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Fabrication, mechanical properties and thermal stability of a novel glass matrix composite material reinforced by short oxycarbide fibres

A. R. BOCCACCINI*
Department of Materials, Imperial College, London SW7 2BP, UK
E-mail: a.boccaccini@ic.ac.uk

R. LIEBALD, W. BEIER
Schott Glas, P.O. Box 2480, D-55014 Mainz, Germany

K. K. CHAWLA
Department of Materials Science and Engineering, University of Alabama, Birmingham AL 35294-4461, USA

An aluminosilicate glass matrix composite material reinforced by randomly oriented SiC-based (Tyranno™) chopped fibres was fabricated. Slurry dipping and hot-pressing techniques were used to prepare dense composites containing 45 vol% fibres uniformly dispersed in the glass matrix. The mechanical properties and fracture mechanisms of the composite under flexion and compression loading were studied. In flexure, the composite showed higher modulus and strength than the unreinforced glass. However, in compression, the strength of the composite was lower than that of the monolithic glass. Considering the potential application of the material at high temperatures, the thermal aging behaviour of the composite in air at temperatures between 500 and 700°C was investigated. The composite retained its room-temperature compressive strength after exposure for 26 h at 500°C. The variation of compressive strength measured after exposures at higher temperatures was ascribed to mechanisms of fibre/matrix interface oxidation and to the softening of the glass matrix.

1. Introduction

The composite approach is an attractive way to the improvement of the thermomechanical properties of glass and glass-ceramics. In a glass matrix composite material, the low-modulus, low-strength, brittle glass matrix is reinforced by a high-modulus, high-strength and/or high-ductility second constituent in the form of continuous or chopped fibres, whiskers, platelets or particulates [1, 2]. The resulting properties of the composite, which are not attainable by the single glass matrix, vary strongly depending on the characteristics, geometry and microstructural arrangement of the reinforcing phase. The best results in term of increasing the fracture tolerance and imparting a pseudo-ductile fracture behaviour to brittle matrices is achieved with continuous fibre reinforcement, including unidirectional and cross-ply fibre alignment, and 2- and 3-dimensional fibre architectures [2–5]. The vast majority of work concerned with fibre reinforcement of glasses and glass-ceramics has focused on using carbon and SiC-based fibres as recently reviewed [2].

Unidirectional fibre reinforced composites are anisotropic and prone to delamination because of the low interlaminar shear strength corresponding to that of the glass matrix. Unidirectionally reinforced composites are therefore not suitable for applications involving complex and multiaxial loads. This limitation can be alleviated by the incorporation of through-thickness reinforcement, i.e., by using 3-D fibre architectures [6, 7], or developing hybrid composites, i.e., with both fibre and particulate or whisker reinforcement [8–10]. Another possibility to obtain isotropic properties in a composite is by dispersing the reinforcing phase randomly in the matrix, i.e., as chopped fibres statistically oriented in the three dimensions. These composites, will have, however, a lower fracture strength than unidirectional composites in the direction of the fibres, but an improved transverse and shear strength. They are also expected to have better wear and abrasive resistance than unidirectional composites, resembling the tribological behaviour of whisker-reinforced ceramics [11]. On the other hand, the compressive strength of chopped fibre reinforced composites may be compromised due to the fibres acting effectively as microindenters and crack nucleators, as in whisker-reinforced brittle matrix composites [12]. It is thus important to investigate

*Author to whom all correspondence should be addressed.

the behaviour of brittle matrix composite materials in compression because the conventional wisdom about superior mechanical behaviour of brittle materials in compression may not necessarily be true for these composites.

In this contribution, the fabrication of an aluminosilicate glass matrix composite material reinforced by SiC-based oxycarbide (Tyranno^{TM}) chopped fibres is presented. The mechanical and fracture properties of the materials have been investigated. Because these composites may find applications involving impact and compressive loads, especial emphasis was given to understand their compressive behaviour. Moreover, considering the potential application of the material at high temperatures, the thermal aging behaviour of the composite in air at temperatures up to 700°C was investigated.

