

Silicon carbide yarn reinforced glass matrix composites

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Continuous silicon carbide fibre yarn has been used as a reinforcement for borosilicate and 96% silica glass matrices. The resultant composites exhibit excellent levels of strength and elastic modulus up to temperatures of 600° C and 1100° C, respectively. At higher temperatures excessive matrix softening causes a significant reduction in composite flexural strength.

1. Introduction

Fibre-reinforced ceramic matrix composites offer significant potential for the development of fracture tough, reliable ceramic materials. One of the most attractive ways of creating these types of materials is through the use of a ceramic in the glassy state as a matrix. The glass can provide several important advantages over crystalline ceramics. First, because of its viscous flow characteristics it can be readily densified with fibres into a composite structure by the application of pressure at elevated temperature. Unlike in the case of crystalline ceramics, this densification can be carried out to achieve very high fibre contents without causing damage to the reinforcing fibres. Second, a glass can be chosen which has an elastic modulus well below that of the intended fibre reinforcement. Thus, during the application of stress to the composite, the fibres provide the main load-bearing composite constituent and, as will be shown, strengths in excess of those of the parent ceramic matrix can be readily achieved. Finally, numerous glass compositions are available to provide a broad selection of chemically compatible matrices to be combined with high performance ceramic fibres. The following paper will demonstrate that high levels of composite structural performance can be maintained up to temperatures well above those normally considered for glass.

In a previous paper [1], it was shown that silicon carbide fibre-reinforced glass matrix composites offer a unique opportunity to achieve high

strength, low density, fracture tough ceramic composites for elevated temperature applications. The work described herein extends these earlier findings. In this case, the work has been limited to the use of silicon carbide yarn as the reinforcement, while in the former paper the use of both the yarn and a silicon carbide monofilament were investigated. Because of the larger fibre surface-to-volume ratio of the yarn and the much finer composite microstructure developed through its use, the general integrity and transverse properties of yarn-reinforced composites were found to be superior to those of monofilament-reinforced material.

The following paper will demonstrate that both borosilicate glass and high silica glass can be used as matrices. In the former case, both unidirectionally- and bi-directionally-reinforced composites were fabricated and tested while in the latter case only unidirectional composites were evaluated. Finally, it will be shown that the reinforcement of a high silica glass can result in a composite with exceptional performance at temperatures up to 1200° C.

2. Composite fabrication and testing

The fibre was manufactured by the Nippon Carbon Co. of Japan and purchased in continuous length on spools which contained approximately 200 g each. The as-received fibre carried an organic binder to minimize any fraying during handling. This material was effectively removed by passing the fibre through the flame of a bunsen burner just prior to infiltration with glass slurry.

TABLE I Constituent materials properties

Property	Borosilicate glass (7740)	96% silica glass (7930)	SiC yarn
Density(g cm^{-3})	2.23	2.18	2.6
Elastic Modulus (GPa)	62.7	65.4	207–234
Thermal expansion coefficient ($\times 10^6 \text{ }^\circ\text{C}^{-1}$)	3.2	0.5	3.1
Annealing point ($^\circ\text{C}$)	560	800–900	–
Softening point ($^\circ\text{C}$)	820	900–1000	–
Working point ($^\circ\text{C}$)	1250	1500	–

This slurry infiltration process consisted of pulling the fibre tow through a continuously stirred mix of – 325 mesh-size glass powder in propanol. The infiltrated fibre was then wound directly onto a mandrel at controlled spacing to achieve a collimated fibre tape. After drying, the tape was cut into 7.5 cm \times 7.5 cm pieces which were stacked in a graphite die and densified in a vacuum hot-press at elevated temperature and pressure. The following three forms of glass matrices were utilized; the constituent glass properties are listed in Table I along with the strength and elastic modulus of the SiC yarn.

2.1. Borosilicate glass

Designated 7740 by the Corning Glass Works, borosilicate glass has been shown in the past [1] to provide an excellent matrix. Composites having this glass as matrix have demonstrated significant structural softening at temperatures above approximately 650 $^\circ\text{C}$ [1–3]. This glass was used in its “as-received” – 325 mesh-size form without any additional processing.

