Original Paper

Mechanical behaviour and environmental stability of continuous fibre-reinforced glass-ceramic matrix composites

Grant West, David M. R. Taplin[1], Aldo R. Boccaccini[1] and Kevin Plucknett
Department of Environmental Sciences, University of Plymouth, Plymouth (Great Britain)

Mike H. Lewis
Department of Physics, Centre for Advanced Materials, University of Warwick, Coventry (Great Britain)

The mechanical behaviour of three continuous silicon carbide fibre-reinforced glass-ceramic matrix composites has been investigated at room and high temperatures. Commercially available composites with magnesium aluminosilicate, calcium aluminosilicate and barium magnesium aluminosilicate glass-ceramic matrices were considered. The materials were tested in the as-received and aged (heat-treated in an oxidizing environment) condition. Four-point bend static tests and flexural creep, fatigue and creep-fatigue tests were carried out as well as a small quantity of tensile tests of aged composites. The experimental results have highlighted the importance of the carbon-rich layer at the fibre/matrix interface for obtaining "graceful" failures. At temperatures of 700 to 800 °C oxidative degradation of the interface results in significant strength reduction and a transition to brittle fracture mode. By rapid heat treatment of the materials at 1100 °C for 1 h it is possible to seal the fibre ends by forming a silica "plug" which prevents oxygen ingress, retaining the carbon-rich interphase and composite behaviour. The results of the creep and creep-fatigue tests indicate low-cycle loading has a strong influence on the life of components at high temperatures.

Mechanisches Verhalten und Umweltbeständigkeit von Verbundwerkstoffen aus endlosfaserverstärkter Glaskeramik

Das mechanische Verhalten von drei mit Siliciumcarbid-Langfasern verstärkten Glaskeramikmatrix-Verbundwerkstoffen wurde bei Raum- bzw. Hochtemperatur untersucht. Handelsübliche Magnesium-Alumosilicat-, Calcium-Alumosilicat- und Barium-Magnesium-Alumosilicat-Glaskeramiken wurden in die Untersuchungen einbezogen. Die Verbundwerkstoffe wurden im Anlieferungszustand und nach einer Wärmebehandlung in oxidierender Atmosphäre getestet. Statische Vier-Punkt-Biegeversuche und Kriech-, Ermüdungs- sowie Kriech-Ermüdungsversuche unter Biegebeanspruchung sowie Zugversuche wurden durchgeführt. Die experimentellen Ergebnisse bestätigen die Bedeutung der kohlenstoffreichen Schicht an der Faser/Matrix-Grenzfläche, die die hohe Rißzähigkeit und das „pseudo-duktile“ Verhalten der Verbundwerkstoffe verursacht. Bei Temperaturen von 700 bis 800 °C findet eine Degradierung der Grenzfläche durch Oxidation statt. Dadurch entsteht bei der Probe Sprödbruch. Mittels einer schnellen Wärmebehandlung bei 1100 °C für 1 h kann man die Faserenden durch Bildung einer Siliciumoxidschicht schützen. Damit wird das Eindringen von Sauerstoff verhindert, die kohlenstoffreiche Schicht erhalten und damit auch das „pseudo-duktile“ Verhalten des Materials. Die Ergebnisse der Kriech- und Kriech-Ermüdungsversuche demonstrieren den starken Einfluß einer zyklischen Beanspruchung auf die Lebensdauer der Komponenten bei Hochtemperatur-Anwendungen.

1. Introduction

Continuous fibre-reinforced ceramic matrix composites and related glass and glass-ceramic matrix composites are candidate materials for various structural, high-temperature and other specialized applications [1 to 5]. The reason for the interest in these materials is their improved mechanical properties, especially fracture toughness, when compared to those of the monolithic materials. To date, the most commonly employed reinforcement for these materials has been silicon carbide (SiC) fibre or yarn.

Glasses can perform the matrix role as demonstrated in early studies [1 and 4]. They can be fabricated at relatively low temperatures, but in practice, the properties are limited by softening of the glass matrix and subsequent viscous flow at moderate temperatures (>550 °C). For low temperature, load-bearing requirements in oxidative atmospheres, however, glass matrix composites, in particular those with a borosilicate glass matrix, may find interesting applications [4 and 6].

The use of glass-ceramics as composite matrices results in a combination of high use temperature and also fabrication ease. A great variety of silicate matrices has been investigated in the literature including Lithium Aluminosilicate (LAS) [7 and 8], Magnesium Aluminosilicate (MAS) [9 and 10], Calcium Aluminosilicate (CAS) [8 and 11], Barium Aluminosilicate (BAS) [12] and Barium Magnesium Aluminosilicate (BMAS) [13]. All of these glass-ceramics offer low density, ease of fabrication and oxidation resistance. Glass-ceramics are

---

Received September 2, 1994, revised manuscript April 4, 1995.
[1] Also affiliated with: School of Metallurgy and Materials, University of Birmingham, Birmingham (Great Britain).

capable of withstanding aggressive environments, high temperatures, being chemically inert, wear resistant and having high strength and stiffness. On the incorporation of a fibre reinforcement, composite densification can occur while the matrix is maintained in a low-viscosity glassy state. The matrix can then undergo a subsequent crystallization or "ceraming" cycle which imparts greater thermal stability.

A major advantage of the aforementioned silicates when used as composite matrices is the fortuitous reaction which occurs with the reinforcing SiC yarn during composite fabrication. A weak carbon interface results which alleviates the need to precoat the fibres, although there is some loss of fibre strength resulting from the reaction.

If the matrix has a coefficient of thermal expansion which differs greatly from that of the SiC reinforcement, then microcracking may occur due to the clamping forces of the matrix. Glass-ceramics, however, have the advantage that their coefficient of thermal expansion can be tailored and hence, fibre/matrix mismatch stresses can be minimized.

An important aspect in the development of glass-ceramic matrix composites is the attainment of an in-depth understanding of their fracture behaviour and, in particular, the necessary requirements for interface design in order to maximize toughness under all operational conditions. The fracture behaviour of these materials is based upon the control of failure via progressive load transfer from the (microcracking) matrix material to the high-modulus fibres, followed by fibre fracture and pull-out [14]. These factors are influenced by the properties of the fibres, matrix and fibre/matrix interface, as well as the residual stress state at the interface. It can be seen, therefore, that these materials exhibit a threshold application stress up to that observed for matrix microcracking, together with an additional design tolerance for stress overload. For optimum composite mechanical behaviour, it is particularly important that a weak fibre/matrix interface is present. In this way, toughness enhancement is due primarily to frictional energy dissipation along the debonded interface [15]. An excellent survey of research aimed at an understanding of the relationship between microstructure, interfacial properties and macromechanical behaviour of glass-ceramics matrix composites has been published recently [5].

