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Effect of heat treatment in air on the thermal properties of SiC fibre reinforced composite: Part 2 A magnesium aluminium silicate (MAS) matrix glass ceramic composite

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Abstract The thermal properties of a magnesium aluminium silicate (MAS) glass ceramic matrix composite reinforced by SiC (Nicalon) fibres have been investigated before and after heat treatment in the temperature range 600–1,200 °C. Within this temperature range, during the heat treatment at lower temperatures such as 600 and 700 °C, the oxidation of the carbon layer occurred and mixture of silicon and carbon was formed in the interface. This results in a decrease in thermal diffusivity values. After heat treatment at the temperatures higher than 1,000 °C, the carbon layer was thickened and resulted in the higher thermal diffusivity values.

Introduction

SiC fibre reinforced glass ceramic matrix composites have been developing over last three decades as possible high performance materials for high temperature applications [1]. Magnesium aluminium silicate (MAS) matrix glass ceramic composites are candidate materials for high temperature applications that have been investigated [2–6].

During the manufacturing stage, due to fibre and matrix reaction, a carbon rich layer is formed [7, 8] in SiC fibre reinforced glass ceramic composites. This carbon rich layer has also been observed in MAS glass ceramic composites. This layer and its effect on the composite behaviour can be affected by the temperature to which the composites have been exposed [2, 6, 9, 10].

A systematic study the effect of heat treatment on the microstructure and thermal properties of a barium osumilite matrix, SiC fibre (Tyronno) reinforced glass ceramic matrix composite has been reported in part 1 of this study [11]. The changes that can occur during heat treatment are influenced by the nature of the interface formed between fibre and matrix during the processing. This in turn will be affected by the fibre and matrix chosen. In this study, a similar investigation has been carried out to monitor the effects of heat treatment on the microstructure and thermal diffusivity of a different system. In this case the system chosen was a magnesium alumina silicate (MAS) matrix composite reinforced with SiC (Nicalon) fibres.

Experimental

Materials

The 0/90/45 degree laminated SiC/MAS cordierite composite was supplied by the National Physical Laboratory. This composite was manufactured by Corning using the glass slurry infiltration route followed by hot pressing. The composite reinforcement was Nicalon fibres of approximately 15 μm in diameter. A fibre yarn was desized in a tube furnace, drawn through a glass slurry and then wound onto a drum. The fibres were then dried to form a tape before it was cut and stacked in a hot press. Hot pressing was carried out at a temperature above the softening point of glass but below the onset of crystallisation. After hot

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pressing, the glass matrix composite was given a two-stage nucleation and growth heat treatment to convert the glass matrix into a glass ceramic matrix.

X-ray diffraction analysis

X-ray diffraction studies were carried out to identify all the phases present in the composite. These were performed using a PHILIPS E'XPERT diffractometer PW 3710. X-ray analyses were carried out on both as fabricated and heat-treated samples using plates 10 mm^2 and 2 mm thick. Scans at a step width of 0.005° for 2θ values from 10° to 70° were used. The diffraction traces were compared against standard XRD patterns of a range of possible matrix constituents.

Microstructural examination

Polished sections of the composite for analysis were prepared by the following procedure. The samples were first cut from the plate. They were prepared by the method mentioned in the first part 1 of this investigation [11]. Mounted samples were ground using by 400 grit SiC abrasive paper followed by successively finer grades of silicon carbide papers from a 400 to 1200 grit. The samples were then lightly polished using 6 and 1 μm diamond paste. Final polishing was carried out with colloidal silica and samples were then washed, cleaned and dried.

The samples were placed on to an aluminium stub and coated with carbon or gold in order to prevent charging in the microscope. A conducting silver paste was used with the carbon-coated samples painted on the edge of the sample connecting it with the stub to improve electrical contact. The surface of the heat-treated samples were examined using Philips 505 and 525 scanning electron microscopes (SEM) operating at 20 kV.

Specimens were prepared for transmission electron microscopes (TEM) by a combination of mechanical polishing and ion beam thinning techniques previously described [11]. The electron microscopy studies were carried out using Philips EM 400 and CM 20 microscopes operated at 120 and 200 kV both were equipped with an energy dispersive spectroscopy (EDS) analysis system.

Thermal properties

Thermal diffusivity measurements were carried out using the laser flash method originally described by Parker et al. [12]. The thermal diffusivity equipment used at UMIST has been previously described in detail in a paper by Taylor [13]. Sample sizes and preparation were as detailed in part 1 and measurements again were carried out over temperature range 100–1,000 °C [11].