2.2. High (96%) silica glass

Frequently referred to as Vycor, high (96%) silica glass was procured in the form of “thirsty” Vycor powder. Designated 7930, this glass was obtained by leaching the boron from the structure of a borosilicate glass, thus raising its effective use temperature. As seen from the data in Table I, this glass offered a significant elevation in composite use temperature above that of the borosilicate glass. Composites could only be fabricated with this glass after it had been ball-milled in propanol for more than 100 h, despite the fact that the as-received powder was also in the – 325 mesh-size form.

2.3. Blended glasses

Combinations of the above two glasses were also used as matrices. In each case, the desired percentages of powders were mixed and then ball-milled for 100 h in propanol prior to fibre infiltration. It was hoped that the blending approach could provide an avenue for maintaining both the ease of composite fabrication characteristic of 7740 glass and also the high use temperature of the 7930 glass. All composite hot-pressing was performed in an inert atmosphere at temperatures in excess of 1200 $^\circ\text{C}$ and pressures in excess of 6.9 MPa.

2.4. Composite flexural testing

All composite specimens were tested in three-point bend flexure using a span-to-depth ratio of 20:1 except where noted. The nominal overall specimen dimensions were 1.9 mm \times 5 mm \times 7.5 cm with the minimum dimension of 1.9 mm used as the specimen depth in the above test ratio. All tests were performed in a laboratory-air environment.

3. Composite properties

3.1. Borosilicate glass matrix composites

3.1.1. Flexural strength

The three-point flexural strengths of both uniaxially (0 $^\circ$) and 0 $^\circ$ /90 $^\circ$ cross-ply reinforced specimens are shown in Fig. 1 and Table II as a function of test temperature. For the 0 $^\circ$ material, the average 22 $^\circ\text{C}$ strength of 470 MPa (35 vol% SiC) and 800 MPa (50 vol% SiC) represents a significant increase in performance over the composites described previously [1]. This may be due to an improvement of fibre quality but it is undoubtedly also due to improved fabrication process control. The earlier work had been performed with short lengths (1 metre) of fibre yarn which were hand dipped in slurry, cut to length, and placed into the hot-press die. In the current programme the use of continuous fibre and the tape making process have undoubtedly resulted in improved fibre collimation and superior translation of fibre properties into the composite.

The shape of the strength against temperature plot in Fig. 1 was assumed based on data obtained previously for 7740 glass matrix composites reinforced with silicon carbide and graphite fibre [1–3]. An observed strength increase in the 500 to 650 $^\circ\text{C}$ temperature range has been typical and has been associated with the decrease in matrix viscosity to the point where either the effective matrix

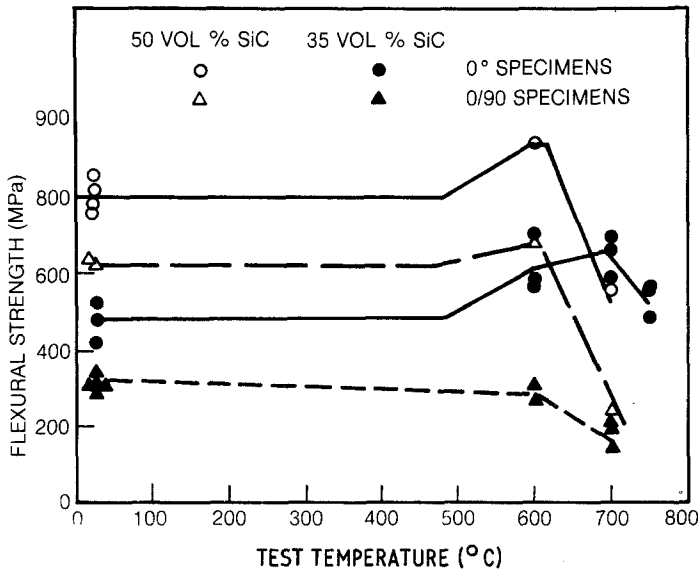


Figure 1 Three-point flexural strength of SiC yarn reinforced borosilicate glass composites as a function of test temperature.