Most of the studies carried out on glass-ceramic matrix composites so far have focussed on the strength and toughness characterization of these materials. The mechanical tests performed have employed quasi-static loads to test the materials in bending, compression and, in some cases, tension. Conditions existing in potential applications, however, warrant the need for characterizing the behaviour of such materials under varying loading and fatigue conditions. Fatigue is a very important property for many sensitive components in engines, for example, particularly those in rotating systems. As stated in a previous conclusive report [16], a major task in the development of advanced composites for high-temperature structural applications is increasing the knowledge of service aspects, including the mechanisms of materials degradation under in-service conditions. Knowledge of the creep and fatigue behaviour of any matrix cracks which may develop during processing or application of initial loads, is of great importance to the designer. The effect of the in-service environment on the physical behaviour of the material is of interest also.

The present work has focussed upon the use of a range of mechanical characterization techniques, including flexural fatigue and creep-fatigue tests, in order to gain a greater understanding of the mechanical behaviour of several glass-ceramic matrix composites in both the as-received and aged (heat-treated in an oxidizing environment) conditions. The results are part of a continuing research programme on ceramic matrix composites.

2. Experimental procedure

Several glass-ceramic matrix materials have been utilized in the current study and details of each of these are given in table 1. The data shown has been given by the manufacturers or are the results from previous studies [17].

The microstructures of the composite materials have been assessed using conventional Scanning and Transmission Electron Microscopy techniques (SEM and REM, respectively). Further phase characterization has also been performed using X-ray Diffraction (XRD). The effects of environmental ageing upon the microstructure and properties of the MAS glass-ceramic composites have been assessed by heat treatment of test bars (nominally $(3 \times 3 \times 50)\,\mathrm{mm}^3$) in air at temperatures of 500, 700 and 1100 °C for periods of 12 h. An investigation of suitable pre-treatments for the prevention, or at least minimization, of environmental ageing effects has also been performed resulting in heat treatment of the samples for 1 h at 1100 °C. These heat treatment parameters were chosen on the basis of previous results [17]. The mechanical behaviour of the composites has been assessed using a range of techniques. Room temperature strength of the composite materials has been determined in four-point bend test (SiC jig, 40 mm outer span, 20 mm inner, fully articulated jig with rotating loading pins) using a servohydraulic testing machine (Instron 8501, Instron, High Wycombe (Great Britain)). The high-temperature strength measurements were carried out by means of a long furnace with a 1600 °C capacity that can be swung in to surround the bend facility. The heating ramps were designed to prevent overshoot and testing was commenced within 5 min of the target temperature being reached. Testing from 500 to 1200 °C was undertaken. Flexural fatigue, creep, and creep-fatigue testing of the BMAS and CAS glass-ceramic composite materials was also performed using the bend facility. The flexural fatigue tests were conducted on the

Table 1. Summary of the glass-ceramic composites investigated [17]

	BMAS	MAS	CAS
supplier	Harwell	Pilkington	Corning
lay-up	0.90	unidirectional	0.90
matrix	BaO, MgO, Al_2O_3, SiO_2	MgO, Al_2O_3, SiO_2	CaO, Al_2O_3, SiO_2
fibre	SiC-Tyranno	SiC-Nicalon	SiC-Nicalon
density in g/cm^3	2.56	2.44	2.67
Young modulus in GPa	73	135	48
coefficient of thermal expansion in 10^{-6} K^{-1}	3.6	4.8	not assessed
fibre volume fraction in vol.%	≈40	≈40	≈40
crystalline phase	barium osumilith, cordierite, celsian	cristobalite, indialite	anorthite, zircon

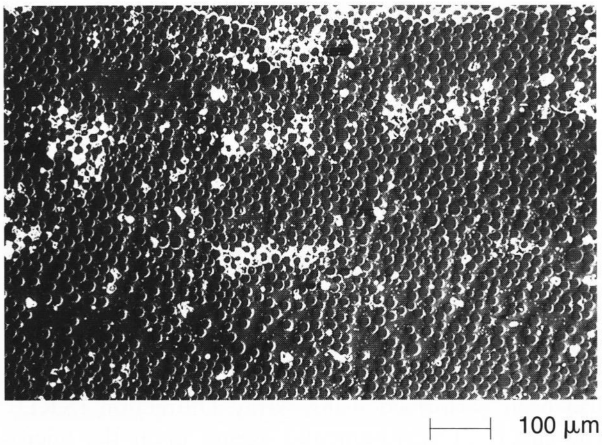


Figure 1. SEM micrograph (secondary electrons) of the MAS glass-ceramic matrix composite. Note micro- and macroporosity.

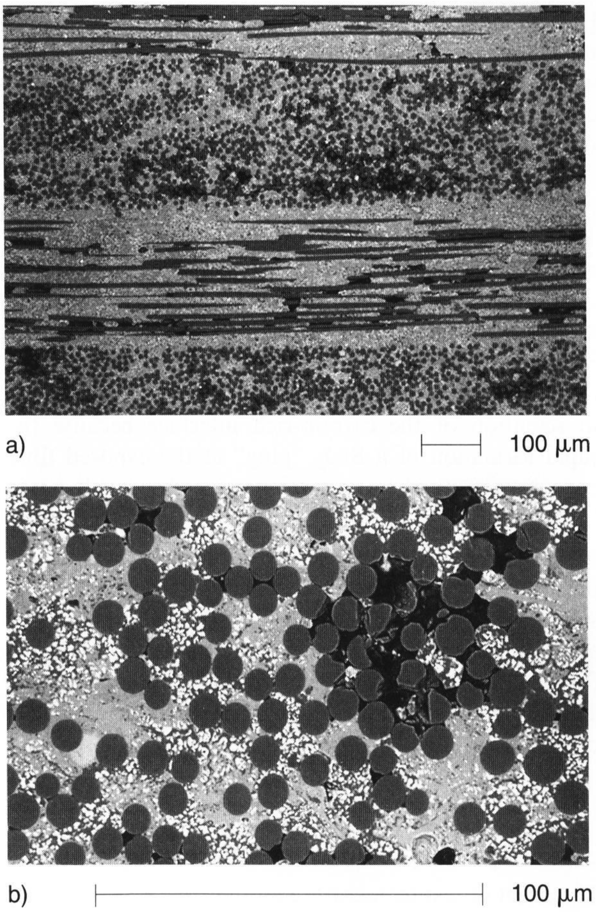
BMAS heat-treated material using a sinusoidal wave form, with the minimum load being 10% of the maximum. The purpose of the creep tests was to measure the creep at specific temperatures and loads for direct imput into the creep-fatigue studies. All creep and creep-fatigue testing to be described here has been for short (<48 h) duration and the studies have focussed on one temperature (1100 °C). The creep-fatigue testing involves the application of a cyclic load at elevated temperature. Cyclic square forms were generated in load control for the creep-fatigue tests. The maximum load equated to 75% of the maximum monotonic bend strength at the working temperature. The lower half of the load cycle is a nominal load to ensure the bend fixture remains in the correct position within the loading push roads. The frequencies used were very low (0.0005 Hz) to give a cycle time of slightly over 30 min.