2. Experimental procedures

The glass matrix material is a commercially available aluminosilicate glass (code 8252, Schott Glas, Mainz, Germany). The oxycarbide fibres used were of type Tyranno^{TM} New Lox M (Ube Industries, Japan). The fabrication involved two steps: fibre impregnation and composite consolidation at high temperatures. Fibre bundles were impregnated with the matrix by drawing them through a bath slurry with air blown from below. The glass powder (mean size <8 μm) and a silicon alkoxide solution were used to form the slurry with an organic binder to "glue" the glass particles to the fibres. The process is similar to that developed for unidirectional reinforced glass matrix composites [13]. Impregnated fibre bundles were chopped to 20–40 mm length, and placed randomly in the die of a hot-press. The densification of the composites took place under an inert atmosphere at a temperature of 1200°C during 2 h. A pressure of 10 MPa was applied during the holding period at the temperature. Specimens ($100 \times 100 \times 3$ mm^3) containing a nominal fibre volume fraction of 45% were fabricated. The density of the composites was 2580 kg/m^3. From the as-hot-pressed discs, samples for measuring mechanical properties were prepared by cutting and polishing.

The three-point flexural strength test was conducted to obtain the fracture strength (modulus of rupture) using samples of dimensions $100 \times 4 \times 3$ mm^3 and a span of 90 mm. Compression strength tests were carried out using prismatic specimens ($4 \times 3 \times 3$ mm^3), with the larger dimension parallel to the compressive stress. It was envisaged that short and thick specimens would prevent the buckling that would invalidate the compressive strength results. The surfaces perpendicular to the compressive stress were parallel polished to a tolerance of 0.05 mm. This was necessary in order to avoid or minimize the problem of specimen misalignment during testing. The specimens were tested in air at room temperature in a standard hydraulic testing machine using a strain rate of 0.001 s^{-1}. The specimens were loaded until fracture and the stress/strain curve was obtained. As-fabricated and thermally aged specimens were tested as well as specimens made from plain glass matrix (without fibre reinforcement). At least seven samples for each condition were used. Thermal-aging experiments involved heating unstressed samples at elevated temperatures (400–700°C) in air for long periods of time (up to 100 hours). After the thermal exposure, the samples were cooled down slowly in the furnace. The weights of the samples before and after the thermal aging were measured using a high-precision electronic balance. The microstructures of as-fabricated and thermally aged samples were characterised using optical microscopy and scanning electron microscopy (SEM) on polished sections and on fracture surfaces.

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the microstructure of the fabricated composites, indicating the random orientation of the fibres. The kind of fibre arrangement depicted in Fig. 1 has not been reported before for glass matrix composites; this may originates from the particular slurry impregnation technique used here. In previous work on chopped fibre reinforced glass matrix composites, extrusion techniques were used in order to obtain a preferred orientation of the fibres [14]. The composites obtained, therefore, were highly anisotropic with the fibres oriented parallel to the extrusion direction [14]. In another processing approach, silica, mullite and alumina short fibres have been incorporated into glass matrices by a tape casting technique [15]. This method also yielded a preferred orientation of the fibres and thus, anisotropic composites. The composites fabricated in the present work, on the contrary, are isotropic because the fibres are randomly oriented. The difficulty for the adequate dispersion of chopped fibres in glass matrices has been considered by other authors by utilising different mixing techniques, including ultrasonic, ball millling and stirring [16]. Particularly troublesome is to achieve sufficient separation of the fibres in the bundle and to get adequate coating of the single fibres through glass powder particles to achieve enhanced densification. Fig. 1 reveals that the impregnation process adopted in this work has led to an adequate glass particle packing around the fibres and in the inter- and intra-tow regions, so that pore-free materials could be fabricated. Fig. 1 also shows that the fibres are homogeneously distributed in the glass matrix and that there are very few fibre-fibre contacts. There are however some matrix-reach regions which could represent weak regions in the material (as discussed below).

3.2. Mechanical properties

3.2.1. Room-temperature flexure strength

Table I shows the mechanical properties of the composite material obtained by flexural strength test. For comparison, the properties of an equivalent unidirectional (UD) fibre reinforced composite [17] and of the unreinforced glass matrix [18] are also shown. It is seen that the mechanical strength of the UD composite, measured parallel to the fibre direction, can be more than four times higher than that of the present random composite. However, the transverse fracture strength of the UD composite was equal to that of the glass matrix (55 MPa) [18], being thus much lower than that of the random composite.

