

Heat conduction characteristics of a carbon-fibre-reinforced lithia-alumino-silicate glass-ceramic

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A study was conducted of the thermal diffusivity, specific heat and thermal conductivity of a uniaxially carbon-fibre-reinforced lithia-alumino-silicate glass-ceramic. The thermal diffusivity and conductivity parallel to the fibre direction was found to be independent of thermal history and more than an order of magnitude higher than in the transverse directions. During the first thermal cycle, the thermal diffusivity transverse to the fibre direction was found to exhibit a decrease attributed to crack formation under the influence of internal stresses. The transverse thermal diffusivity on thermal cycling to 1000°C exhibited lower values during heating than during subsequent cooling. This hysteresis was attributed to a thermal history-dependent barrier to heat flow at the matrix-fibre interface. The thermal conductivity of the fibres along their length inferred from composite theory was found to be much lower than the corresponding value for pyrolytic graphite, attributed to less than complete graphitization and associated high density of lattice defects which act as phonon scatterers.

1. Introduction

Glasses, glass-ceramics and ceramic matrices reinforced with fibres or whiskers represent a new class of refractory composites for service conditions involving high temperatures. These composites are characterized by greatly improved fracture toughness, impact resistance and greatly increased tolerance to mechanical surface damage compared to many single-phase brittle materials for structural purposes [1-4]. Service at elevated temperatures frequently requires that the materials of construction be subjected to high levels of transient or steady-state heat flow. Some designs such as heat exchangers require that candidate materials have thermal conductivity and thermal diffusivity as high as possible. This latter requirement also is essential for high resistance to catastrophic failure by thermal shock [5]. In contrast, other designs require the thermal conductivity to be as low as possible to keep heat losses to a minimum for purposes of energy conservation. For this reason, a knowledge of the thermo-physical behaviour of refractory fibre- or whisker-reinforced composites is essential for purposes of engineering design. For performance predictions and the development of new composites with specified values of thermal conductivity or diffusivity for a given application, a detailed understanding of the underlying variables which control their thermo-physical characteristics is required.

An earlier study [5] of the thermal diffusivity of fibre-reinforced composites showed that a lithia-alumino-silicate glass-ceramic uniaxially reinforced

by amorphous silicon carbide fibres showed excellent thermal insulating behaviour due to the low thermal diffusivity of both the matrix phase as well as the silicon carbide fibres.

In a further study [6] it was observed that for composites of amorphous silicon-carbide-fibre-reinforced CVD-SiC heated to temperatures in excess of 1400°C, the thermal diffusivity on return to room temperature exhibited a permanent increase, attributed to the crystallization and compositional changes in the silicon carbide fibres. CVD-SiC reinforced with carbon fibres, however, showed only a slight increase in thermal diffusivity on heating to temperatures as high as 1800°C, as the result of the much higher thermal stability of the carbon fibres compared to the amorphous silicon carbide fibres. Pertinent to the results of this investigation, it was found in another study [7] that the thermal conductivity of carbon-fibre-reinforced epoxy resins could be described by the appropriate theory for the thermal conductivity of composites.

The purpose of the present study was to establish some of the variables which affect the conduction of heat in a composite of a unidirectionally carbon fibre-reinforced lithia-alumino-silicate glass-ceramic.

2. Experimental procedures

2.1. Materials

The matrix phase of the composites of this study consisted of a lithia-alumino-silicate glass-ceramic with molar ratios of the Li_2O , Al_2O_3 and SiO_2 of

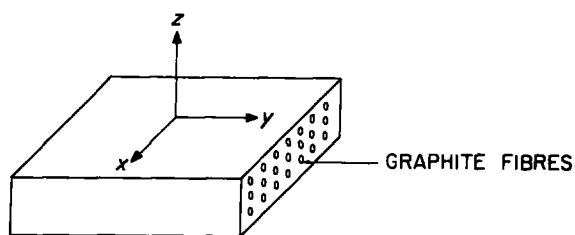


Figure 1 Orientation of carbon-fibre reinforced lithium-alumina-silicate glass-ceramic.

1:1.2:6, with minor amounts of MgO and ZnO substituted for the Li_2O , and with TiO_2 and ZrO_2 added as nucleating agents. Crystallization was carried out at 1000°C for 2 h which resulted in the stuffed α -quartz crystal structure with density of $\sim 2.50\text{ g cm}^{-2}$.

The carbon fibres made by the pyrolysis of polyacrylonitrile (PAN) fibres (Hercules HMS PAN-based fibres with Young's modulus $\sim 350\text{ GPa}$) were in the form of tows of yarn with about 6000 fibres per tow. The average fibre diameter was $\sim 7.3\ \mu\text{m}$ and had a density of $\sim 1.877\text{ g cm}^{-2}$. The cross-section of the fibre was generally circularly symmetric with the basal plane concentric around the centre of the fibre. With this orientation, the axis of each fibre corresponded to the crystallographic directions within the basal plane of the graphite crystal structure.

