Environmental Degradation of a Continuous Oxide Fibre-Reinforced Oxide Matrix Composite

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ABSTRACT

Thermal aging of a Nextel[TM] 720 aluminosilicate fibre reinforced alumina matrix material (N720/Al$_2$O$_3$) has been studied. The as-received composite has a woven fibre architecture in a porous matrix. Samples of the composite were subjected to a range of thermal aging regimes ranging from 2000 hours at 1100 ^{o}C to 100 hours at 1500 ^{o}C. On completion of the thermal aging treatments, the microstructures of the samples were characterised, principally using scanning and transmission electron microscopy. Initial scanning electron microscopy results indicate that the 1100°C thermal aging treatment has little effect on the microstructure of the N720/Al$_2$O$_3$ material, whereas transmission electron microscopy investigations reveal very slight changes to the fibres and matrix. In contrast, much shorter exposures to higher temperatures lead to significant changes to the microstructure, principally in terms of the reduction in porosity and grain growth in the matrix regions and the reaction of the fibres with the matrix. Further, it appears that there may be a variation in the microstructural characteristics across the sample.

1. INTRODUCTION

A significant driving force for the development of ceramic matrix composites (CMCs) for engineering applications is provided by the aerospace industry, where there is a continued demand for increased materials performance and reduced costs. One particular field of interest that is pushing the limitations of current materials are turbine engines.

Limitations associated with non-oxide ceramic matrix composites, in particular their susceptibility to oxidation, has led to increased interest in oxide-oxide CMCs as these materials are inherently more oxidation resistant. The majority of these systems are based upon various combinations of alumina and mullite used as both the matrix and fibre reinforcement. In general terms, there are two possible approaches to the creation of an oxide-oxide CMC. One approach is to follow the principles used in other CMCs and create a weak interface, so that fibre/matrix debonding occurs and thus the material is able to sustain multiple cracks without catastrophic failure.

The other, more novel, approach is to promote crack deflection through the use of a porous matrix [1, 2]. In the porous matrix composites, strong fibre/matrix bonding is allowable so fewer issues associated with chemical compatibility arise. There are, however, other issues associated with the potential long-term use of these porous matrix composites in aerospace applications that do need to be addressed. One of these is the stability of the microstructure following long exposures to elevated temperatures. Thus, the aim of the current investigation was to assess the effect of various temperature regimes on the microstructure of a specific oxide-oxide CMC.

2. MATERIAL AND EXPERIMENTAL METHODS

The material investigated was a Nextel 720 fibre reinforced porous alumina matrix composite (designated N720/Al$_2$O$_3$) manufactured by COI Ceramics Ltd. The fibre reinforcement was in the form of an 8 harness satin woven cloth. The supplied material was in the form of a plate, approximately 3mm thick.

A thermal aging temperature of 1100°C was chosen for the initial long-term thermal exposures as this temperature approaches the limit of the stability of the fibres, although a wide range of temperatures has been reported [3, 4, 5, 6]. Two sets of samples were thermally aged at 1100°C for 500, 1000, 1500, and 2000 hours. A set of samples consisted of one piece of material measuring approximately 3 mm x 3 mm x 55 mm and two pieces of material measuring approximately 3 mm x 1 mm x 55 mm. The thicker pieces of material are to be used for mechanical testing whilst the thinner sections were used for microstructural observations. An additional two sets of samples were also aged for 2000 hours with the intention of conducting further thermal aging in order to investigate the effect of even longer thermal exposures. Additional thermal aging treatments were conducted at 1500°C for 100 hours and 1400°C for 200 hours. The thermal aging at 1500°C for 100 hours was an attempt to simulate a 'worst-case' scenario of an over-temperature excursion of the material. This was also intended to act as an accelerated exposure in an attempt to predict the final state of the material after very long thermal exposures at lower temperatures.

Two furnaces were used for the thermal aging exposures. A three-zone alumina tube furnace (Carbolite Furnaces Ltd, model TZF 12/100) was utilised for the thermal aging at 1100°C. The central furnace zone was controlled by a Eurotherm 818 controller whilst the two outer zones were controlled by Eurotherm 815 controllers. Thermal aging experiments conducted at temperatures over 1100°C were performed in a single zone alumina tube furnace (Elite Thermal Systems Ltd., model TSH15/75/450). The furnace was commissioned specifically for this project to minimise the possibility of contaminants affecting the thermal aging effects. The furnace was controlled by a Eurotherm 2416 controller with a Eurotherm 2116 controller fitted as an over temperature controller.