Results and discussions

X ray diffraction analysis

An XRD trace of the as fabricated material from $10 < 2\theta < 70$ is shown in Fig. 1. Two phases can be detected α-cordierite ($Mg_2Al_4Si_5O_{18}$) and surprisingly celsian ($BaAl_2Si_2O_8$). This provides clear evidence that the base frit from which this glass ceramic composite was fabricated contains some BaO. The presence of a peak at $2\theta = 34.5$ shows that some crystalline SiC was present in the fibre. Examination of the mound between 30 and 40 shows a significant glassy phase content was present. The formation of α-cordierite from mullite + liquid is time and temperature dependent and favoured by a slow cooling rate [4].

Thermal properties

Based on experience learned from studies of the BMAS composite [11] only heat treatment times and temperatures which are thought to be informative were selected. These were 600, 700, 1,000 and 1,200 °C for 30 h. All heat treatments were carried out in air.

Figure 2 shows thermal diffusivity results obtained after heat treatment for 30 h at each of the four selected temperatures. After the heat treatment at 1,000 °C, the thermal diffusivity results were consistently higher than that of the as-received material whereas the material heat treated at 1,200 °C shows very similar values. The results, obtained for 600 and 700 °C, show lower thermal diffusivities than the as-received material and moreover show negligible difference between the two heat treatment temperatures. The thermal diffusivity for all heat treatment temperature converges on the as received results at a measurement temperatures for 1,000 and 1,200 °C. This is in marked contrast to the results for SiC/BMAS composite where after all heat treatment temperatures the diffusivity maintains the same consistent difference over the whole temperature

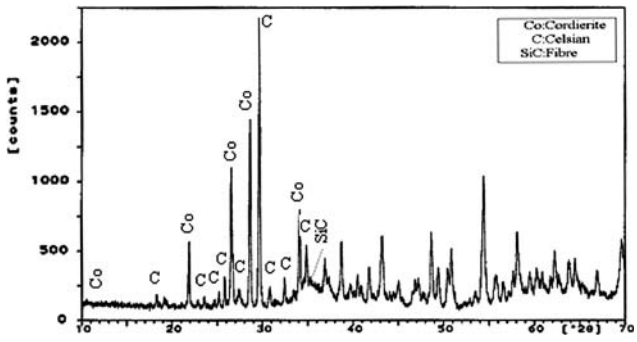

Fig. 1 X-ray spectrum of as-received material of MAS/SiC composites

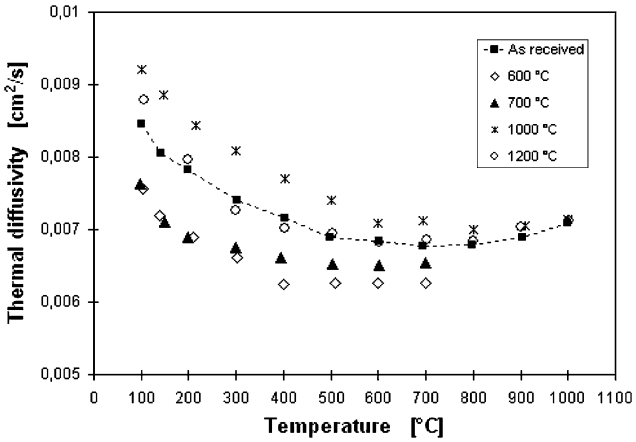

Fig. 2 Measurement of thermal diffusivity of MAS/SiC CMC after heat treatment in air for 30 h

range [11]. To illustrate these points we compare, in Table 1 the results for two composites that heat treated in air for 30 h for three selected temperatures 100, 500, 900 °C.

Microstructural studies

SEM studies were carried out on the heat-treated samples. As can be seen in Fig. 3, the sample heated at the lower temperature (600 °C) showed significant amount of glassy phase on the surface of the sample. Some glassy phase was present around the fibre was also evident. The same situation seems to be occurring here. After removal of the carbon around the fibre gaps and voids occurred and these were filled by the residual glassy phases present as in the matrix. Here also cracks in the interface and debonding between the fibre and matrix were observed (Fig. 4). Similar observations were obtained in other studies [3, 9]. After the higher temperature heat treatment at 1,000 and 1,200 °C the gaps around the fibre appeared to have disappeared (Fig. 5a, b) and also fine grain phases were observed. The higher temperature heat treatment seems to provide improved bonding at the interface, which results in higher values of the thermal diffusivity. These SEM results were in good agreement with the previous findings except that recrystalisation was not as obvious as for the SEM results of SiC/BMAS composites. This may be because this composite does not contain as much residual glassy phase as the SiC/BMAS composite does [11].