TABLE I Mechanical properties measured in flexural strength test of the random composite fabricated in this study and of equivalent unidirectional composites

Composite	Fibre architecture	Fibre volume fraction (%)	Ultimate flexure strength (MPa)	Young's modulus (GPa)	Coefficient of thermal expansion (ppm K^{-1})
SiC fibre/aluminosilicate glass matrix (Code 8252 Schott) (this study)	Random	45	150 (measured in two perpendicular directions)	90 (measured in two perpendicular directions)	3.0
SiC fibre/borosilicate glass matrix (DURAN®) [17]	Unidirectional	45	700 (tensile load parallel to fibre direction)	120 (tensile load parallel to fibre direction)	3.0
Unreinforced DURAN® glass matrix [18]	Not applicable	Not applicable	55	79	Not measured

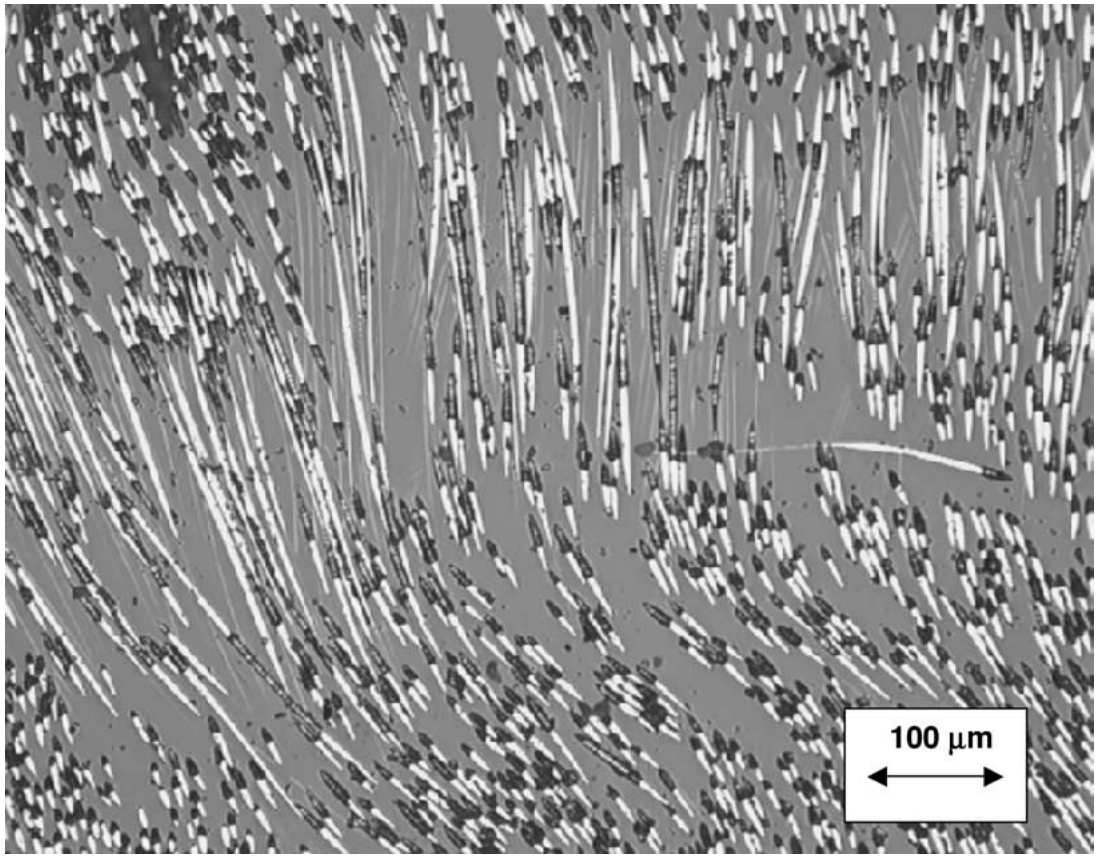


Figure 1 Optical micrograph showing the microstructure of the composite material, exhibiting homogeneous distribution and random orientation of chopped Tyranno(TM) fibres and high matrix density.