Two different scanning electron microscopes were used to characterise the microstructure of the samples. One was a variable pressure Hitachi environmental S-3200N scanning electron microscope (SEM) and the other was a JEOL 8600 Superprobe. Both SEMs were used with a low accelerating voltage, typically 10 kV in order to produce a small irradiated volume. The JEOL Superprobe was preferred for some of the investigations as it has a chemical analysis capability and very good beam stability. Chemical analysis was performed using energy dispersive x-ray (EDX) analysis in conjunction with Oxford Instruments Ltd INCA system. Samples that were to be observed in a scanning electron microscope were vacuum mounted in an epoxy resin. The samples were ground and polished to a 1μm finish using diamond abrasive pads. The samples were then coated with a thin layer of carbon in order to prevent charging and hence aid observation in the SEM.

A Philips 400T transmission electron microscope (TEM) was also used to investigate the microstructure of the as-received and thermally aged material. An accelerating voltage of 120 kV was used. Samples were mechanically thinned by grinding and then polishing to a thickness of less than 80 μm using silicon carbide abrasive paper. Once sufficiently thin, the samples were placed into a Gatan PIPS (Precision Ion Polishing System) to be further thinned by ion beam milling. The ion beam angle was varied from 6° to 3° during thinning in order to create a hole within the sample, surrounded by a thin, electron transparent region. The material was supported on slotted nickel grids as it was too fragile to be handled without support.

3. RESULTS AND DISCUSSION

3.1. Long Term Thermal Aging

The microstructure of the as-received material can be seen in Fig. 1a. A microstructural feature common to all of the as-received samples is the presence of large scale voids within the material. These voids are likely to have been created during the manufacture of the material as a result of incomplete slurry infiltration into the reinforcing cloth. Also visible in Fig. 1a is the woven nature of the reinforcing fibres. An SEM micrograph of the material that has been thermally aged for 2000 hours at 1100°C can be seen in Fig. 1b. Comparison of the cracking present in Figs. 1a and 1b indicates that the thermal aging does not appear to have had an effect on the crack distribution within the material. The majority of the cracks are perpendicular to the reinforcing cloth layers and would have been created either during the manufacture or pre-test handling of the material.

An SEM micrograph of the as-received material at a higher magnification can be seen in Fig. 2a and this enables the matrix porosity to be seen more clearly. The fine scale porosity is homogeneously distributed. It is also possible to observe the presence of micro-cracks around the fibres as well as in the matrix. An SEM micrograph of the thermally aged material at a higher magnification can be seen in Fig. 2b. When the matrix porosity in Fig. 2b is compared with that of the as-received material, it can be seen that there is no apparent difference in either pore size or distribution. There also appears to be no difference in the fibres.


(a)   (b)
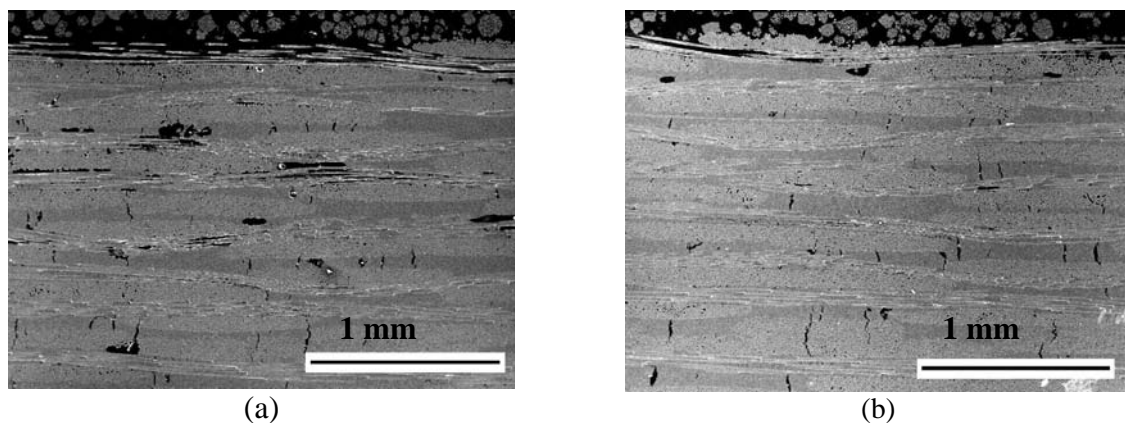
Fig. 1. SEM micrographs of the microstructure of (a) the as-received material and
(b) the material aged for 2000 hours at 1100°C, showing the presence of large scale porosity.