A block of the uniaxially reinforced composite was made by passing the yarn through a slurry of the powder of the uncrystallized glass suspended in an aqueous medium. Following drying the coated yarns were cut to the proper length and laid parallel in a graphite die followed by hot-pressing in a nitrogen atmosphere at a temperature of $\sim 1300^\circ\text{C}$ and pressure of $\sim 6.9\text{ MPa}$. Following densification, the die was cooled to 1000°C while under pressure and held for 2 h to assure complete crystallization. The die was then cooled to room temperature with the pressure gradually released as cooling proceeded. The fibre volume fraction of the hot-pressed composite was $\sim 30\%$. The composite final density was $\sim 2.15\text{ g cm}^{-3}$. For purposes of convenience of reporting the data relative to the fibre direction, Fig. 1 shows the xyz -coordinate system with the axes of the fibres coinciding with the y axis.

Figs 2a and b show photomicrographs of a polished section of the composite perpendicular to the fibre direction. The inhomogeneous distribution of the fibres indicated by Fig. 2a is thought to be reflective of the original existence of the carbon fibres in tow form as well as the specific procedure selected for the manufacture of the composite. Fig. 2b shows an area within the composite with a relatively high fibre concentration, which indicates the full penetration of the matrix material between the fibres of each tow.

Figs 3a and b show SEM fractographs perpendicular and parallel to the fibre direction, respectively. The generally clean fracture along the interface indicates a low degree of adhesion between the carbon fibres and LAS matrix. Some areas of actual physical separation between the fibres and matrix are clearly evident.

2.2. Measurement of thermophysical properties

The thermal diffusivity was measured by the flash method [8] using a neodymium-glass laser as the flash source. The specimens for these measurements were in the form of $\sim 8 \times 10 \times 2\text{ mm}$ rectangular platelets cut from the hot-pressed billet with a slow speed precision diamond saw. Possible transmission of the laser beam was prevented by coating the specimens with a thin layer of colloidal carbon. The transient temperature response of the specimen rear surface was monitored by remote optical sensing, with a viewing spot size on the specimen approximately 5 mm in diameter. This viewing area is sufficiently large compared to the scale of the microstructure for the detector to sense the average temperature of the specimen surface. For this reason, complexities are avoided in evaluating the thermal diffusivity due to local surface temperature differences which arise from differences in the thermal conductivity and diffusivity of the fibres and the matrix [9, 10]. For measurements above room temperature the specimens were held in a carbon resistance furnace with nitrogen atmosphere. In the evaluation of the thermal diffusivity from the transient temperature response, the corrections for the finite laser pulse width and heat losses were taken into account using the analysis of Heckman [11].

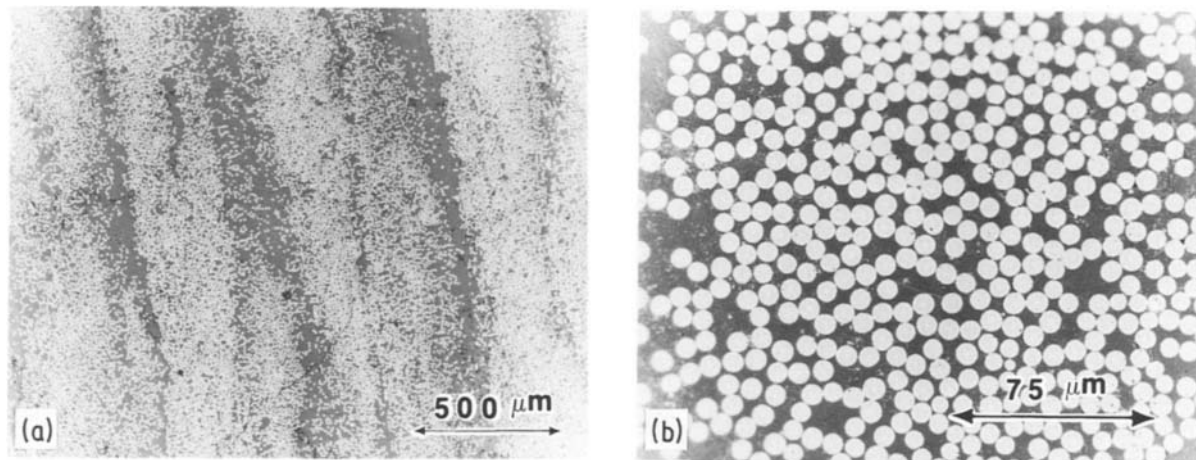


Figure 2 Photomicrographs of carbon fibre-reinforced lithia-alumino-silicate glass-ceramic at two different magnifications.

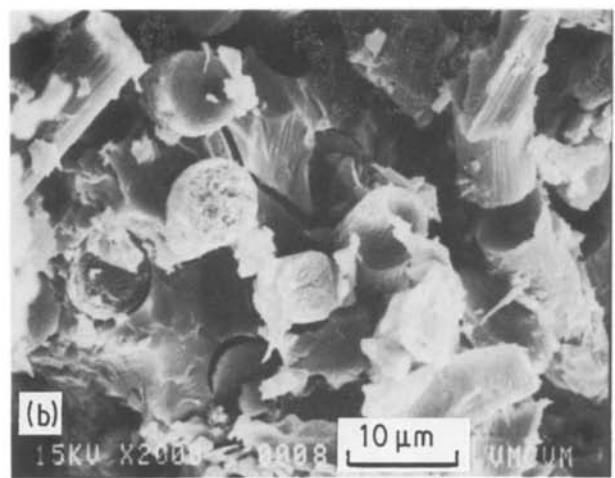
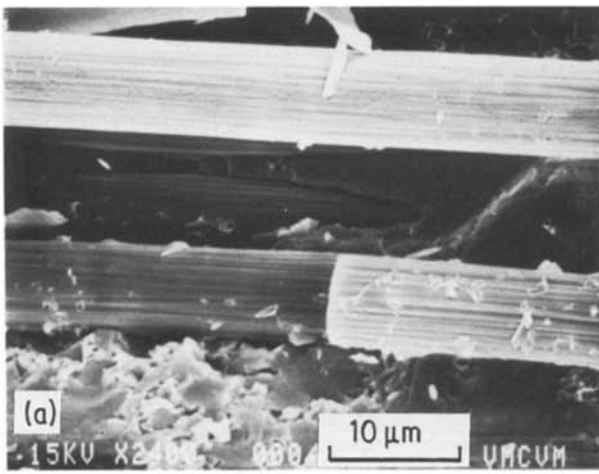