Additionally some strength data on heat-treated BMAS composites at room temperature has been obtained in direct tension, using a "dog-bone" type test piece similar to that specified by Holmes [18]. A screw-driven testing machine (Instron 1175) has been used in these experiments.

3. Results and discussion

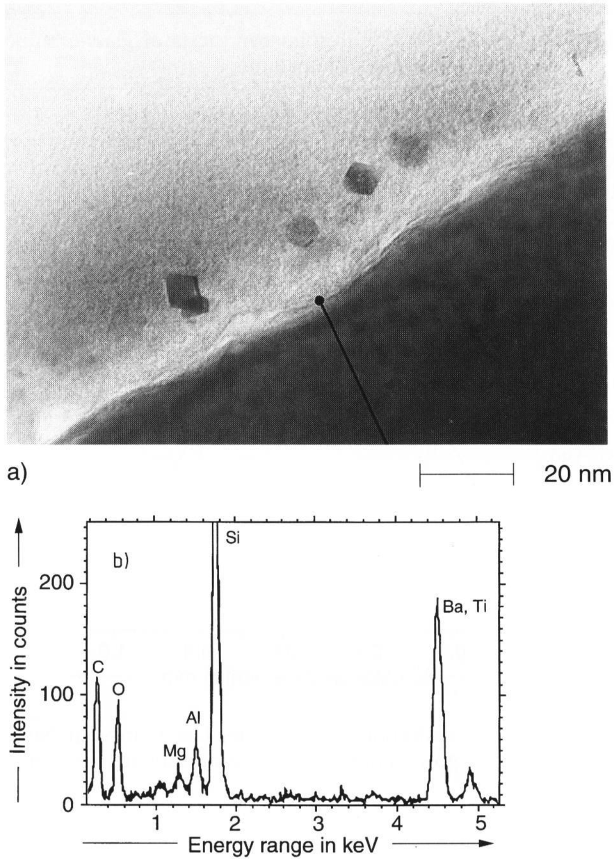
3.1 Materials characterization

In the case of the MAS and BMAS materials details of the processing route were not specified and the specific matrix compositions were not provided by the manufacturers. The MAS material was poorly processed as can be seen in the SEM micrograph shown in figure 1, where both macro- and microporosity is evident. It was available in (100 × 100 × 3) mm^3 plates and had a undirectional architecture. The high-porosity volume is believed to arise from bloating during an incorrectly applied crystallization stage conducted by the manufacturer. The matrix phase is primarily devitrified to a mixture of cristobalite and indialite ($Mg_2Al_4Si_5O_{18}$) as found in the previous investigation [17]. The BMAS material was available as cross-ply laminates. The material is of superior quality with respect to the MAS composite although residual porosity, primarily within the core of fibre bundles is present. In addition "fibre-free" regions were also apparent in this material. Figure 2a shows the 0.90 lay-up and figure 2b the matrix crystallization and intra-bundle voids. The BMAS composite exhibits a similar microstructure to the MAS material, with three different crystallization products identified by X-ray diffraction and electron microscopy, namely: cordierite ($Mg_2Al_4Si_5O_{18}$), celsian ($BaAl_2Si_2O_8$) and barium osumilith ($BaMg_2Al_6Si_9O_{30}$). Transmission electron microscopy and Energy Dispersive X-ray (EDX) analysis of the as-received BMAS material reveal a carbon-rich interface between the fibre and matrix as shown in figures 3a and b. This has also been previously reported for other SiC fibre/glass-ceramic matrix systems [3, 8 and 10]. The presence of this carbon-rich interface typically results in low debond and sliding shear stress values be-



Figures 2a and b. SEM micrographs of the BMAS glass-ceramic matrix composite showing a) the 0.90 lay-up (low magnification), b) the matrix crystallization and the intrabundle voids. 0.90 lay-up means the arrangement of the fibres in the composite: fibres in 0° and in 90° directions.

tween matrix and fibre, thus enhancing composite properties related to fibre pull-out, as will be discussed in section 3.2. A more detailed microstructural investigation of the BMAS material has been reported elsewhere [19]. The CAS material is similar to that studied in a separate programme [20]. The composite has a 0.90 architecture and a section of it can be seen in figure 4. The CAS matrix phase exhibits a very low porosity and it has been almost fully crystallized to anorthite ($CaAl_2Si_2O_8$) with small precipitates of zircon ($ZrSiO_4$) at the fibre/matrix interface as shown in figure 4. This presumably forms from the addition of ZrO_2 as a nucleating agent for the glass.



Figures 3a and b. Carbon-rich interfacial layer between the fibre and the matrix in the BMAS material; a) TEM micrograph, b) EDX analysis at the marked point in figure a.

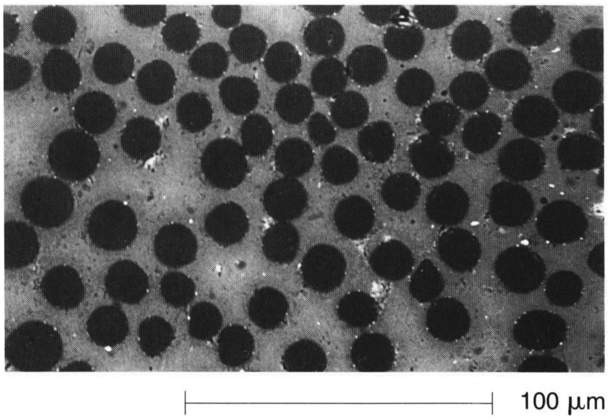


Figure 4. Backscattered electron SEM image of the microstructure of the CAS glass-ceramic matrix composite. Note the white zircon ($ZrSiO_4$) precipitates at the fibre/matrix interface.