TEM studies were only carried out on the samples of SiC/MAS, which were heat treated at 700 and 1,200 °C. Figure 6 shows the interface between fibre and matrix together with EDS data and a selected area diffraction pattern from a region near to the matrix for the sample heated to 700 °C. At the interface there is a clear peak for silicon with traces of oxygen and carbon. The selected area diffraction pattern shows that region is amorphous.

A TEM micrograph from the fibre/matrix interface of a region heated to 1,200 °C is shown in Fig. 7 together with a SAD pattern, which shows the region to be amorphous and two EDS analyses, one from near the fibre the other from the centre of the interfacial region. Near to the fibre interface can be seen a large Si peak and smaller peaks due to Mg, Al, O and C. The interface is also much thicker (150 nm) than that observed after the lower temperature heat treatment and also much thicker than that observed in the BMAS material after a similar heat treatment [11].

Discussion

In spite of the limited experimental data generated from this study it is clear that there are significant differences in thermal diffusivity values after at higher and lower temperature heat treatments. After heat treatment at low temperatures (600 and 700 °C), thermal diffusivity values decrease significantly. After heat treatment at these temperatures, as noted in the TEM micrographs, there is a gap in the interface. This is a result of the oxidation of the carbon to leave a silicon rich region noted in previous studies [10, 11].

The reduction in oxygen content of the interfacial layer suggests that this mechanism may be a contributory factor although not the only one to account for the dramatic decrease in thermal diffusivity values after heat treatment at 700 °C. The rate of oxidation of C increases with the temperature and the degradation is slower due to the kinetics of oxidation. Residual glassy phases in the matrix begin to soften with the temperature and flow into the gaps. At lower temperature, this flow was limited therefore, at

Table 1 The summary of the thermal diffusivity results measured at 100, 500 and 900 °C after heat treatment in air for 30 h

Measurement temperature (°C)	Heat treatment temperature (°C)				
	As received	600	700	1000	1200
	Thermal diffusivity (cm^2/s) × 10^3				
100	8.5	7.4	7.4	9.2	8.7
500	6.9	6.3	6.5	7.4	6.9
900	7.1	7.1	–	7.1	7.1

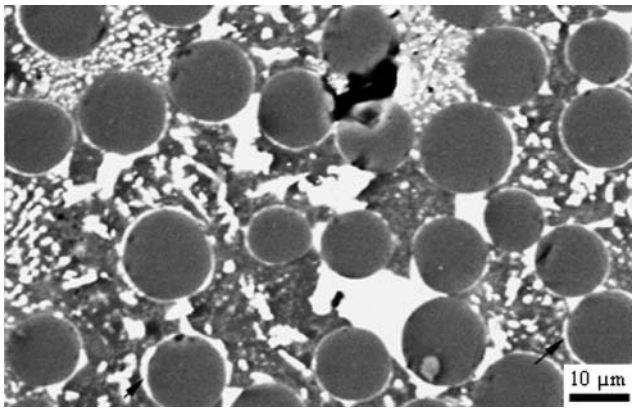

Fig. 3 Back-scattered electron SEM images of the MAS matrix composite heated at 600 °C general microstructure showing glassy phase distribution in the matrix and around fibres

lower heat treatment temperature such as 600 or 700 °C, the residual glassy phases attempt to flow to fill the voids at the interface or concentrate at local regions in the matrix.

After heat treatment to higher temperatures such as 1,000 and 1,200 °C, the microstructure of the interface changes and the thickness increases to ~150 nm. This is much higher then that noted 30 nm for SiC (Nicalon)/MAS composite [14] and 20 nm noted for SiC (Tyranno)/BMAS composite Plucknett et al. [10], Yilmaz et al. [11]. The thermal diffusivity increases for the composite annealed at 1,000 °C but is largely unchanged for the composite annealed at 1,200 °C.