Figure 3 SEM-fractographs of uniaxial carbon fibre reinforced lithia-alumino-silicate glass-ceramic: (a) parallel and (b) perpendicular to fibre direction.

Preliminary data indicated that for heat flow perpendicular to the fibre-direction a permanent decrease in thermal diffusivity was obtained, which also was found to be a function of the maximum temperature reached. For this reason, measurements were made over two successive thermal cycles up to temperatures of approximately 350, 600 and 1000°C. Furthermore, data were also obtained for one specimen held at approximately 300°C over a period of about 4 h.

The specific heat was determined by differential scanning calorimetry from room temperature to 600°C. The combined data for the thermal diffusivity, specific heat and density were used to calculate the effective thermal conductivity, K by means of the relation:

$$K = \kappa \rho c \quad (1)$$

where κ is the thermal diffusivity, ρ is the density and c is the specific heat. Basically, such a calculation of the thermal conductivity involves multiplication of the thermal diffusivity by a constant. For the purpose of conservation of space, this calculation is left to the reader, with the exception of heat flow parallel to the fibre direction in order to calculate the corresponding value of the thermal conductivity of the fibres themselves.

3. Experimental results, discussion and conclusions

3.1. Thermal diffusivity

Fig. 4 shows the experimental data for the thermal diffusivity at room temperature as a function of specimen thickness for the LAS matrix without fibres and for the x , y and z directions for the carbon fibre-LAS composites. These data indicate that the value for the thermal diffusivity of the composite in the y axis parallel to the fibre direction is much higher than in the x and z directions and also much higher than the corresponding value of the matrix phase. Such differences in thermal diffusivity can be attributed to two effects. Firstly, as indicated by the theory [12] for the thermal conductivity of composites of isotropic materials, the thermal conductivity parallel to the fibre direction corresponds to the maximum value

(upper bound) for such a composite, regardless of the relative value of the thermal conductivity of the components. For the present composite, by far the major contributing factor for the much higher thermal diffusivity in the y direction is that the axes of the fibres coincide with the graphite basal plane, which as indicated by corresponding data for pyrolytic graphite [13, 14, 15] coincides with the direction of maximum thermal conductivity/diffusivity in the graphite crystal structure. Perpendicular to this direction, the thermal conductivity/diffusivity can be less by as much as a few orders of magnitude. For this reason, for heat flow perpendicular to the fibre direction, the presence of the fibres is expected to have a much smaller effect on the thermal diffusivity, as observed. In fact, in the x and z directions the thermal diffusivity is increased by less than a factor of two over the corresponding value of the matrix. As will be shown later, perpendicular to the fibre direction the conduction of heat also appears to be affected by the presence of a thermal barrier resistance.

The data shown in Fig. 4 also indicate the existence of a specimen size effect on the thermal diffusivity of the LAS-matrix but the absence of such an effect in the carbon fibre-LAS composites for all three directions. The finding of such a size effect for the matrix agrees with similar findings in earlier studies [5, 19, 15]. The existence of such a size effect is indicative of a contribution of radiative heat transfer directly across the specimen to the total thermal conductivity. The absence of a specimen size effect on the thermal diffusivity in all three directions within the composite most probably can be attributed to the high value of the absorption coefficient of the carbon fibres which effectively suppresses the radiative contribution to the total heat being conducted.

Fig. 5 shows the data for the temperature dependence of the thermal diffusivity of the LAS-matrix without fibres up to 900°C for a specimen with thickness of 1.97 mm, which is outside the range of thickness for which the thermal diffusivity is thickness dependent as shown in Fig. 4a. Up to about 300 to 400°C, the data in Fig. 5 show a negative temperature dependence expected for a dielectric crystalline solid