failure strain has been increased substantially or matrix deformation permits a redistribution of stress throughout the three-point bend beam. In both of these cases the effect would be to increase the load required to fracture the specimen and thus also increase the calculated value of composite flexural strength. The 0° specimens tested at 700° C or greater were characterized by extensive beam deformation, clearly indicating that the calculation of flexural strength is questionable, and in three out of the seven specimens no fracture occurred. For all of the lower temperature tests, specimen fracture was incomplete and specimens retained some integrity after crack initiation at

the tensile surface. This was due to diversion of the primary crack into the direction parallel to the fibres.

The 0°/90° cross-ply material strength and elastic modulus both indicate that, at 22° C, values equal to 65 to 75% of the 0° material properties are achievable. Thus, the 90° plys can contribute significantly to composite performance. Also of interest, however, was the fact that very little, if any, increase in strength was measurable at the elevated temperatures, although at 700° C the specimens did exhibit some evidence of local plastic deformation near the loading nose. In all cases the primary fracture occurred on the tensile

TABLE II Three-point flexural strength, σ , and elastic modulus, E , of SiC yarn reinforced 7740 glass

Test temperature (°C)	0° specimens				0°/90° specimens			
	35 vol% SiC		50 vol% SiC		35 vol% SiC*		50 vol% SiC	
	σ (MPa)	E (GPa)	σ (MPa)	E (GPa)	σ (MPa)	E (GPa)	σ (MPa)	E (GPa)
22	414	97	814	116	347	53	619	98
	476	102	840	120	299	59	629	101
	520	99	763	118	339	71		
			786	119	320	78		
					301	72		
600	702	136	940	101	272	33	685	81
	584	95			303	52		
	569	104						
700	698	80	545	76	192	21	200	45
	593	82			192	22		
	663	88			145	16		
750	556	60						
	476	62						
	561	69						

*Span: depth ratio of 12:1 while all others tested at 20:1.

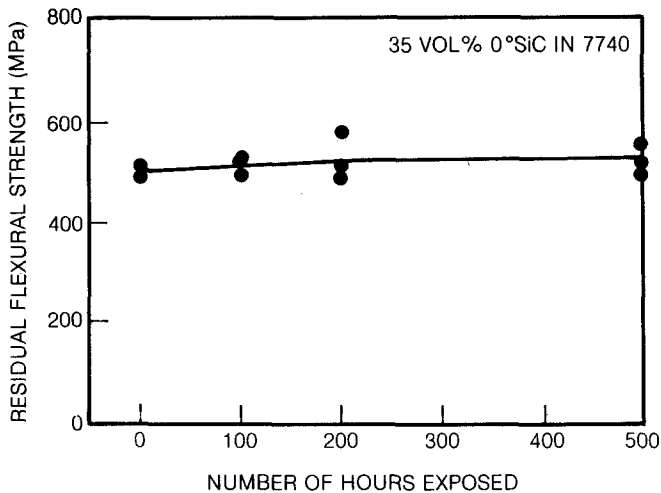


Figure 2 Composite residual flexural strength (at 22° C) after exposure to air at 540° C.

surface and was diverted in a direction parallel to the fibres as it attempted to propagate through the specimen.

3.1.2. Oxidative stability

A series of 0° reinforced three-point bend specimens was subjected to continuous exposure in air at 540° C for times of up to 500 h. The specimens were precut and ground to final dimensions (1.9 mm × 5 mm × 7.5 cm) prior to exposure and their residual flexural strength and modulus were measured in three-point bend at 22° C. The resultant data, shown in Fig. 2, indicate that the composites were totally unaffected by these exposure conditions. Similarly, measurements of specimen mass prior to and after exposure indicated no change had taken place. This oxidative stability is significantly different from that of graphite fibre-reinforced glass [2, 3] where a significant composite strength loss was noted after similar exposure conditions.