3.2 Mechanical behaviour of as-received and heat-treated composites

3.2.1 Room temperature bending strength

The results of the four-point bend strength tests for the three materials investigated are shown in table 2. The large scatter in the values of the MAS composite is directly related to the inhomogeneous microstructure of this material and high volume of randomly distributed porosity acting as strength-controlling flaws. The measured values are lower than previous strength data determined in three-point bending [17] for similar composites. The as-received materials exhibited typical "composite" behaviour as a typical load deflection curve of the MAS material in figure 5 shows.

Table 2. Results of the four-point bend tests of glass-ceramic matrix composites at room temperature

material	bending strength in MPa
MAS	620 ± 75
BMAS	360 ± 50
CAS	490 ± 40

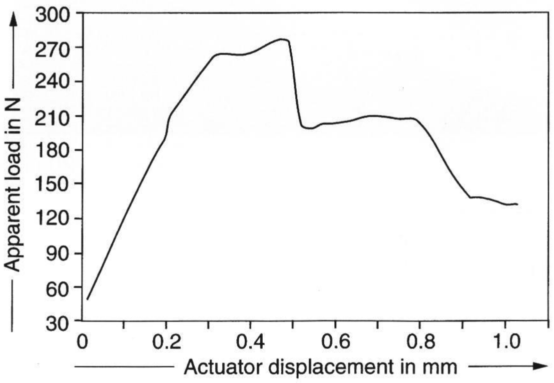


Figure 5. Load deflection curve obtained in four-point bend tests for MAS glass-ceramic matrix composite at room temperature.

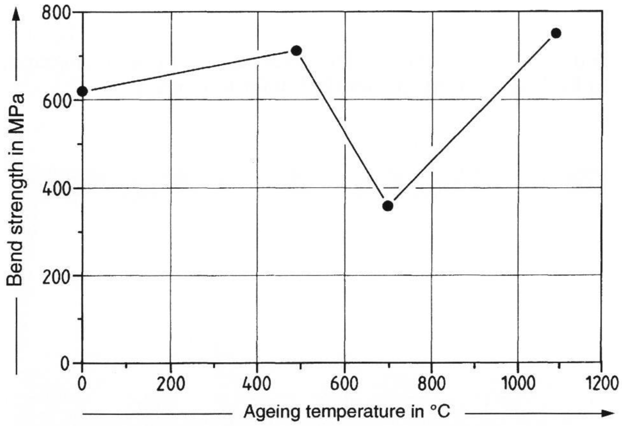


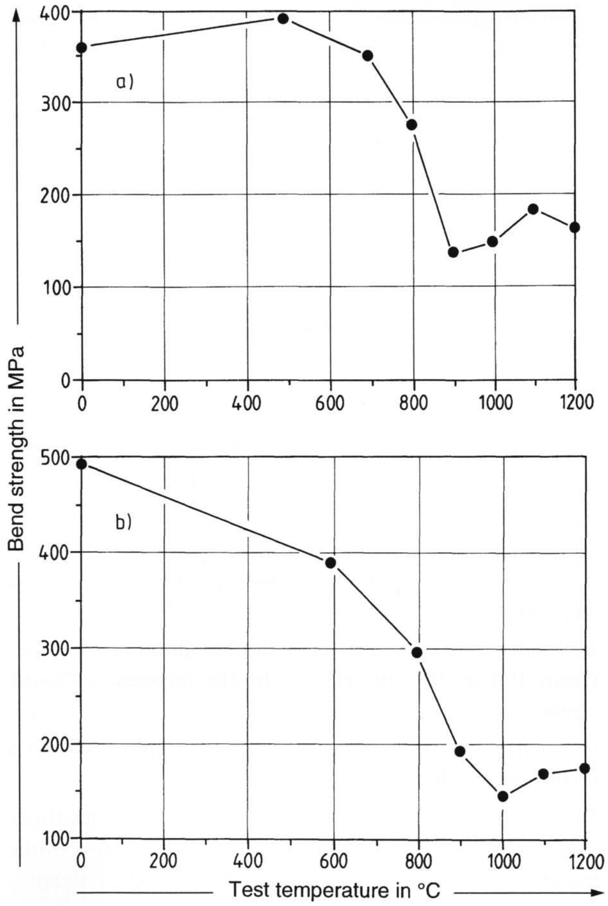
Figure 6. Flexural strength against ageing temperature for MAS glass-ceramic matrix composites. Specimens were aged at different temperatures for 12 h and tested at room temperature. The line serves only as a guide to the eye.

The effects of a post-fabrication ageing heat treatment upon the room temperature strength of the MAS glass-ceramic matrix composites is shown in figure 6. A considerable drop in ultimate bend strength for a heat treatment at 700 °C is noted, in agreement with the results of a similar investigation on the CAS and BMAS materials [17]. At higher ageing temperatures (1100 °C), however, the measured room temperature strength is comparable to the material in the as-fabricated condition. These observations are similar to those made in previous investigations on BMAS and CAS material [17], which exhibited a strength degradation at ageing temperatures above 600 °C with increasing strength above 1000 °C. Although not measured here, post-fabrication heat treatment should have a significant effect upon both the frictional stress (τ) at the interface and the debond energy (2Γ) as shown previously for BMAS glass-ceramic composites [17]. After heat treatment for 12 h at 700 °C there is a significantly stronger bond between fibre and matrix phase. Oxidative degradation of the carbon-rich interface occurs at this temperature and subsequent oxidation of the surface of the SiC fibre to SiO_2 occurs slowly, with partial bridging of the interface [17]. The use of an ageing temperature of 1100 °C results in retention of the carbon-rich interface because the rapid formation of a SiO_2 "plug" at the exposed fibre ends prevents further oxygen ingress as previously noted [17 and 20].

The as-received material exhibited typical "composite" behaviour (figure 5) while ageing at 700 °C resulted in brittle failure, with negligible "pull-out". At an ageing temperature of 1100 °C a return to more "graceful" failure was noted when tested at room temperature. The mechanism for this change in failure behaviour will be discussed more fully in section 3.2.2.