The random composite exhibited a flexure strength more than two times higher than that of the unreinforced glass. In a flexure test, the fracture process is dominated by the tensile stress state, although the specimen will be in compression in one half and in tension in the other half. The short fibres will contribute to the modulus and strength under tensile loading. It is understandable that compared to a unidirectionally reinforced composite, the present isotropic composite will be less efficient in strength and modulus in the direction of continuous fibres but more efficient in all other directions. Compared to the monolithic glass, the isotropic composite showed superior mechanical properties. Thus, the normal fibre loading by shear lag mechanism would be operative under tensile and flexural loading. Since this composite has a weak fibre/matrix interface, which is typical for all glass matrices reinforced by oxycarbide fibres of type Nicalon™ or Tyranno™ [17], it is expected that the material will also exhibit higher fracture toughness than the unreinforced glass.

3.2.2. Room-temperature compressive strength

Typical stress-strain curves recorded during compressive strength tests for an as-fabricated composite specimen and for a plain glass matrix sample are shown in Fig. 2. Clearly, the incorporation of randomly oriented chopped fibres degraded the compressive strength of the material, which was four times lower than that of the unreinforced glass. Similar results have been obtained in whisker-reinforced ceramic matrix composites, as reported by Lankford *et al.* [12, 19]. The stress-strain curve of the composite deviated from the linear elastic behaviour before reaching the ultimate strength, indicating resistance to catastrophic crack propagation typical of fibre composites. Moreover after the attainment of the ultimate strength, the material tended to drop off in a stable manner. Typical failure mechanisms occurring during compression of composites include fibre buckling and local crushing of the test specimens [20]. In composites with discontinuous reinforcement

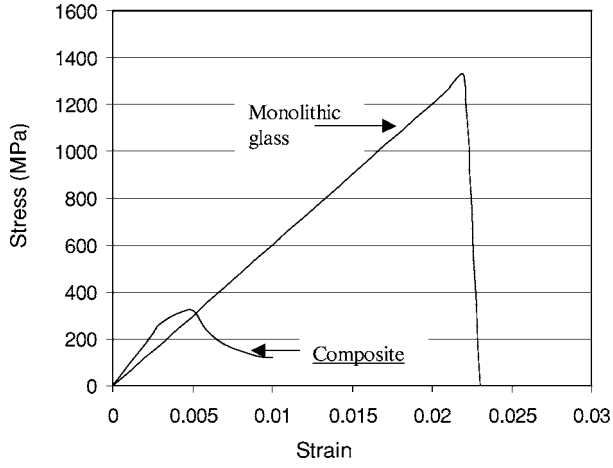
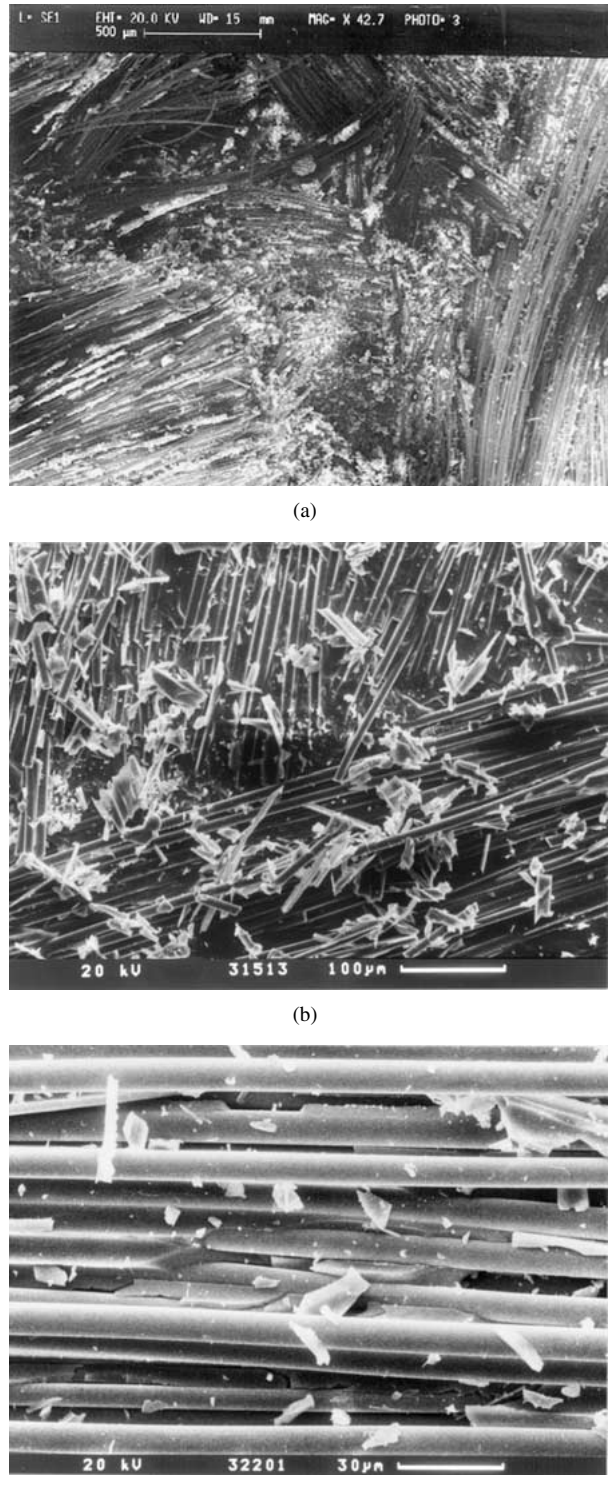