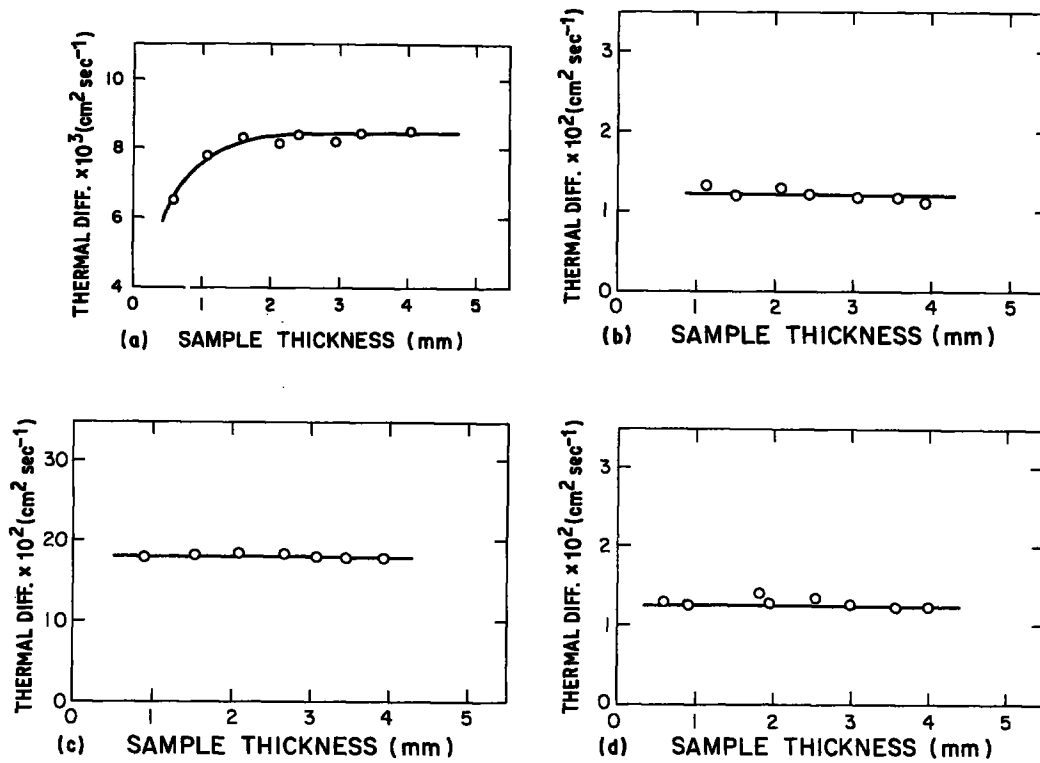


Figure 4 Dependence of thermal diffusivity at room temperature on specimen thickness for: (a) lithia-alumina-silicate (LAS) matrix and (b), (c), (d) carbon fibre-reinforced LAS matrix for the three fibre directions indicated in Fig. 1; (b) x axis; (c) y axis; (d) z axis.

in which heat is conducted primarily by phonon conduction. Above 400°C, however, the thermal diffusivity appears to be independent of temperature, most likely due to an increased contribution of radiation, with its associated positive temperature dependence, to the total heat transferred. It should be noted that on heating and cooling the data coincide, which indicates that over the temperature involved the specimen did not undergo any permanent changes which affected the conduction of heat.

Fig. 6 shows the experimental data for the thermal diffusivity of the carbon fibre-LAS composite along

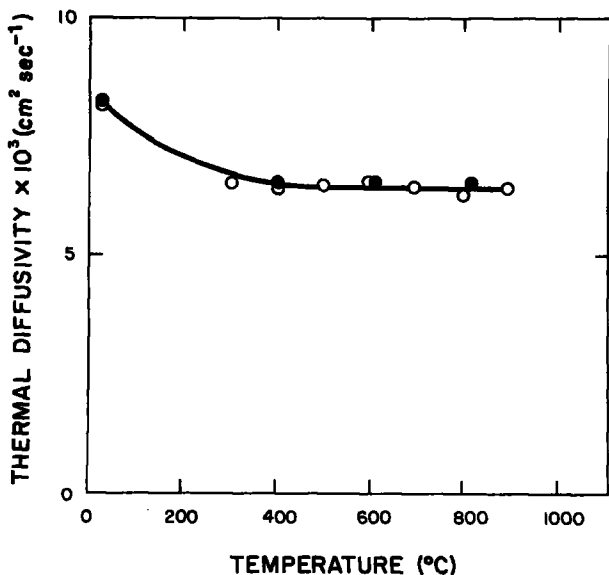


Figure 5 Temperature dependence of the thermal diffusivity of lithia-alumina-silicate glass-ceramic matrix. (○) heating, (●) cooling.

the y axis (parallel to the direction of the fibres) as a function of temperature for two samples heated to 600 or 1000°C. These data indicate the existence of a negative temperature dependence of the thermal diffusivity over the total range of temperature. In addition, the data obtained on heating or cooling are identical within the experimental error. It was also found that on re-measurement of the thermal diffusivity over subsequent thermal cycles, the data were identical within the experimental error. These observations suggest that for heat flow parallel to the fibre axis, the thermal diffusivity is not affected by permanent structural or compositional changes in the fibres or matrix phase.

Figs 7a-c show the experimental data for the thermal diffusivity along the x axis, perpendicular to the axes of the fibres, for separate specimens heated and cooled to ~350, 600 and 1000°C, respectively, over two successive thermal cycles. The data for heat flow in the z-direction were essentially identical to those in the x direction shown in Fig. 7. Also, the data for subsequent cycles were the same as those for the second cycle within experimental error.