(a)   (b)
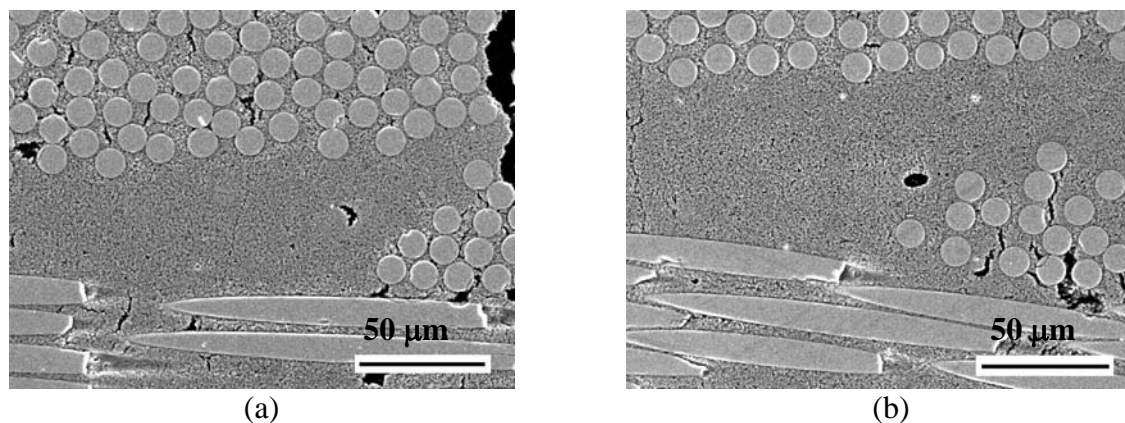
Fig. 2. SEM micrographs of the microstructure of (a) the as-received material and
(b) the material aged for 2000 hours at 1100°C, showing the homogeneous nature of the fine scale matrix
porosity as well as the presence of micro-cracks.

Fig. 3 is a TEM micrograph of the as-received material. The porous alumina matrix can be seen on the left, whilst the Nextel 720 fibre reinforcement is on the right. The presence of porosity, and its varied size and shape, within the matrix can be seen in Fig. 3. The matrix grains of Al_2O_3 appear rounded whilst it is possible to see distinct crystals within the fibre.
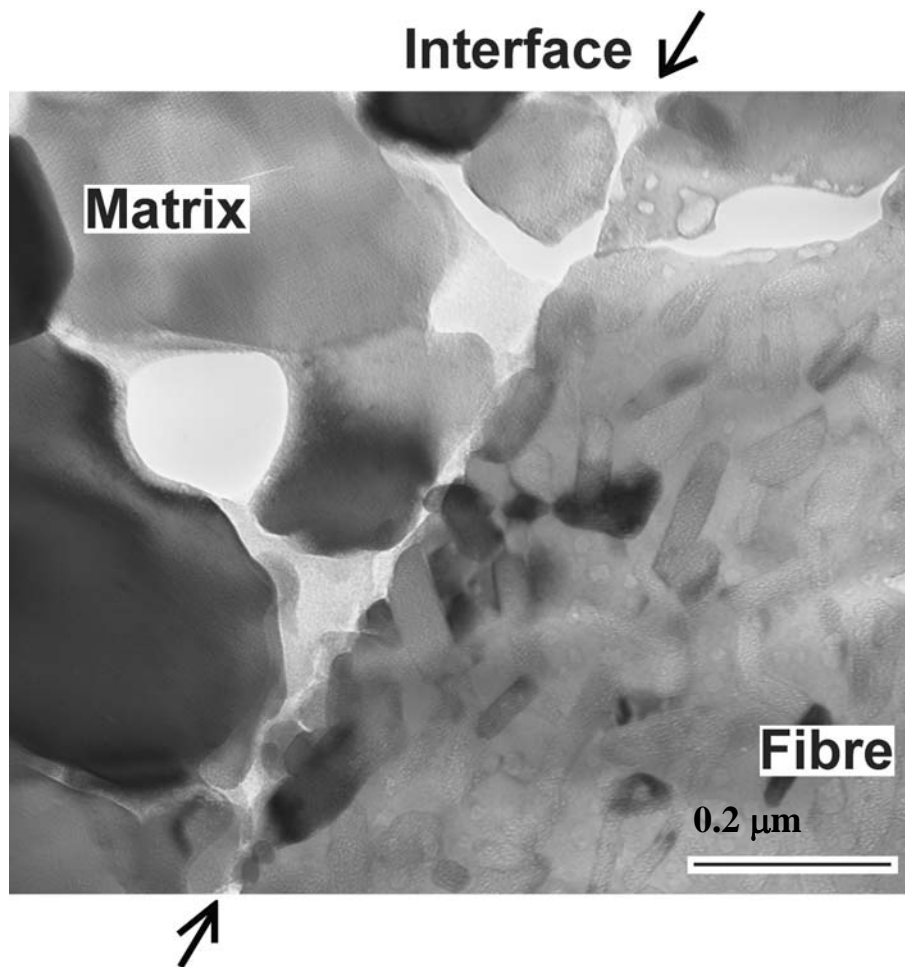
Fig. 3. TEM micrograph showing the microstructure of the as-received material.