3.2.2 High-temperature fracture

The effect of test temperature on the flexural strength of both the BMAS and CAS composites is shown in figures 7a and b. Both materials demonstrate a significant decrease in ultimate bend strength at test temperatures above 500 °C similar to the results of MAS unidirectional glass-ceramic composites reported previously [17]. These observations are similar to those obtained by Prewo [7] on LAS glass-ceramic matrix composites reinforced with Nicalon fibres. He observed that the strength reduction did not occur when the LAS materials were tested in argon environment, indicating an oxidation-induced degradation mechanism. The load deflection traces obtained here at several test temperatures, for the CAS composites, are presented in figures 8a to c. Observation of these figures reveals that a transition in failure mode occurs with increasing temperature, from a typical "graceful" failure as exhibited in the load deflection curve at room temperature (figure 8a) through to an essentially "brittle" failure mode at 1100 °C as exemplified by figure 8c. Similar observations to these were made for the MAS and BMAS materials [17]. The apparent change in failure mode is also particularly notable when studying the resultant fracture surfaces. Considerable "pull-out" is apparent in samples broken at room temperature, however, at higher temperatures "brittle" fracture with minimal "pull-out" is observed. It is clear that the fibres become strongly bonded to the matrix phase during the high-temperature test cycle and hence, it is more energetically favourable for impinging cracks to go through the fibres rather than around with subsequent debonding.



Figures 7a and b. Flexural strength against test temperature for a) BMAS material, b) CAS material.

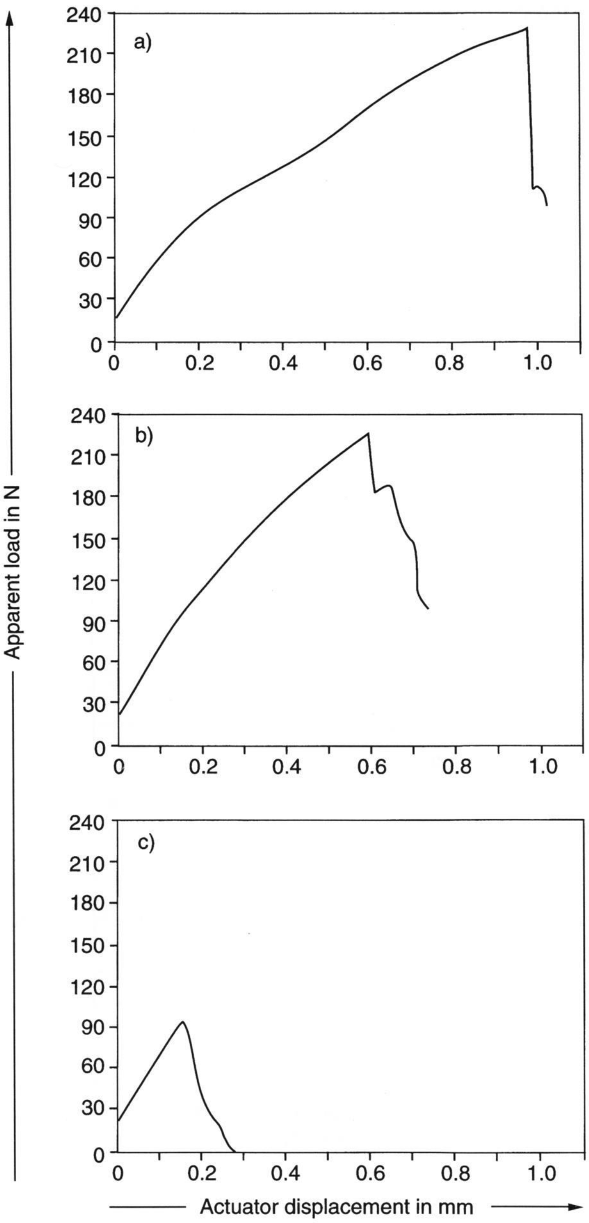
It is the onset of matrix cracking which permits the atmosphere to enter the composite and attack the fibre/matrix interface; because of this "environmental" penetration the fracture mode changes. It is well-known that the ingress of oxygen into the composite via "piped" diffusion from the exposed fibre ends or from cracks within the matrix causes the removal of the carbon-rich layer at temperatures above 600 °C [8]. This is because the oxygen reacts with the carbon according to the reaction:

$$C + O_2 \rightarrow CO_2 \,. \qquad (1)$$

Following interface oxidation the space is filled by a reaction between the fibre and oxygen as described earlier [8 and 20 to 23]:

$$SiC + 2O_2 \rightarrow SiO_2 + CO_2 \,. \qquad (2)$$

The discontinuity between the matrix and fibre is the reason a single crack can propagate through the composite unimpeded. The explanation for the better strength above 900 °C can be given following a suggestion of Pharaoh et al. [20]. The two oxidation reactions (equations (1 and 2)) are still effective over 900 °C but the oxidation of the SiC competes with that of the interface reaction. The carbon interface removal initiates at the exposed fibre ends but immediately upon the formation of a void around the end, the fibre oxidation fills the gap and prevents further oxygen ingress. The silica bridging therefore forms a passivating plug which protects the interface from oxidation. The matrix at these higher temperatures strains more prior to matrix cracking and oxygen ingress. The higher strengths than at intermediate temperatures can be partly attributed to reduced matrix rigidity due to residual glassy phase becoming softer. Thus, matrix cracking is delayed and when cracking eventually takes place the interface degradation takes a finite time to complete. If this is so,



Figures 8a to c. Load deflection curves obtained in four-point bend tests for the CAS glass-ceramic matrix composite at a) room temperature, b) 700 °C, c) 1100 °C.

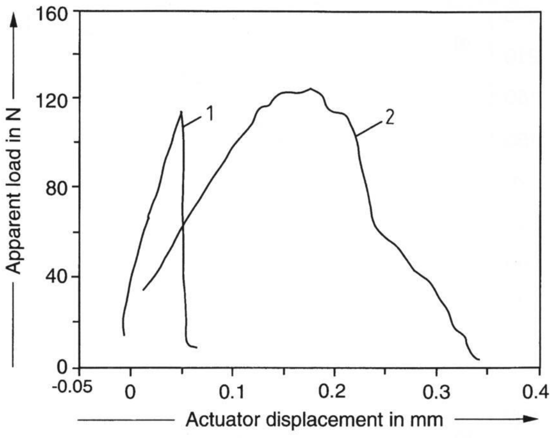


Figure 9. Load deflection curves of the BMAS material tested in four-point bend tests at 1100 °C for two strain rates. Curve 1: 0.01 mm/min, curve 2: 0.5 mm/min.