The data shown in Fig. 7 indicate a totally different relative dependence of the thermal diffusivity on temperature compared to the data shown in Fig. 6 for heat flow parallel to the fibre length. Two effects appear to be operative for heat flow perpendicular to the fibre direction. Firstly, on heating during the first cycle the thermal diffusivity appears to undergo a permanent decrease which is not recovered on cooling. Secondly, during the second cycle on heating and cooling to 1000°C the thermal diffusivity appears to exhibit a

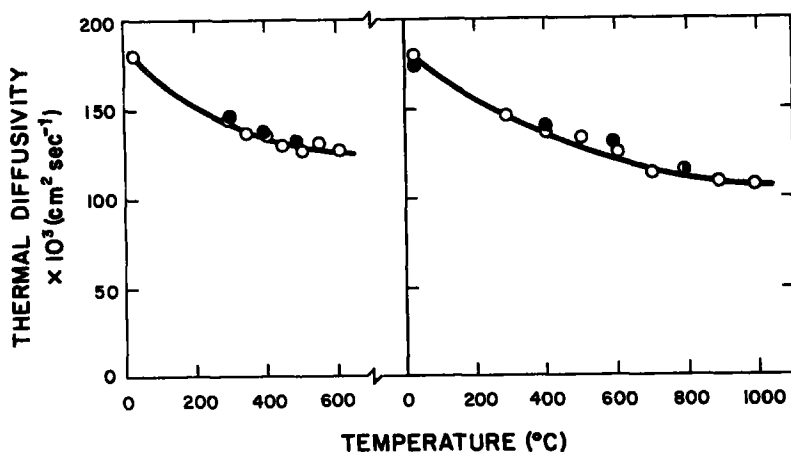


Figure 6 Temperature dependence of the thermal diffusivity of uniaxial carbon fibre reinforced lithia-alumina-silicate glass-ceramic parallel to fibre direction. (y axis) (○) heating, (●) cooling.

hysteresis with the data on cooling exceeding the data on heating.

The permanent decrease in thermal diffusivity during the first thermal cycle must be attributed to the formation of structural discontinuities which inhibit the conduction of heat. It was found, as shown in Fig. 8, that this decrease in thermal diffusivity was time-dependent during an isothermal anneal at 300°C for 4 h. Because the formation of these discontinuities appears to require an elevated temperature above room temperature, it appears to be governed by a thermally activated process. As shown in Fig. 9, optical microscopy of a polished 8 × 2 mm side-surface of the specimen used for the generation of the data shown in Fig. 8, revealed the formation of cracks following the 4 h anneal at 300°C. Such cracks were not present prior to the annealing treatment. As clearly indicated by Fig. 8, the cracks form perpendicular to the surface and parallel to the fibre direction. It also appears that whenever possible the fibre-matrix interface was the preferred path of crack propagation. Such fracture along the interface would be promoted by incomplete adhesion between the matrix and the fibres. Cracks have been shown to be very effective in lowering the thermal conductivity [18]. Furthermore, the sub-critical growth of cracks is governed by a time- and temperature-dependent thermally activated process [19]. For these combined reasons, the permanent decrease in thermal diffusivity during the first thermal cycle is most likely due to the formation of cracks.

The permanent crack-opening displacement evident in Fig. 9 suggests that residual stresses provide the driving force for crack formation. As established in an earlier study [20], crack formation represents a possible mechanism for residual stress relief. In the present composites, residual stresses can arise from a number of sources. The thermal expansion mismatch between the fibres with a coefficient of thermal expansion perpendicular to the fibre direction $\sim 18 \times 10^{-6} \text{C}^{-1}$ [21] greatly exceeds the corresponding value for the matrix with $\alpha < 1 \times 10^{-6} \text{C}^{-1}$. The direction of this mismatch is such that cooling from the crystallization temperature results in localized radial tensile stresses within the fibres and in the matrix immediately surrounding the fibres. Especially for less than perfect adhesion between the matrix and fibres, such radial

stresses would promote interfacial fracture and separation. However, because of the simultaneous existence of compressive tangential stresses, it is not clear why the thermal expansion mismatch would promote crack formation between a number of adjacent fibres. Internal stresses which arise on cooling to thermal equilibrium at room temperature from spatially non-uniform temperatures during hot-pressing and crystallization are thought to be a further source for the crack formation. These stresses are expected to exist over larger regions of the composite and therefore can result in cracks which can propagate along a number of neighbouring fibres as shown in Fig. 9. Another possible source of internal stresses is the elastic bending of bundles of carbon fibres during hot-pressing and cooling under load, which cannot be relieved by creep of the fibres themselves at the temperatures at which the matrix can undergo significant non-linear deformation. Finally, the approximately 6% decrease in volume of the glass-ceramic during crystallization is expected to result in internal stresses of high magnitude and may well be the primary reason for the formation of the cracks shown in Fig. 9.

The hysteresis in thermal diffusivity on heating and cooling evident on heating to $\sim 1000^\circ \text{C}$ and absent on heating to 350 and 600°C, as shown in Fig. 7, is thought to be related to the existence of a thermal history-dependent thermal barrier resistance at the matrix-fibre interface, which arises from the thermal expansion mismatch between the matrix and the fibre perpendicular to the fibre direction. Because of this mismatch in thermal expansion, on cooling from the processing temperature the fibres will undergo a relatively greater decrease in dimensions than the surrounding matrix. As the result of poor adhesion, an interfacial gap with poor thermal conductance will develop between the fibres and the matrix. Because of the existence of this interfacial gap the fibres cannot contribute to the overall thermal diffusivity to the extent that would be seen if perfect thermal contact existed between the matrix and the fibres. On heating, however, the interfacial gap will narrow with a corresponding decrease in the thermal resistance at the interface. If so, the temperature dependence of the thermal diffusivity is expected to be governed by the corresponding temperature dependence of the matrix and the fibres as well as the interface. The experimental