3.2. Blended glass matrix composites

Blended glass matrices were synthesized with 0, 25, 50 and 75 wt% of 7930 glass, the balance being 7740 borosilicate glass. The three-point bend data obtained for unidirectionally-reinforced specimens are presented in Table III. It can be seen that the addition of the Vycor to the 7740 borosilicate did not adversely affect low-temperature composite properties, but did increase the high-temperature performance. Where 100% 7740 matrix specimens deformed excessively at 750° C, specimens of 75 wt% Vycor exhibited no large deformations even at 850° C.

3.3. High silica glass matrix composites

Preliminary fabrication experiments demonstrated the need for both ball-milling and an inert atmosphere in composite fabrication. Once established, the fabrication procedure succeeded in achieving high room-temperature strength composites which also demonstrated the improvements in high-temperature performance achievable using a high silica glass matrix. These superior properties were obtained despite the fact that the composite microstructure, shown in Fig. 3, exhibited both porosity and non-uniform fibre distribution.

Composite flexural properties measured over the temperature range of 22° C to 1250° C are presented in Table IV and Fig. 4. The 22° C composite strength and elastic modulus values are nearly identical to those presented previously (Table II and Fig. 1) for 0° 7740 matrix composite specimens (35 vol% fibres). Thus, despite a substantial change in matrix, the overall composite performance has not been altered. A major extension of maximum use temperature, however, has been achieved by this switch. Where the 7740

TABLE III Three-point bend strength of SiC yarn reinforced blended glass matrix composites

Temperature (°C)	Flexural strength (MPa)			
	Blend: 7930 Vycor/7740 borosilicate (wt%/wt%)			
	0/100	25/75	50/50	75/25
22	470	550	608	535
750	531*	560	670	433
850	—	160*	470	382

*Specimens bent extensively during test

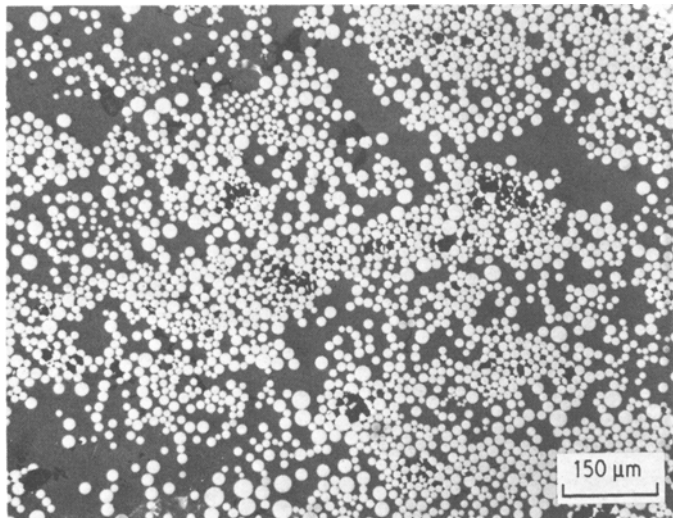


Figure 3 Microstructure of SiC yarn reinforced high silica glass.

matrix composites were limited to approximately 700° C, the 7930 matrix composites exhibited a peak strength level at around 1050° C and evidence of specimen deformation could only be found after testing at 1150° C and above.

It should be noted that the data in Fig. 4 have been presented with drawn curves that assume a behaviour similar in form to that of 7740 glass composites, i.e., the relatively sudden increase in strength near the temperature of maximum performance. The true nature of this curve for 7930 matrix composites is yet to be determined. Also indicated in Fig. 4 is the nature of the specimen deformation mode; below 1050° C there was no sign of specimen plastic deformation prior to fracture. A typical 1050° C fracture surface is

shown in Fig. 5 and indicates the extremely fibrous nature of composite failure in this and also the other glass matrix–SiC fibre systems.