The changes occurring after heat treatment and differences with the results for BMAS are of particular interest with special emphasis on the changes occurring at the fibre/matrix interface. The first noteworthy feature is that after heat treatments with all samples, the microstructure of the interface changes. In particular at high temperatures (above 1,000 °C) the thickness of the interface increases mark-

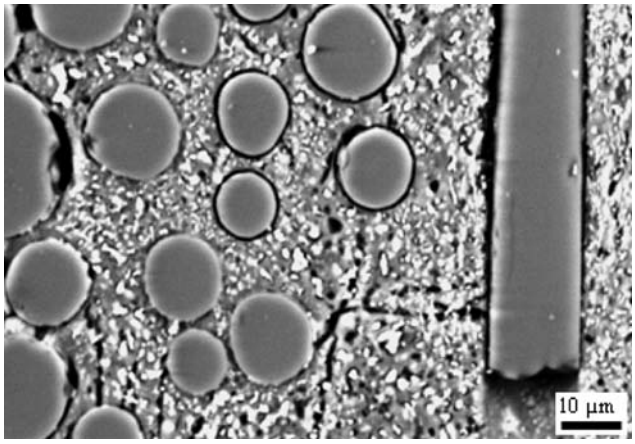

Fig. 4 Back-scattered electron SEM images of SiC/MAS composite showing crack in the matrix and gap around the fibre heat treatment at 700 °C

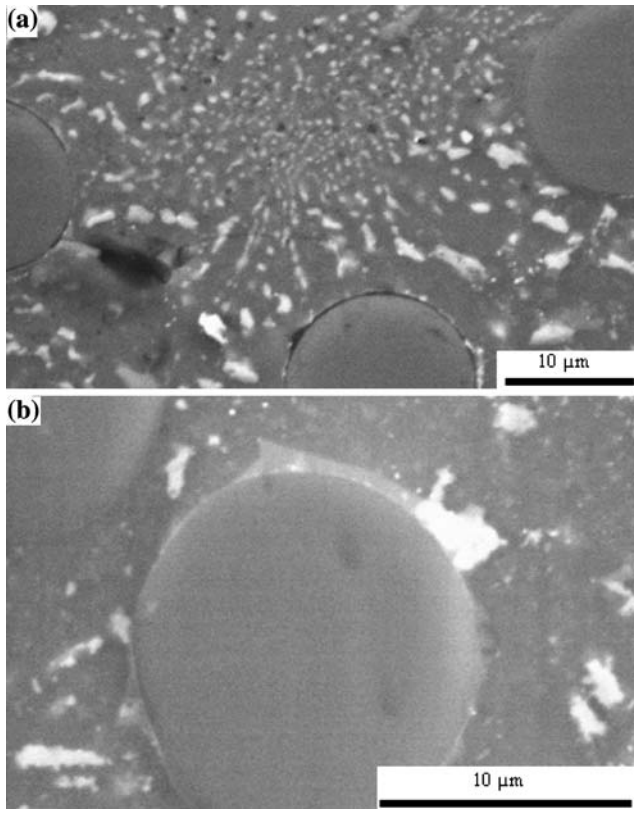

Fig. 5 Back-scattered electron SEM images of the MAS matrix composite heated at (**a**) 1,000 °C and (**b**) 1,200 °C

edly, this is much larger than the change observed for BMAS [11]. The EDS data are particularly revealing and show:

(a) For the 700 °C heat treatment, the carbon content of the interface has decreased significantly. However, the carbon content increased after the 1200 °C annealing.
(b) The Si content of the annealed samples has similar.
(c) Heat treatment of the sample at 1200 °C resulted in Mg, Al and Si exist in the interfacial layer, which suggested a concentration gradient inward from the matrix.

Conclusions

The following conclusion can be drawn from this study:

1. Thermal properties were determined after heat treatment of composites at various temperatures in the air. It has been found that heat treatment at lower temperatures (600 and 700 °C) causes a degradation in the thermal diffusivity.
2. Higher heat treatment temperatures (>1,000 °C) resulted in a retention in the thermal property values and sometimes even higher thermal diffusivity values were obtained.