Figure 2 Typical stress-strain curves recorded during compression strength tests for composite and monolithic glass matrix specimens.

tensile stresses can be generated in a compressive field if microstructural inhomogeneities are present. Previous work on compression strength of fibre reinforced glass and glass-ceramics has concentrated mainly on continuous fibre reinforcement [21, 22], where fibre buckling and matrix microfracture were shown to be the main failure mechanisms. Only limited work has been conducted on compression strength of whisker- and chopped-fibre-reinforced brittle materials [12, 19]. A common finding of these works is that the composites may be weaker than the monolithic matrices. In the case of whisker-reinforced glass-ceramics this behaviour was observed when the materials were tested under low strain rates ($<1\ s^{-1}$) [12], in agreement with the present results (Fig. 2). Moreover, it was shown that chopped fibres or whiskers oriented normal to the compressive axis may behave as micro-indenters, leading to the formation of cracks at lower applied stresses than for the unreinforced monolithic matrices. In particular for SiC-whisker-reinforced lithium aluminosilicate glass-ceramics, Lankford [12] showed that small whiskers ($<1\ \mu$m diameter) could lead to an increase of the compressive strength, but large whiskers ($>3\ \mu$m diameter) were detrimental because they served as microcrack-nucleating inclusions.

In the present investigation, failed specimens consisted of two fragments. Observation of the fracture surfaces by SEM revealed that the crack propagated through matrix regions or along fibre/matrix interfaces but in no case fibre breaking was observed. Typical fracture surface images are shown in Fig. 3a–c. Following the explanation of Lankford [12] for whisker-reinforced glass-ceramics, it is proposed that initial axial microcracks nucleated at the surface of fibres, and propagated subsequently through matrix-rich regions and fibre/matrix interfaces, with minimal interaction with other fibres that they might encounter. The compressive failure mode of this kind of composites is in reality a series of more-or-less simultaneous local microcrack nucleation events, producing an initial ensemble of axial cracks. This damage development may lead to the loss of stiffness of the composite before failure, as detected here (Fig. 2). Upon further loading, the cracks would then coalesce leading to fracture. This fracture mechanism is supported by observation of fracture surfaces



(a)

(b)

(c)

Figure 3 Typical fracture surface images of composites after compression strength tests at low (a) and high magnifications (b,c). Note absence of fibre breakage and fibre pull-out.

of specimen fragments at high magnification (Fig. 3b and c), which revealed practically no fibre pull-out or fibre breakage, suggesting that crack propagation has occured through the matrix and around fibre/matrix interfaces.