Fig. 4 is a TEM micrograph of material that has been aged for 2000 hours at $1100^{o}C$. The porous alumina matrix can be seen on the left, whilst the Nextel 720 fibre reinforcement is on the right.

When a comparison is made between the Figs. 3 and 4, it is possible to conclude that the interface between the fibre and the matrix is quite distinct in the as-received material, whilst it appears to be rougher and less well defined after aging. This may indicate a reaction between the fibre and matrix as a result of the thermal aging treatment. Further, the Al_2O_3 matrix grains in Fig. 4 have a more faceted shape than those in Fig. 3. The microstructure of the fibre also appears to have changed slightly and the crystals have become more rounded and less distinct.
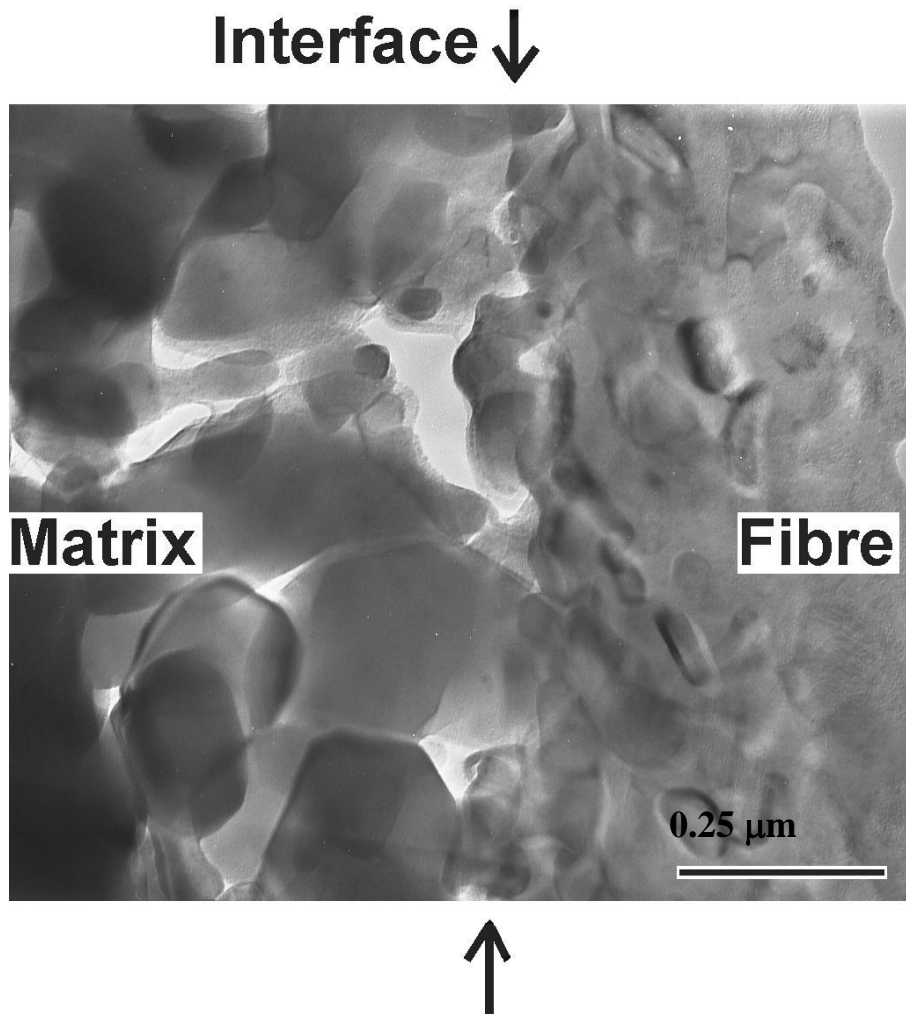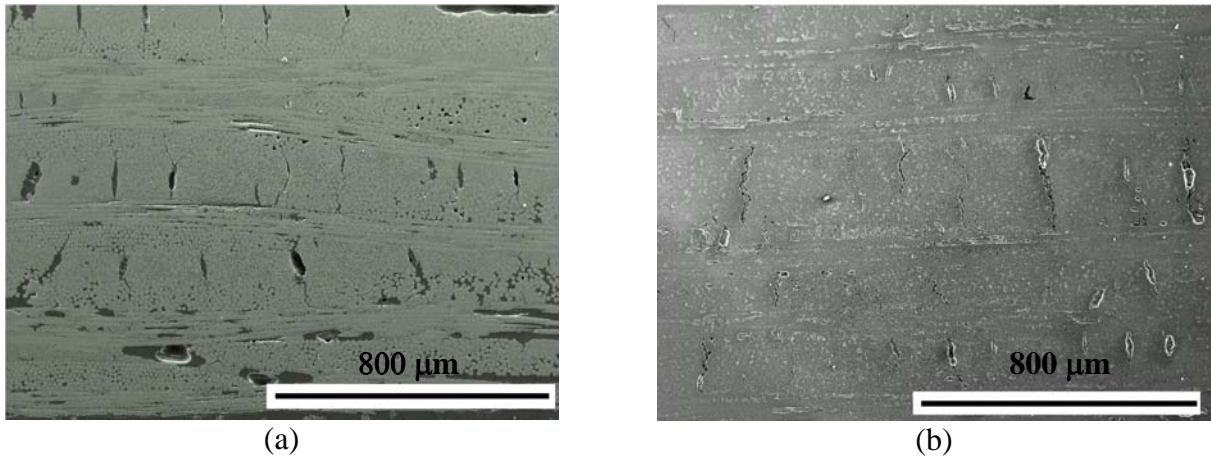
Fig. 4. TEM micrograph showing the microstructure of the material thermally aged for 2000 hours at 1100°C.

Thus, although the scanning electron microscopy study of the material did not reveal any significant changes to the microstructure after aging at 1100°C for 2000 hours, the transmission electron microscopy investigation indicates that small changes to the microstructure have occurred. These should be more apparent in the samples aged for longer times (or at higher temperatures, provided that the same mechanisms are in operation).

3.2. Short Term Thermal Aging

The microstructure of the material thermally aged at 1400°C for 200 hours and 1500°C for 100 hours can be seen in Figs. 5a and 5b, respectively. Cracks are clearly present in the material, and appear to be similar to those observed in the as-received material and the material thermally aged at 1100°C for 200 hours (Figs. 1a and 1b, respectively). On closer examination, it was noted that the cracks present in the material aged at 1500°C are less open than those in the as-received material and those in the material aged at 1100°C and 1400°C.

| (a) | (b) |

Fig. 5. SEM micrographs of the microstructures of (a) the material aged for 200 hours at 1400°C and (b) the material aged for 100 hours at 1500°C, showing the presence of large scale porosity and cracking.