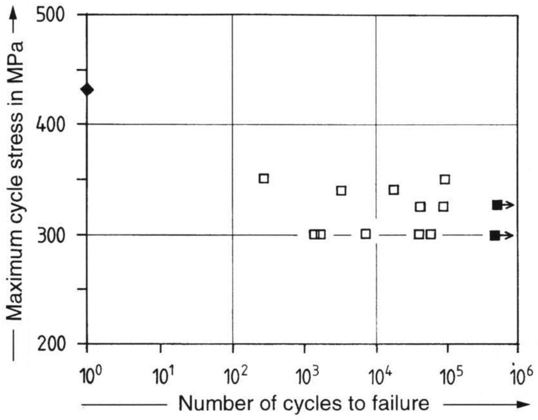


Figure 10. Maximum cycle stress against number of cycles to failure for BMAS material in four-point flexural fatigue tests; ◆: static test failure, □: fatigue fracture, ■→: fatigue run out. Each point represents a single experiment.

the composite strength at these temperatures will be highly strain rate-dependent. A test with the BMAS material at 1100 °C for two different strain rates (0.5 and 0.01 mm/min), as shown in figure 9, supports this approach. Superimposing the two load/displacement responses clearly shows a marked decrease in ductility for the low-strain rate specimen. Although the tests are not strictly comparable because of slight dimensional differences of the samples, the stiffness is much greater for the slower tested specimen, probably due to the more rigid interfacial bond due to silica bridging. The strength is also much reduced from the average at 1100 °C for the slow-strain rate sample. Certainly, new experimental work is needed to further support this approach. It is worth to point out that the influence of strain rates on the fracture of brittle matrix composites, being of great importance, in only beginning to be considered in detail in the literature [24].

On the basis of previous work [17] the possibility of sealing the fibre ends of the BMAS and CAS composite samples was studied. This involves exposing the composite to a temperature between 1000 and 1200 °C (1100 °C in this study) instantaneously (sometimes called an up-quench) to form the passivating plug at the exposed fibre ends. The interface can be shielded from the oxidizing environment in this way. Heat-treated samples were used for the fatigue, creep and creep-fatigue testing and for the tensile tests, the results being discussed in the sections 3.2.3 and 3.2.4.

3.2.3 Fatigue, creep and creep-fatigue tests

Fatigue results in beding for the BMAS material are presented in figure 10. Depending on the maximum stress applied, three stages are observed, similarly to earlier investigations on LAS glass-ceramic composites [25 and 26]:

a) samples broken at first loading (ultimate bending strength);

b) fractures occurred after a limited number of cycles (from 100 to 10^5) in relation to the maximum fatigue stress;

c) no fracture occurred after a given number of cycles (typically $5 \cdot 10^5$).

While these results are in general comparable with those obtained under tension-tension fatigue of glass-ceramic matrix composites [27], most samples failed by delamination and not on the tensile side. Therefore, tensile fatigue results are in general preferable and current theoretical end experimental work on the fatigue behaviour of glass-ceramic matrix composites is focussed on this testing mode [28].

Creep tests in four-point bend of BMAS and CAS heat-treated composites were conducted at 1100 °C. Creep loads were chosen so as to apply a bend stress of 75 % of the maximum instantaneous bend strength at the selected temperature. The results of the creep response of the BMAS and CAS glass-ceramics are shown in figures 11a and b. Pseudo-steady-state creep is reached after approximately one quarter of the test duration of 12 h. An in-depth investigation of the creep response of CAS and BMAS glass-ceramic composites is being conducted in a parallel programme [29].

The results of the creep testing were used here in designing the creep-fatigue experiments, which involved the application of a cyclic load in the form of a square wave at 1100 °C. Application of the first load cycle gives comparable strain to the creep tests under the same load and temperature conditions, as expected. With removal of the load the composite recovers most of the creep strain ($\varepsilon_{cr,R} \approx \varepsilon_{cr}$, where ε_{cr} is creep strain and $\varepsilon_{cr,R}$ is the strain recovered), as shown in figures 12a and b for the creep-fatigue response of the BMAS and CAS materials, respectively. The creep strains which are nor recovered on each cycle accumulate and lead to an increase in the overall strain. The recovery of the creep strain when unloaded at temperature can be explained by the load transfer from the creeping viscoelastic matrix to the fibres which, at these temperatures, do not creep significantly within the time span and stresses involved [30]. The load is therefore stored elastically in the fibres. When the lower load half of the cycle is acting the fibres may provide the mechanism for matrix creep in reverse, thus enabling creep strain recovery. A more detailed study of creep recovery behaviour is beyond the scope of this work. This has been the subject of previous work [31], where the creep strain recovery of BMAS glass-ceramic matrix composites has been quantified for different loading conditions in terms of strain recovery ratios [32].

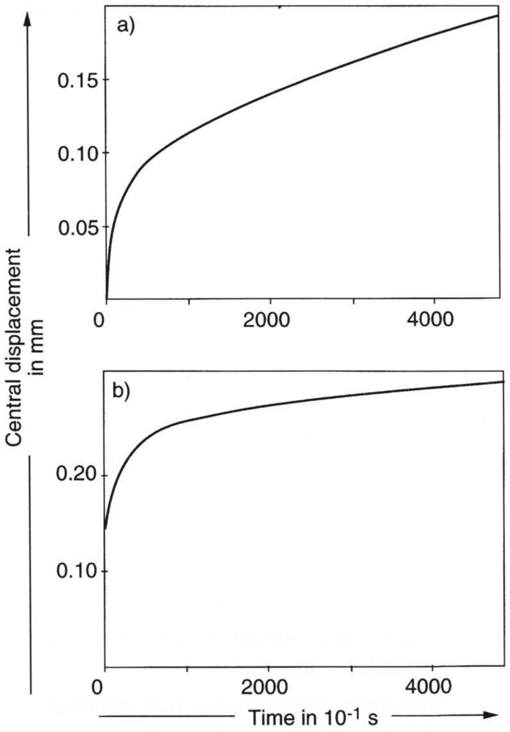
At the maximum cyclic load, equivalent to 75 % of the ultimate bend strength, all creep-fatigue test specimens have failed within 3 h. The intended test duration in creep-fatigue has been selected as twice the duration of the creep tests. This is to ensure the maximum creep stress is applied for the same period in both tests (12 h). While the specimens in creep can endure this period it seems the creep-fatigue specimens cannot at this stress level. A possible explanation for the premature failures within the first few cycles could be embrittlement caused by exposure to the oxidizing atmosphere. It should be noted, however, that creep tests at this temperature last for the whole testing period of 12 h so it is the repetitive loading or the actual load cycle which causes the premature failures. The results indicate a strong influence of cyclic loading on the life of components undergoing simultaneously creep. More experimental testing on this topic, including the use of different cyclic frequencies, wave forms and loads is needed, in order to more accurately assess the materials response under these complex loading conditions.

