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The Oxidation Behaviour of Carbon Reinforced Glass Matrix Composites

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Abstract: Oxidation experiments have been performed on carbon fibre reinforced glass matrix composites as a function of glass composition. The oxidation resistance of the carbon fibres has been shown to be related to the microstructure of the glass and the adherence of the glass to the carbon fibres. Coating of the fibres with a SiC CVD precursor has been shown to improve the oxidation resistance of the fibres. However, post-exposure mechanical characterization has shown an inverse relationship between oxidation resistance and the ability of the composites to exhibit "graceful" failures. © 1997 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

The demand for stiffer, stronger and lighter materials has resulted in the development of a large number of aligned fibre composites. The matrices for these materials can be polymeric, metallic, ceramic, or, as in the material described here, glass. The reinforcing phases are generally selected for high stiffnesses and, accordingly, are often ceramic materials, although there are a few composites that utilize metals, and a number of polymer based composites utilize graphite as the reinforcing phase. Graphite is seldom used with metal matrix composites because it reacts with most metals. For composites that are intended for use at elevated temperatures, graphite has the added disadvantage of extraordinary oxidation rates at temperatures greater than a few hundred degrees Celsius. The carbon fibres can be, and are, incorporated into ceramic matrices, but the fabricability of such materials is difficult. An alternative to ceramic matrices is glass. Glass has the advantage of being relatively easy to fabricate and to form into structural shapes. It is also generally chemically inert, has a low density and is relatively inexpensive. The disadvantages of glass are its inherent low toughness at low and intermediate temperatures and its low viscosity as temperature is increased. Incorporation of graphite fibres in glass serves to protect the relatively stiff and high strength fibres from oxidation while lending strength and stiffness to the glass matrix. Early work that examined this concept showed that the incorporation of graphite fibres in Pyrex® glass resulted in a significant increase in the work of fracture.[1–8] However, these same studies indicated that the use of glass/graphite composites was oxidation limited, oxygen attacking the fibres through cracks in the glass matrix, or at fibre ends.[2,9] The cracks in the glass matrix generally form during fabrication because of the coefficient of thermal expansion (CTE) difference between the glass and the graphite. Typical glasses have CTE values of 1.7–3.2 ppm/K, while PAN-based carbon fibres have CTE values of 5.5 – 8.4 ppm/K in the transverse direction and −0.5 to −1.3 ppm/K in the longitudinal direction.[10] The objective of this work was to attempt to understand the oxidation behaviour of carbon fibres in glass matrices as a function of glass composition, and to attempt to develop protective coatings for the fibres.

2 EXPERIMENTAL

The carbon fibres used in this investigation were PAN-based 5C fibres provided by Fiberfil Fibers, Inc., a subsidiary of AKZO International. The

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Table 1. Properties of glass matrices

Glass	T_g (°C)	Density (g/cm^3)	CTE (10^{-6}/K)	E (GPa)
7070	495	2.13	3.2	51
B10	590	2.10	1.7	60
B15	510	2.10	2.2	60

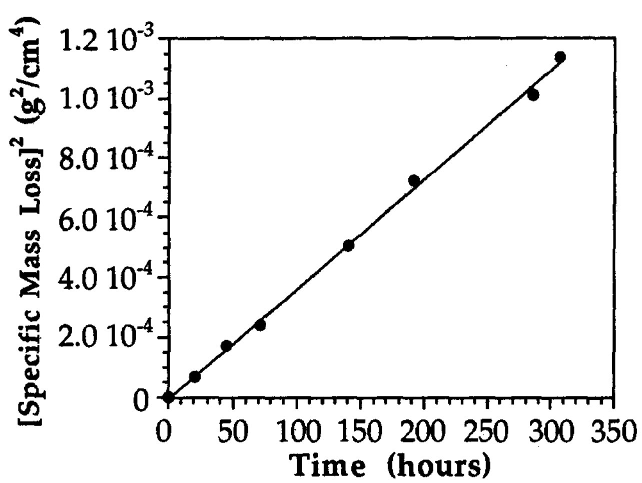

Fig. 1. Oxidation behaviour of a 7070 glass/carbon fibre composite at 450 °C.