A higher magnification micrograph of the matrix of the as-received material can be seen in Fig. 6a. When compared to the matrix of the material aged at 1400°C for 200 hours, shown in Fig. 6b, it is apparent that the thermal aging has had an effect on the matrix. It would appear that the matrix has densified, although no change in the bulk density of the sample was detected when it was measured using the Archimedes's principle. Therefore, it may be more appropriate to suggest that the matrix has coarsened and that densification of the overall sample has not occurred due to the constraint of the fibre reinforcement [6]. A change in the matrix was not unexpected due to its very porous nature in the as-manufactured state.


| (a) | (b) |
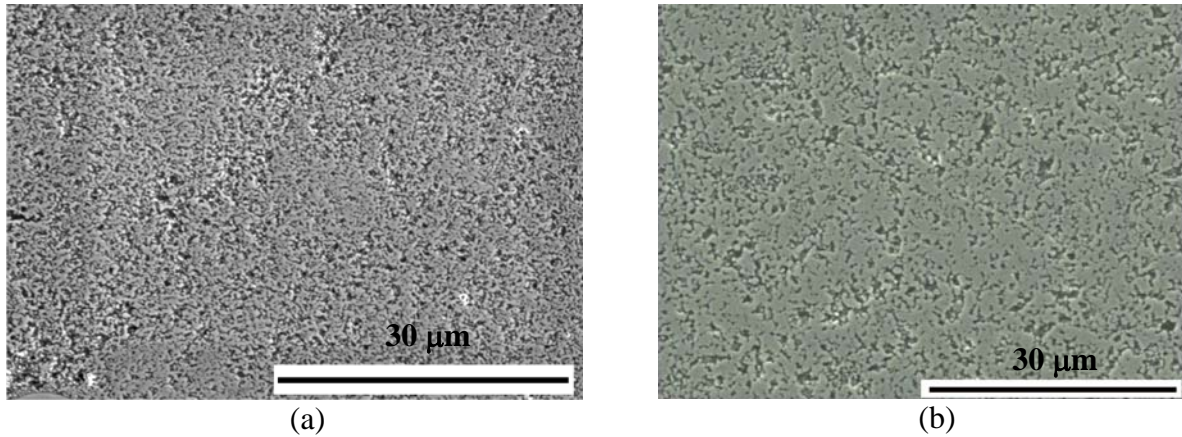
Fig. 6. SEM micrographs of the microstructure of (a) the as-received material and (b) the material aged at 1400°C for 200 hours.

Fig. 7 is a high magnification micrograph of the material aged at 1500°C for 100 hours and shows that there has been a significant change in the microstructure of the material. It appears that the matrix of this sample has densified to a greater extent than the material aged at 1400°C. The micrograph was recorded towards the centre of the sample. However, further examination of the material thermally aged at 1500°C showed that there was a variation in the microstructure across the sample.
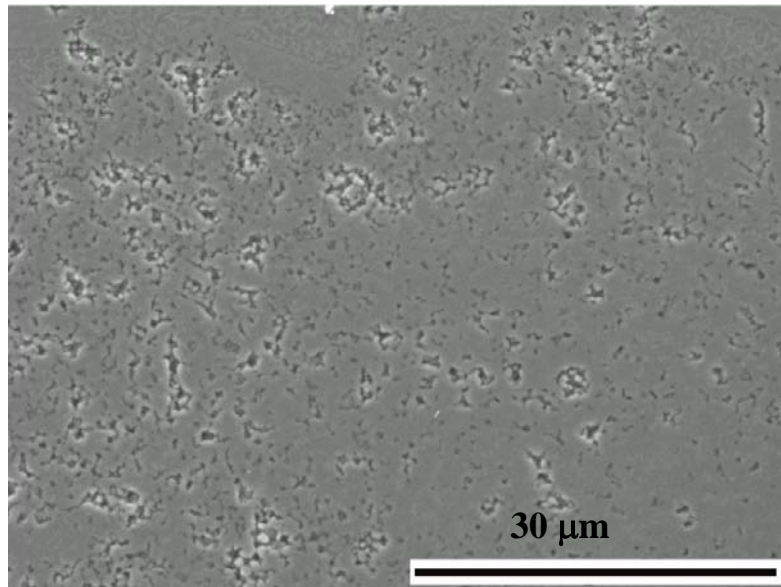
Fig. 7. SEM micrograph of the microstructure of the material aged for 100 hours at 1500°C.