3.2.4 Tensile tests

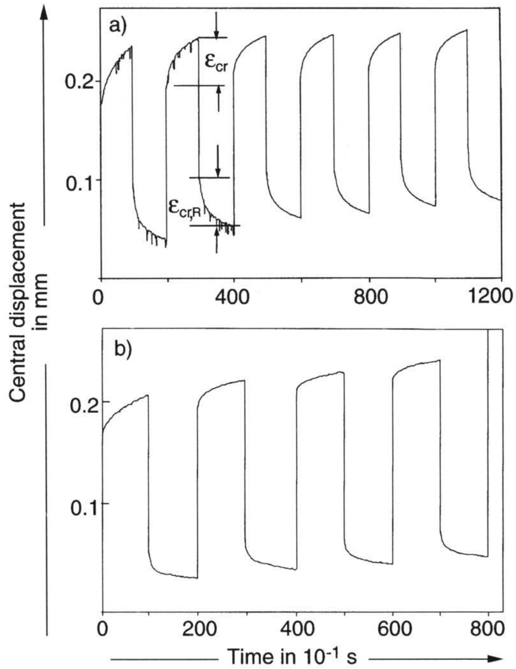
The ultimate strength of heat-treated BMAS composites has been assessed in direct tension at room temperature with tensile strength values of ≈ 400 MPa, and much less scatter than for the bend tests. A typical tensile load deflection curve is shown in figure 13, indicating the "graceful" mechanical behaviour of the composite. Extensive "pull-out" was observed. Work is in progress to assess the high-temperature tensile behaviour of BMAS and CAS heat-treated materials. At elevated temperatures less brittle behaviour than that of as-received (i.e. untreated) materials is expected.

4. Conclusions

An assessment of the mechanical behaviour of several continuous fibre-reinforced glass-ceramic matrix composites has been undertaken. Particular emphasis has been placed upon obtaining a greater understanding of the influence of environmental ageing upon mechanical



Figures 11a and b. Creep behaviour of glass-ceramic matrix composites at 1100 °C under applied stress equivalent to 75 % of average flexural strength at this temperature; a) BMAS material, b) CAS material.



Figures 12a and b. Creep-fatigue behaviour of glass-ceramic composites at 1100 °C. Maximum stress equivalent to 75 % of average flexural strength at this temperature and minimum nominal load of 0.01 kN were applied. ε_{cr} is the creep strain, and $\varepsilon_{cr,R}$ is the creep strain recovered; a) BMAS material, b) CAS material.

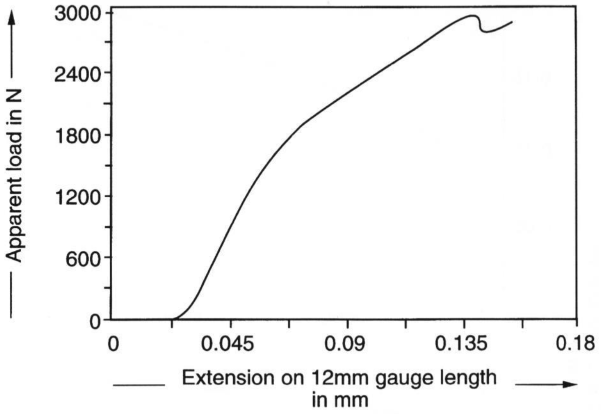


Figure 13. Typical tensile load deflection curve for the aged BMAS glass-ceramic matrix composite at room temperature.

behaviour, which has been assessed by different macromechanical tests and microstructure characterization. The principal conclusions are:

a) Oxidative degradation of the carbon-rich interface occurs during fast-fracture testing at elevated temperature, resulting in significant strength reduction and a transition to brittle failure mode at temperatures greater than 800 °C.

b) Similar effects are apparent after high-temperature ageing. However, minimum strength is observed at 700 °C, with a strength increase to levels approaching the as-received material at higher temperatures. A mechanism of oxidation of the carbon-rich interface and its removal at 700 °C followed by the development of SiO_2 bridges between the matrix and the fibre can explain this behaviour. At higher ageing temperatures the formation of a SiO_2 "plug" at exposed fibre ends inhibits further interface degradation by acting as a barrier against further oxygen ingress. This fact can conveniently be used to seal the exposed fibre ends of the samples by a rapid heat treatment (up-quench) at 1100 °C for 1 h.

c) Flexural fatigue testing of composite materials is subject to undesirable delamination failure mode of most samples. Tensile fatigue tests are therefore preferable.

d) From the results of the creep and creep-fatigue tests, a creep-fatigue synergism effect can be inferred, with cyclic loading being detrimental for the behaviour of the composite at high temperature and under creep conditions. The existence of creep recovery, however, would indicate a reduction of the total strain accumulated, and therefore, a positive contribution to the life of the components undergoing cyclic creep. More experimental work is clearly needed for an in-depth study of the creep-fatigue behaviour of glass-ceramic matrix composite materials and this will be the subject of future investigations.

e) The tensile tests provided more realistic tensile strength data than the bend tests, since only tensile failures were observed. Heat-treated samples showed "composite" failure mode at room temperature with extensive fibre "pull-out". The effectiveness of the heat treatment for 1 h at 1100 °C in sealing the fibre ends and preventing extensive degradation of the carbon-rich interface will be assessed carrying out tensile tests at high temperatures.

*

The authors acknowledge the financial support of the European Commission with the provision of Brite-Euram contracts (no. BE4610 and BRE2 CT94 3064).

5. References

[1] Prewo, K. M.; Brennan, J. J.: High strength silicon carbide fiber-reinforced glass-ceramic composites. J. Mater. Sci. **15** (1980) no. 2, p. 463–468.

[2] Prewo, K. M.; Brennan, J. J.: Silicon carbide yarn-reinforced glass matrix composites. J. Mater. Sci. **17** (1982) no. 4, p. 1201–1206.

[3] Brennan, J. J.: Interfacial chemistry and bonding in fiber reinforced glass-ceramic matrix composites. In: Tressler, R. E.; Lessing, G. L.; Newnham, G. C. (eds.): Tailoring multiphase and composite ceramics. New York: Plenum Press 1988. p. 387–400.

[4] Spallek, M.; Pannhorst, W.: Starke Partner für Hochtemperatur-Verbundwerkstoffe. Werkst. Konstr. **3** (1989) p. 505–508.

[5] Lewis, M. H.; Chamberlain, A. et al.: Microstructure-property relationships in silicate matrix composites. J. Microsc. **169** (1993) p. 109–118.

[6] Klug, T.; Reichert, J.; Brückner, R.: Thermal shock behaviour of SiC-fibre-reinforced glasses. Glastech. Ber. **65** (1992) no. 2, p. 41–49.