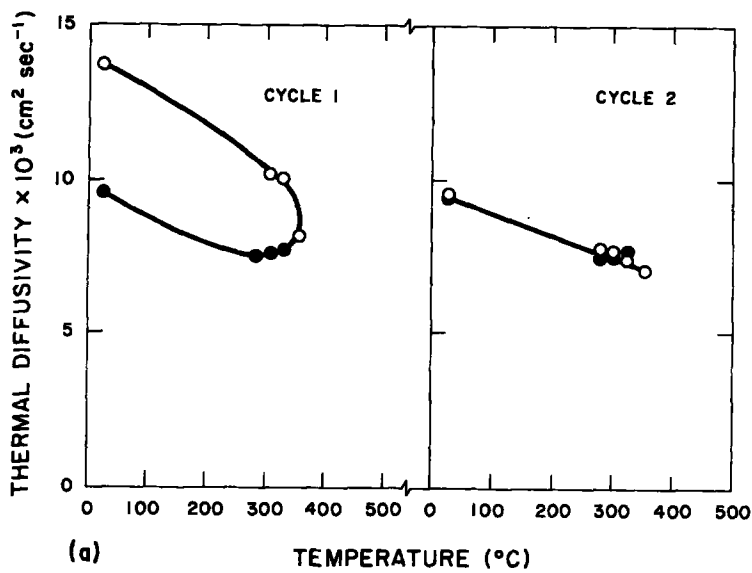
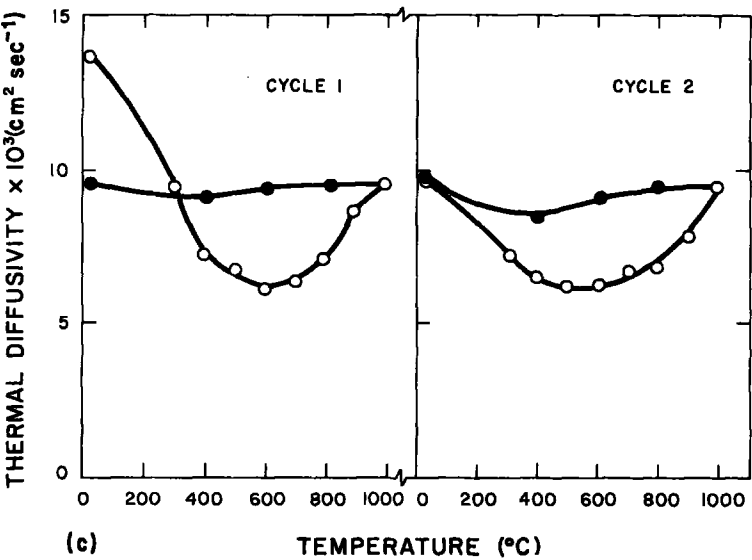
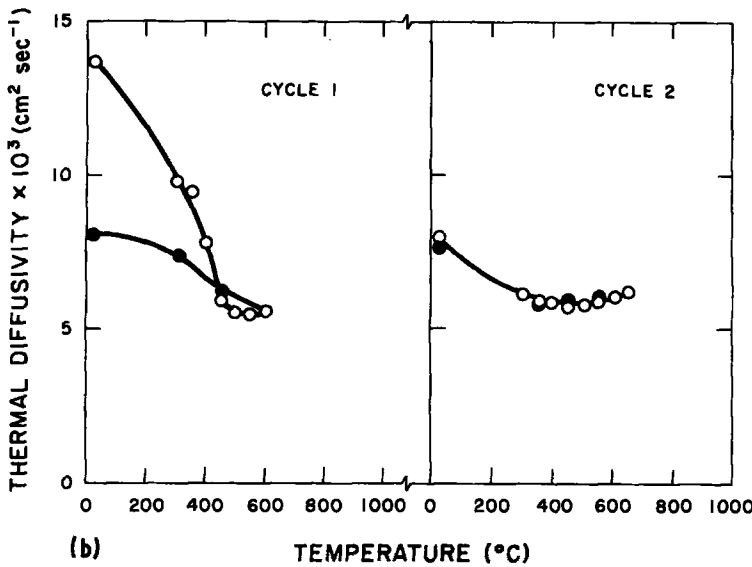


Figure 7 Temperature dependence of the thermal diffusivity of carbon fibre-reinforced lithia-alumino-silicate glass-ceramics, perpendicular to fibre direction (x axis), to temperatures of (a) 350, (b) 600 and (c) 1000° C. (○) heating, (●) cooling.



data shown in Fig. 7 suggest that at least qualitatively up to approximately 600° C the negative temperature dependence of the thermal diffusivity is governed primarily by the corresponding negative temperature dependence of the thermal diffusivity of the matrix and the fibres. Above 600 to 1000° C, however, the effectiveness of the interfacial thermal barrier resistance

decreases sufficiently rapidly with temperature to result in a strongly positive temperature dependence of the overall thermal diffusivity of the composite. A similar positive temperature dependence of the thermal diffusivity was observed for a composite of a low thermal expansion borosilicate glass with non-bonding nickel dispersions [22].