When the material at the edges of the sample was examined, it was found that there was a significant difference in the microstructure compared with the central region of material. This can be seen in Figs. 8a and 8b, respectively. Fig. 8a is a micrograph of the material towards the very edge of the sample where the material appears to have densified to such an extent that the fine porosity has disappeared and large voids have formed. Furthermore, it is not possible to discern any of the fibre reinforcement present with the material. It is also evident that there have been significant changes in the grain size and shape. It is possible to observe the presence of long, rectangular shaped grains, which appear to be randomly orientated.

(a)   (b)
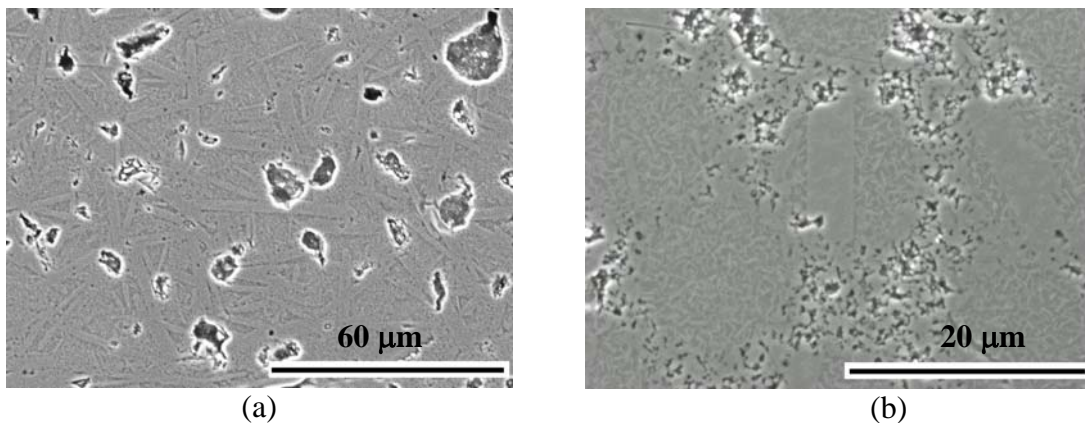
Fig. 8. SEM micrographs of the microstructure of the material aged for 100 hours at 1500°C showing (a) material at the edge of the sample, (b) material at the centre of the sample.

In contrast, it can be seen in Fig. 8b that the fibre reinforcement and matrix porosity are still visible at the centre of the sample. Of particular interest in Fig. 8b is the development of what appears to be 'grain-like' structures within the fibre reinforcement. A similar fibre structure has been reported previously for a thermal aging regime of 2 hours at 1600°C [5].

The variation in microstructure across the sample may have been a result of a thermal gradient in the furnace. This is, however, unlikely due to the small size of the samples being thermally aged and their proximity to the furnace tube wall. A second possibility is that the manufacturing technique has resulted in a non-uniform microstructure across the sample and

although this is not readily apparent in the as-received material this has become manifest on thermal aging. Further work is required before definite conclusions on the reasons for this variation can be drawn.

The initial results of the short-term thermal aging at 1400°C suggest that similar processes are occurring to those in the lower temperature/longer time specimens. Aging at this temperature may be a valid tool for predicting the behaviour of the same material at lower temperatures for extended lifetimes. Tests at intermediate temperatures are underway to examine this possibility. The initial results of the thermal aging at 1500°C indicate that very significant microstructural changes can occur within the $N720/Al_2O_3$ material and that this temperature may not be appropriate temperature for accelerated aging experiments.

4. CONCLUDING REMARKS

The thermal aging of the $N720/Al_2O_3$ material at 1100°C appears to be causing changes to the microstructure of the material. There is microstructural evidence of a possible interaction between the fibre and matrix and a change in the matrix grain shapes. The thermal aging at 1400°C has caused a densification of the matrix regions within the composite material but appears to have had no major effect on the fibre. The thermal aging at 1500°C has caused a significant change in the microstructure of the material. However, further investigations are required before any definite conclusions are reached.

ACKNOWLEDGEMENTS

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