3.3. Thermal aging behaviour

Fig. 4 shows a summary of the results obtained for the compressive strength and weight loss of samples thermally aged at 600°C. It is seen that the variation of sample weight parallels the variation of compressive

strength for different aging durations. Fig. 5 shows the compression strength of samples aged at different temperatures for different durations. For aging at 400 and 500°C, the compressive strength has not changed significantly in comparison with the as-received condition. For aging at 600°C, the compressive strength depended on the duration of the exposure, while for aging at 700°C, a strong degradation of the compressive strength was observed.

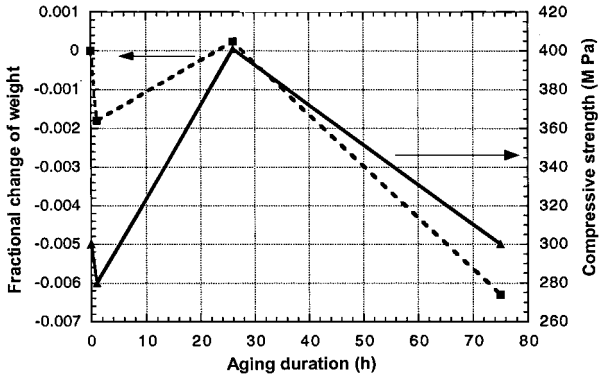


Figure 4 The compressive strength and weight loss for composite samples thermally aged at 600°C. It is seen that the variation of sample weight parallels the variation of compressive strength for different aging durations.

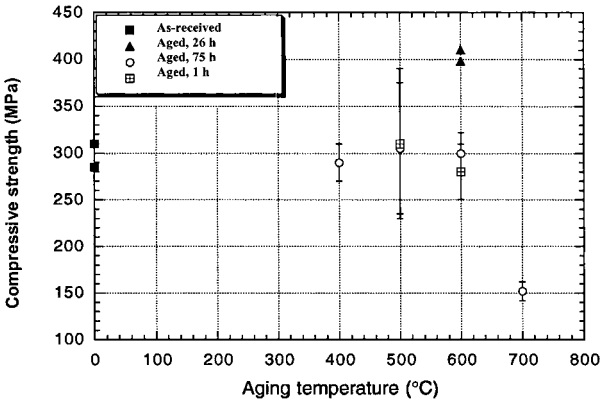


Figure 5 Compressive strength of samples aged at different temperatures for different durations.

Several mechanisms can contribute to the behaviour observed. For example, the oxidation of the carbon-rich interface, which is characteristic of oxycarbide fibre reinforced glass matrix composites [2, 18], could be responsible for the loss of compressive strength after short exposures at 600°C (<10 h) (Fig. 4). This form of microstructural damage, characterized by the formation of annular pores around the fibres, has been observed in aging experiments of similar (unidirectional) composites [23]. In addition to the oxidation reaction of the carbon-rich interface layer, another competing reaction involving oxygen takes place during thermal aging; namely, the surface oxidation of the oxycarbide fibre, which leads to the formation of SiO_2 at the interface. It has been shown that with increasing temperature or exposure duration, fibre surface oxidation begins to predominate over oxygen transport through the annular pore [24]. When this occurs, the pore will be sealed by the SiO_2formed and a strong fibre/matrix bonding will develop [23, 24]. Thus, in the present experiments, the increase of compressive strength at intermediate exposures (20–30 h) could be related to this stronger fibre/matrix interfacial bonding. For longer aging duration at 600°C or for aging at higher temperatures (700°C), partial oxidation of the fibres may start to occur. This, in combination with accelerated formation of SiO_2 on the fibre surface and thus degradation of the interface, may explain the low compressive strength measured under these conditions. As found by other authors [25], the presence of a silica surface layer may induce some fibre notch-sensitivity, which will contribute to microcrack development at the fibre/matrix interfaces. Moreover, exposure of the material for long durations above the glass transition temperature of the glass matrix, can also result in viscous flow of the glass with consequent cavity or pore formation, which is exacerbated by the presence of the rigid, constraining fibres [26, 27]. This form of microstructural damage can be deduced from the SEM micrograph (Fig. 6) for the polished section of a sample aged for 75 h at 700°C. It is evident that viscous flow of the matrix at this temperature has resulted in the formation of cavities, as well