4. Conclusions

It has been demonstrated that silicon carbide yarn-reinforced glass matrix composites can be fabricated with both borosilicate and high silica glass matrices. In both cases high levels of flexural strength have been obtained with these matrices providing limitations in maximum use temperature through their gradual decrease in viscosity with increasing test temperature. In the case of the borosilicate matrix this limitation is reached at about 700° C while for the high silica glass it is not reached until approximately 1100° C. The

TABLE IV Three-point flexural strength and elastic modulus of SiC yarn reinforced 7930 glass

Test temperature (°C)	Specimens fabricated at 1500° C		Specimens fabricated at 1600° C	
	Flexural strength (MPa)	Flexural modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)
22	467	111	509	109
	413	107	482	97.1
	447	112	527	101
950	643	108	724	101
	565	88	657	102
1050			742	83
			668	87
1150	541	64		
	498	65		
1200	419	60		
1250	243	48		
	280	52		

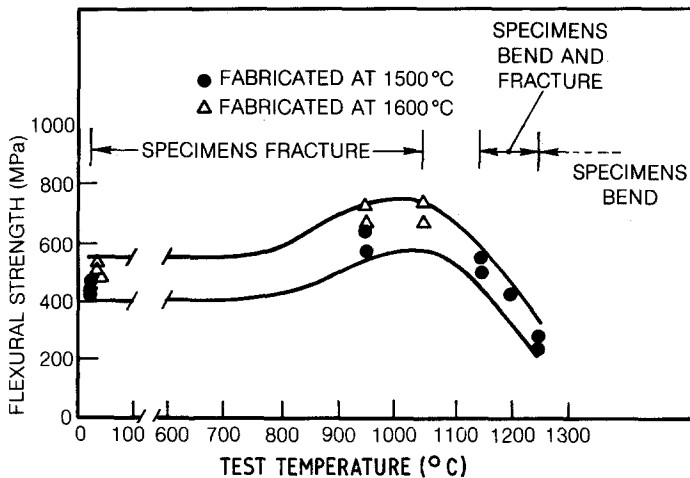


Figure 4 Three-point bend flexural strength of SiC yarn reinforced high silica glass matrix composites as a function of test temperature.

demonstrated levels of elevated temperature strength and exceptional low composite density of approximately 2.4 g cm^{-3} (for 60 vol% high silica glass) should make this composite system extremely attractive for a broad range of applications. Its temperature capability should place it in direct competition with iron- and nickel-base alloys that are three to four times as dense and which contain costly elements such as tantalum, cobalt and chromium.

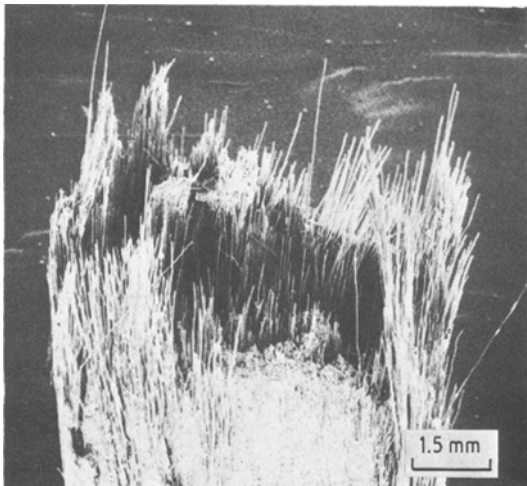


Figure 5 Fracture surface of a 0° SiC yarn reinforced high silica glass matrix composite.

In addition, although not documented in this report, it has already been shown that silicon carbide-reinforced glass matrix composites exhibit excellent fracture toughness [1]. This demonstration is critical in that it separates these composites from traditional ceramic materials whose reliability would be of serious concern. The presence of discreet high strength and stiffness fibres within the glass microstructure provides an effective network of crack stoppers. Similarly, their presence permits a new degree of flexibility for the designer who must contend with regions of high stress in the vicinity of transitions and attachments.

References

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