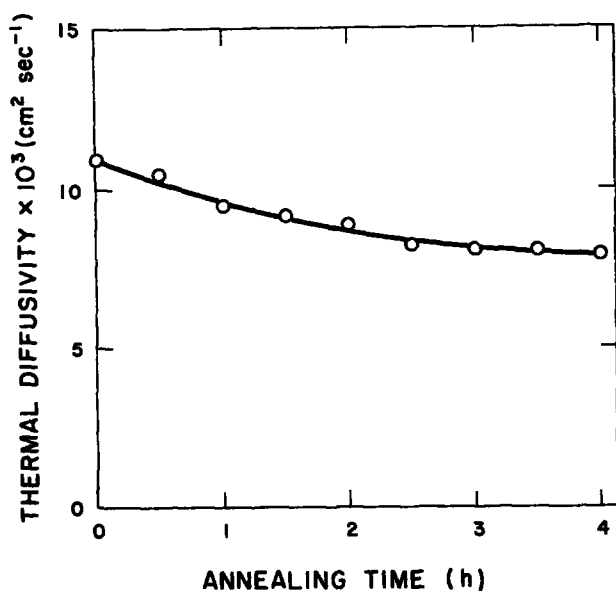


Figure 8 Time dependence of thermal diffusivity of uniaxial carbon fibre reinforced lithia-alumina-silicate glass-ceramic perpendicular to fibre direction at 300°C.

If the magnitude of the interfacial thermal barrier resistance was strictly a function of the absolute value of temperature, the thermal diffusivity at any temperature would be independent of thermal history. However, the existence of a pronounced hysteresis in thermal diffusivity on heating to and cooling from 1000°C suggests that the thermal barrier resistance indeed is a function of thermal history. It is speculated here that the existence of the hysteresis in thermal diffusivity represents evidence for the existence of some degree of adhesion between the fibres and matrix at the higher levels of temperature. Such adhesion is re-established on reaching the temperature of 1000°C. Cooling from this temperature must occur over some range of temperature before the internal stresses which arise from the thermal expansion mismatch become sufficiently high to exceed the adhesive forces

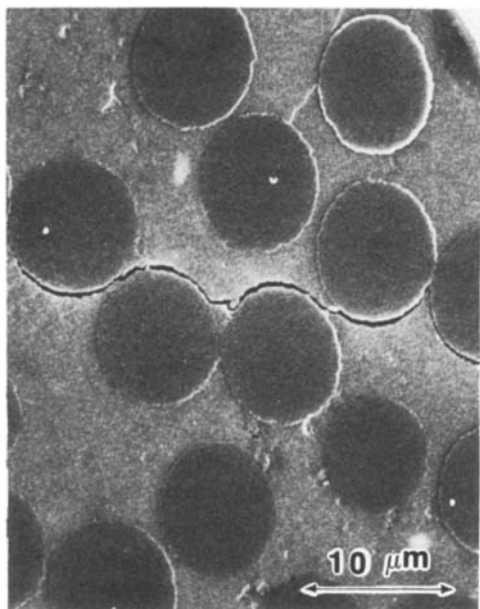


Figure 9 Crack formation in uniaxial carbon fibre reinforced lithia-alumina-silicate glass-ceramic annealed for 4 h at 1000°C.

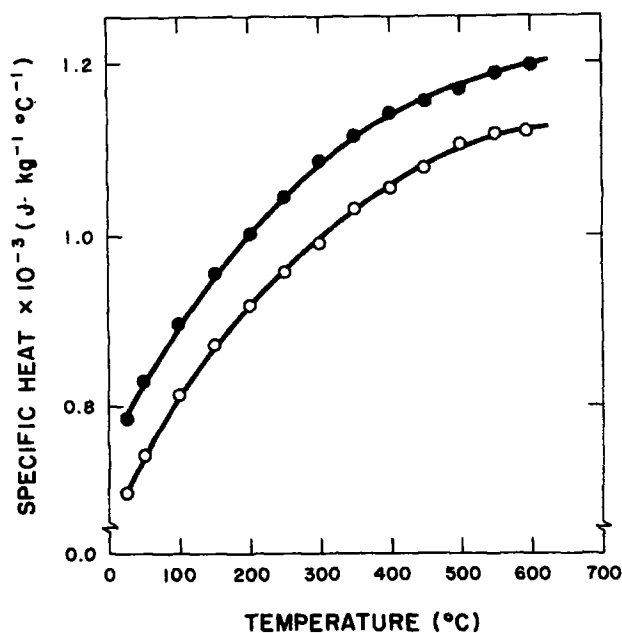


Figure 10 Specific heat of lithia-alumina-silicate glass-ceramic matrix ●, without and ○, with uniaxial carbon fibre reinforcement (~30 vol %).

at the interface. For this reason, on cooling from any temperature at which interfacial adhesion has been partially or completely re-established, the values of the thermal diffusivity will exceed the corresponding values obtained during the heating part of the cycle over which the thermal barrier resistance of the interfacial gap was still fully effective. A similar hysteresis in the thermal diffusivity on heating and cooling was observed for heavily microcracked brittle single-phase and composite materials, which was attributed to the closure and healing of the microcracks at the higher levels of temperature [23–26].

3.2. Specific heat

Fig. 10 shows the experimental data for the specific heat of the matrix without and with the ~30 vol % carbon fibres. These data indicate that the specific heat of the composite is less than that of the matrix. This is to be expected because the specific heat of graphite or diamond as indicated by literature data [27] is less than that of the LAS matrix over the temperature range of this study.