[7] Prewo, K. M.: Tension and flexural strength of SiC fiber reinforced glass-ceramics. J. Mater. Sci. **21** (1986) p. 3590–3600.

[8] Cooper, R. F.; Chyung, K.: Structure and chemistry of fiber-matrix interfaces in silicon carbide fiber reinforced glass-ceramic matrix composites: An electron microscopy study. J. Mater. Sci. **22** (1987) p. 3148–3160.

[9] Metcalfe, B. L.: Donald, I. W.; Bradley, D. J.: Development and properties of a SiC fiber-reinforced magnesium aluminosilicate glass-ceramic matrix composite. J. Mater. Sci. **27** (1992) p. 3075–3081.

[10] Murthy, V. S. R.; Lie, J.; Lewis, M. H.: Interfacial microstructure and crystallization in SiC glass-ceramic composites. Ceram. Eng. Sci. Proc. **10** (1989) p. 938–951.

[11] Bleay, S. M.; Scott, V. D.; Harris, B. et al.: Interface characterization and fracture of calcium aluminosilicate glass-ceramic reinforced with Nicalon fibers. J. Mater. Sci. **27** (1992) p. 2811–2822.

[12] Murthy, V. S. R.; Pharaoh, M. W.; Lewis, M. H.: Interface, matrix and fibre microstructure in SiC-reinforced glass-ceramic matrix composites. In: Proc. International Conference on New Materials and their Applications, Warwick (Great Britain) 1990. p. 185–196. (Institute of Physics, Conf. Ser. 111.)

[13] Sun, E. Y.; Nutt, S. R.; Brennan, J. J.: Interfacial microstructure and chemistry of SiC/BN dual-coated Nicalon-fiber-reinforced glass-ceramic matrix composites. J. Am. Ceram. Soc. **77** (1994) no. 5, p. 1329–1339.

[14] Evans, A. G.; Marshall, D. B.: The mechanical behaviour of ceramic matrix composites. Acta Metall. **37** (1989) p. 2567–2583.

[15] Evans, A. G.; Zok, F. W.; Davis, J. B.: The role of interfaces in fibre-reinforced brittle matrix composites. Comp. Sci. Technol. **42** (1991) p. 3–24.

[16] Casteels, F.; Sleurs, J.; Lecocq, R.: Ceramic composites materials: A contribution to an overall technology assessment. In: Davidge, R. W.; Voorde, M. H. van de (eds.): Designing with Structural Ceramics. London (et al.): Elsevier 1990. p. 336–342.

[17] Plucknett, K. P.; West, G.; Taplin, D. M. R. et al.: Continuous fibre reinforced glass-ceramic matrix composites: Microstructure, mechanical behaviour and environmental stability. In: Proc. 8th International Conference on Fracture, Kiev (Ukraine) 1993. Oxford (et al.): Pergamon Press. (In press.)

[18] Holmes, J. W.: Tensile creep behavior of a fiber reinforced SiC–Si_3N_4 composite. J. Mater. Sci. **26** (1991) p. 1808–1814.

[19] Plucknett, K. P.; Sutherland, S.; Daniel, A. M. et al.: Environmental ageing effects in a silicon carbide fibre reinforced glass-ceramic matrix composite. J. Microsc. **177** (1995) p. 251–260.

[20] Pharaoh, M. W.; Daniel, A. M.; Lewis, M. H.: Stability of interfaces in calcium aluminosilicate matrix/Nicalon SiC fiber composite. J. Mater. Sci. Lett. **12** (1993) p. 998–1001.

[21] Prewo, K. M.; Batt, J. A.: The oxidative stability of carbon fiber reinforced glass-matrix composites. J. Mater. Sci. **23** (1988) p. 523–527.

[22] Bischoff, E.; Rühle, M.; Sbaizero, O. et al.: Microstructural studies of the interfacial zone of a SiC-fiber-reinforced lithium aluminum silicate glass-ceramic. J. Am. Ceram. Soc. **72** (1989) no. 5, p. 741–745.

[23] Cao, H. C.; Bischoff, E.; Sbaizero, O. et al.: Effect of interfaces on the properties of fiber-reinforced ceramics. J. Am. Ceram. Soc. **73** (1990) no. 6, p. 1691–1699.

[24] Vaidya, R. U.; Chawla, K. K.: Effect of strain rate on the fracture of ceramic fiber reinforced glass matrix composites. J. Mater. Sci. **29** (1994) p. 3535–3541.

[25] Prewo, K. M.: Fatigue and stress rupture of silicon carbide fiber-reinforced glass-ceramics. J. Mater. Sci. **22** (1987) p. 2695–2701.

[26] Prewo, K. M.; Johnson, B.; Starrett, S.: Silicon carbide fiber-reinforced ceramic composite tensile behavior at elevated temperature. J. Mater. Sci. **24** (1989) p. 1373–1379.

[27] Rouby, D.; Reynaud, P.: Role of interfaces on the cycle fatigue behavior of ceramic matrix composites. In: AGARD Report 795: Introduction of ceramics into aerospace structural composites. 1993. p. 6.1–6.10.

[28] Vanswijgenhoven, E.; Wevers, M.; Biest, O. van der: Modelling of the stress-strain behaviour during tensile and tension-tension fatigue testing of uni-directional SiC fibre reinforced glass-ceramic matrix composites. Presented at: 3rd International Conference on Ceramic-Ceramic Composites, Mons (Belgium) 1994.

[29] Sutherland, S.; Lewis, M. H.: Engineered fibre strengthened ceramic composites structural integrity and performance in energy conversion and processing systems. Brite Euram Report 4610-09, 1994.

[30] Simon, G.; Bunsell, A. R.: Creep of silicon carbide fibers. J. Mater. Sci. Lett. **2** (1983) p. 80–82.

[31] West, G.; Boccaccini, A. R.; Taplin, D. M. R.: Creep and creep-fatigue behaviour of continuous fibre reinforced glass-ceramic matrix composites. Materialwiss. Werkstofftech. **26** (1995) p. 368–373.

[32] Holmes, J. W.; Park, Y. H.; Jones, J. W.: Tensile creep and creep-recovery behavior of a SiC-fiber–Si_3N_4-matrix composite. J. Am. Ceram. Soc. **76** (1993) no. 5, p. 1281–1293.

0296P002

Addresses of the authors:
G. West, D. M. R. Taplin, A. R. Boccaccini, K. Plucknett
Department of Environmental Sciences
University of Plymouth
Plymouth PL4 8AA (Great Britain)

M. H. Lewis
Department of Physics, Centre for Advanced Materials
University of Warwick, Coventry CV4 7AL (Great Britain)