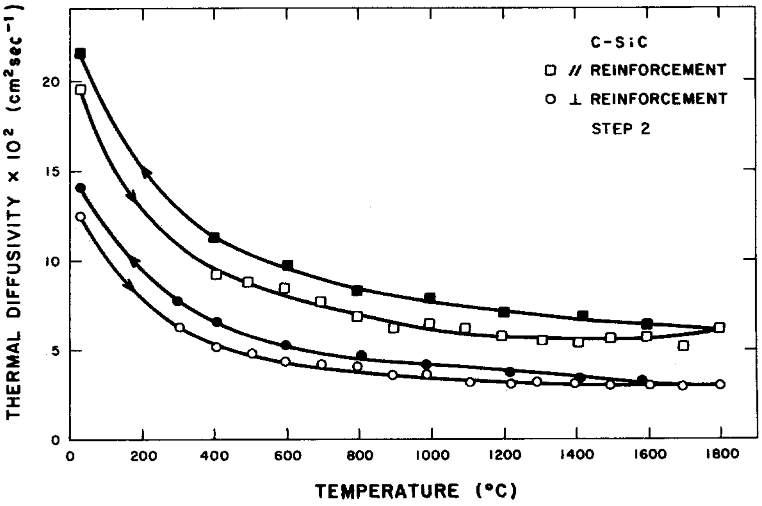

Figure 11 Temperature dependence of the thermal diffusivity parallel and perpendicular to the reinforcement in step 2 C–SiC specimens of intermediate density cycled to 1800° C. Open (closed) symbols indicate data taken during heating (cooling).

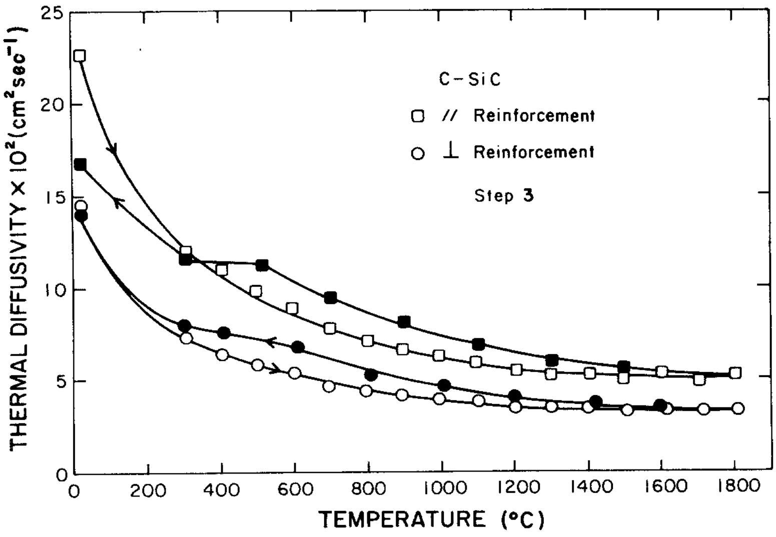

Figure 12 Temperature dependence of the thermal diffusivity parallel and perpendicular to the reinforcement in step 3 C–SiC specimens cycled to 1800° C. Open (closed) symbols indicate data taken during heating (cooling).

graph of the sample used for the measurement of thermal diffusivity parallel to the reinforcement. This micrograph depicts a crack through the SiC matrix perpendicular to the direction of heat flow. The presence of such a crack or cracks would tend to lower the thermal diffusivity [13].

4. Conclusions

The thermal diffusivity of SiC–SiC and C–SiC composites was found to depend on the degree of densification and the direction relative to the fibre orientation. Compositional and structural modifications in the SiC fibres and the CVD SiC matrix resulting in permanent changes in the thermal diffusivity were produced by heating SiC–SiC composites to temperature above 1200° C and C–SiC composites to temperatures above 1500° C. The modifications to the Nicalon fibres, and thus to the SiC–SiC composites, were found to be time-dependent, whereas, over the time period of the measurement, the modifications in the C–SiC composites had considerably less effect on the overall thermal diffusivity and were dependent only on the maximum temperature attained. Crystallization in the SiC–SiC composites was accompanied by pronounced mass losses which were not observed in the C–SiC composites. The theory for the thermal conductivity of composites revealed that the CVD SiC matrix had a conductivity that was much larger than for the C or SiC fibres and was of intermediate value compared to CVD SiC materials from other sources.

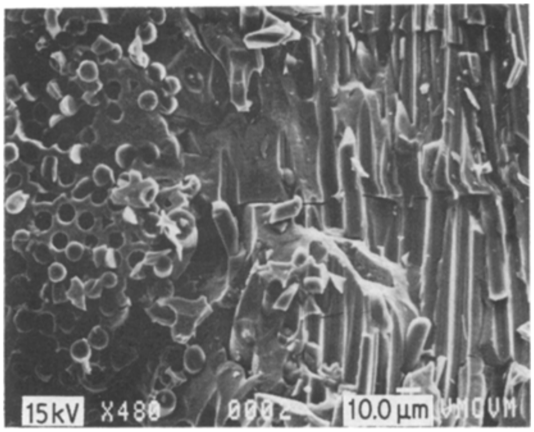

Figure 13 Scanning electron fractograph of a step 3 C–SiC specimen showing a crack in the SiC matrix perpendicular to the direction of heat flow.

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