3.3. Thermal conductivity

The values of thermal conductivity which correspond to the experimental data for the thermal diffusivity can be calculated by means of Equation 1, taking into account the changes in density due to the effects of thermal expansion. Because the specific heat and density are scalar quantities, the data for thermal conductivity for the different directions of heat flow and thermal histories at any temperature will show the identical quantitative difference. The thermal conductivity, primarily as the result of the positive temperature dependence of the specific heat, will exhibit a more positive relative temperature dependence than the thermal diffusivity.

For purposes of evaluating the thermal conductivity of the fibres parallel to their axes, Fig. 11 shows

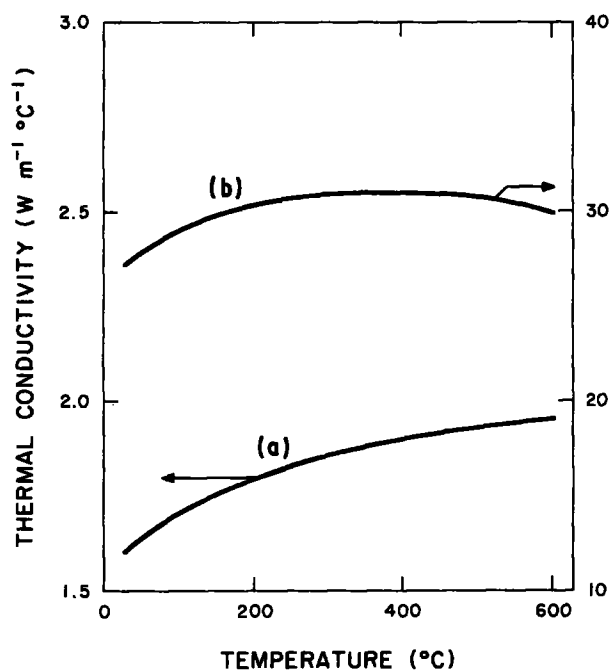


Figure 11 Thermal conductivity of lithia-alumina-silicate glass-ceramic matrix (a) without and (b) with uniaxial carbon fibre reinforcement parallel to fibre direction.

the calculated values of the thermal conductivity from room temperature to $\sim 600^\circ\text{C}$ for the LAS matrix without and with the carbon fibres calculated from the smooth curve drawn through the corresponding data for the thermal diffusivity shown in Figs 5 and 6. The LAS matrix phase shows a positive dependence of thermal conductivity on temperature over the total temperature range. This effect arises because the relative positive temperature dependence of the specific heat exceeds the relative negative temperature dependence of the thermal conductivity. At least surprising at first sight to the present authors, a similar positive temperature dependence is also exhibited by the composite, with the exception of the highest temperature levels over which the thermal conductivity exhibits a slight negative temperature dependence. Because of the strongly negative temperature dependence of polycrystalline graphite [28] and especially of pyrolytic graphite within the basal plane [13, 14, 15], it was expected that the thermal conductivity of the LAS-carbon fibre composite also would exhibit a strong negative temperature dependence. A partial answer to this apparent discrepancy can be provided by an estimate of the thermal conductivity of the fibres themselves.

For a two-component uniaxially fibre-reinforced composite with heat flow along the fibres, the effective thermal conductivity is:

$$K_c = K_1 V_1 + K_2 V_2 \quad (2)$$

where K is the thermal conductivity, V is the volume fraction and the subscripts c, 1 and 2 refer to the composite, matrix and fibres, respectively. Fig. 11 shows that at room temperature, $K_c \sim 27 \text{ W m}^{-1} \text{ K}^{-1}$, and $K_1 \sim 1.6 \text{ W m}^{-1} \text{ K}^{-1}$. For $V_2 \sim 30 \text{ vol } \%$, Equation 2 yields for the thermal conductivity of the fibres along their axial direction, $K_2 \sim 90 \text{ W m}^{-1} \text{ K}^{-1}$. This value is much less than the values of thermal

conductivity of 306 and $1840 \text{ W m}^{-1} \text{ K}^{-1}$ and comparable values for as-deposited and annealed pyrolytic graphite, respectively, within the basal plane at room temperature as found by Null *et al.* [15] and others [29, 30, 31, 32], but compares more favourably with the value of $\sim 150 \text{ W m}^{-1} \text{ K}^{-1}$, found by Heremans *et al.* [33] and $\sim 175 \text{ W m}^{-1} \text{ K}^{-1}$ found by Nysten *et al.* [34], by the direct measurement of the thermal conductivity of PAN-based carbon fibres. These low values for the thermal conductivity and associated relatively small temperature dependence are attributed to the high concentration of lattice defects in these PAN-based carbon fibres [34].

As a final comment, it should be noted that, at least in principle, with the aid of composite theory the transverse thermal conductivity of the fibres can be calculated as well. However, the solutions for the effective thermal conductivity of fibrous composites of which these authors are aware, do not take into account the existence of an interfacial barrier resistance nor the effect of crack formation. Ignoring these effects would result in values of the transverse thermal conductivity of the fibres which are too low and not representative of the actual behaviour of the fibres. The inclusion of these effects will require the development of the appropriate theory.

Acknowledgements

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