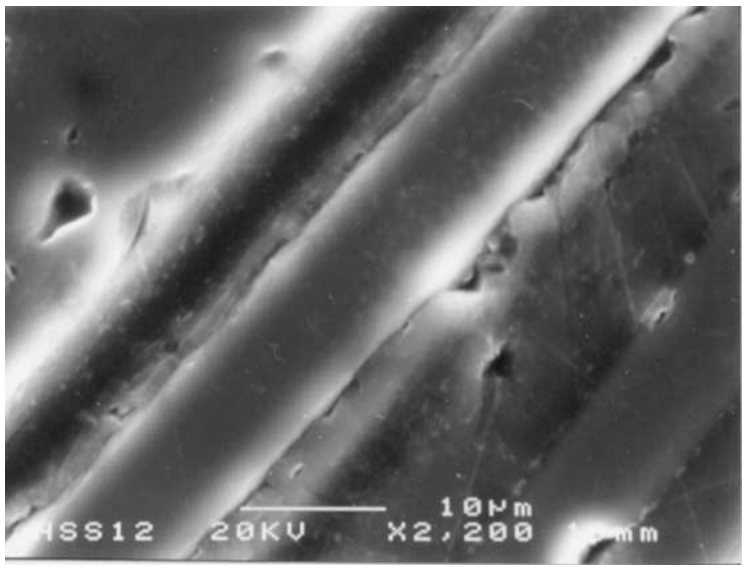


Figure 6 SEM micrograph of a polished section of the sample aged for 75 h at 700°C showing formation of cavities, as well as local separation of fibre and matrix due to softening of the glass matrix.

as local separation of fibre and matrix and development of interfacial cracking. Thermal aging may also cause displacement and rearrangement of the fibres within the composite. Such effects have also been found in similar (unidirectional) composites thermally aged in hot air at temperatures >500°C [23]. These mechanisms, in particular the formation of pores and microcracks, are likely to lead to a loss of composite stiffness and also explain the observed weight loss of the specimens. Softening of the matrix may also indirectly contribute to the loss of compressive strength measured for long aging durations at 600°C and 700°C. For example, extensive fibre-fibre contact is a probable consequence of the matrix softening and subsequent fibre displacement. This could generate local stress concentrations at the points of contact, increasing the likelihood of microcrack formation and hence reduced composite compressive strength. Furthermore, the formation of cavities within the matrix in the vicinity of the fibres may produce some surface damage on the fibres (see Fig. 6), increasing their flaw populations, thus further weakening the composites. Note that this effect occurs in addition to the induced notch-sensitivity caused by the silica layer formed on the partially oxidized fibre surfaces, as mentioned above. Microstructural damage development based on cavity formation and matrix softening has also been invoked to explain the degradation of flexure strength in similar (unidirectional) oxycarbide-fibre reinforced glass and glass-ceramic matrix composites after thermal aging [23, 28].

4. Conclusions

A novel glass matrix composite material consisting of randomly dispersed chopped oxycarbide (Tyranno^{TM}) fibres in an aluminosilicate glass matrix was produced by slurry processing and hot-pressing. The composite showed isotropic mechanical properties. In flexure, the strength and modulus of the composite were higher than those of the monolithic glass as expected on the basis of a load-transfer mechanism. The compressive strength of the composite was lower than that of the unreinforced glass matrix. The compressive fracture of the composite was explained on the basis of initial microcracks nucleating at fibres surfaces and subsequent propagation of cracks through matrix-rich regions and fibre/matrix interfaces, with no fibre breakage or pull-out. The variation of compressive strength after exposure of the material to high temperatures in air was studied. The composite retained its room-temperature compressive strength after exposure for 75 h at 500°C. The variation of compressive strength after exposure at higher temperatures is related to mechnanisms of fibre/matrix interface oxidation and softening of the glass matrix, which led to pore formation. An increase of compressive strength was measured for composites thermally aged at 600°C for 26 h, which was explained by the formation of a strong fibre/matrix interface due to oxidation of the carbon-rich interface.

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