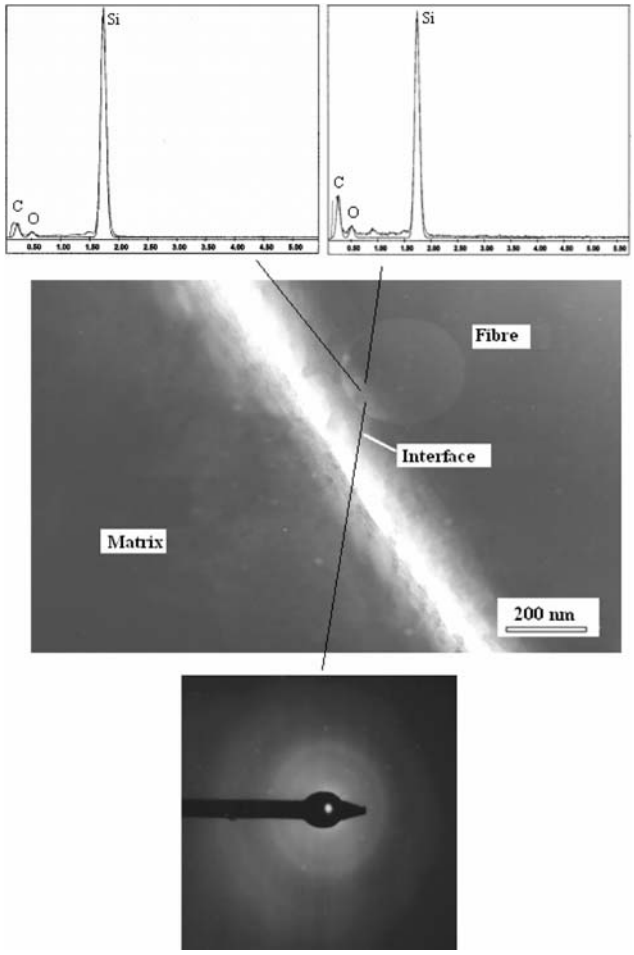

Fig. 6 TEM bright field image, energy dispersive spectrometry spectra and SAD pattern from interfaces of the sample heated at 700 °C

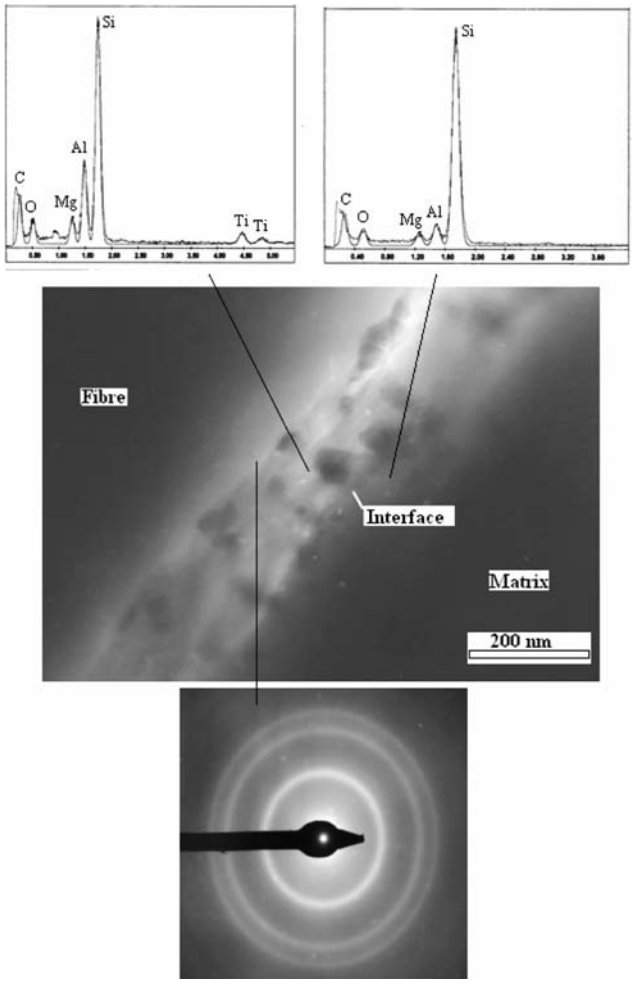

Fig. 7 TEM bright field image, SAD pattern and energy dispersive spectrometry spectra from interfaces of the sample heated at 1,200 °C

3. TEM analysis after higher heat treatment temperatures such as 1,200 °C showed that the interfacial reaction layer was much thicker which sometimes resulted in higher values in the thermal diffusivity.
4. Thermal diffusivity values of the composites exposed heat treatments at lower temperatures between 600 and 700°°C, resulted in significant decrease in the values of thermal diffusivity.
5. SEM studies show that at lower heat treatment temperatures (600–700 °C) residual glass in the matrix migrated to voids in particular to interfaces after degradation of carbon layer at interfaces.

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