fibres were received as "tapes" consisting of 4 fibre tows with 50,000 fibres per tow. The tensile strength of the fibres was 2760 MPa and the tensile modulus was 345 GPa, according to the manufacturer's specifications. The fibres are circular in cross-section, with a diameter of 6.7 ± 0.5 μm. The fibres exhibit an "onion skin" structure, with the outer skin consisting of graphene with a (0002) texture, and the core consisting of amorphous carbon. Some of the fibres were coated either by chemical vapour deposition (CVD) or simply by dipping the coatings in a CVD precursor. The precursor used for CVD was 1,3-dimethyl-3-methylsilamethylene-1,3-disilacyclobutane. This precursor deposits amorphous SiC at temperatures less than 1000 °C.[11] The dip coating was a highly branched hydridopolycarbosilane developed at Rensselaer Polytechnic Institute.[12]

Three glass compositions were used as matrix materials: Corning Glass Works 7070, a sodium borosilicate glass containing 1% Al_2O_3, 26% B_2O_3, 0.5% Li_2O and 1% K_2O; B10 glass containing 10% B_2O_3; and B15 glass containing 15% B_2O_3. The glasses containing B_2O_3 as the sole additive were selected because Na_2O is believed to be a catalyst for the oxidation of carbon. The 7070 glass was obtained commercially in powder form, while the B10 and B15 glasses were fabricated from a sol–gel process.[13] The properties of the glasses are shown in Table 1.

The composites were fabricated by aligning the fibres in a metal frame and infiltrating the fibres with a slurry of glass powder, an organic surfactant, an organic binder and distilled water. After infiltration the water was driven off with a heat lamp, resulting in a single composite ply. The plies were cut to size (5 mm×5 mm) and heated in air at 325 °C for 3 h to remove the surfactant and binder. Seven plies were stacked together and hot pressed in an argon atmosphere at 1200 °C for 7070, 1400 °C for B10 and 1350 °C for B15. A pressure of 7 MPa was applied throughout the heating and cooling cycle of approximately 120 min. This fabrication process resulted in fibre reinforced glass matrix composites approximately 3 mm thick, containing approximately 30–40% fibres by volume, depending on the nature of the glass and of the fibres (coated vs uncoated). The actual volume fractions were determined utilizing an image processing program and an optical microscope.

Oxidation studies were performed on 45 mm square samples cut from the hot pressed composite samples, in dried laboratory air, at 450 and 550 °C. Oxidation rates were determined from thermogravimetric measurements. Physical observations indicted that all of the oxidation damage occurred on the fibres and the oxidation rates reported here are normalized for the fibre volume fractions in the composites.

The effects of oxidation on the mechanical properties of carbon fibre reinforced glass composites were also examined. For these tests composite samples were tested in three-point bending at room temperature. The samples tested were 32 mm × 3 mm × 2 mm rectangular samples. Unoxidized samples were compared with samples that had been oxidized for 300 h at either 450 °C or at 550 °C. The mechanical properties were determined from the standard elastic bent beam formula: $\sigma = \frac{3Pl}{2bd^2}$, where σ is the flexural strength, P is the applied load and l, b and d are the physical dimensions of the sample.

3 RESULTS AND DISCUSSION

Figure 1 shows the results of oxidation of a 7070 glass/uncoated carbon fibre composite at 450 °C, plotted as the square of the weight loss vs time, indicating that the oxidation rate is parabolic. Figure 2 compares the data at 450 °C with data at 550 °C. Note that the oxidation rate at the higher temperature is linear, indicating a change in the rate determining mechanism.

Figure 3 shows the weight loss vs time plots for the B15 glass at 450 and 550 °C and demonstrates

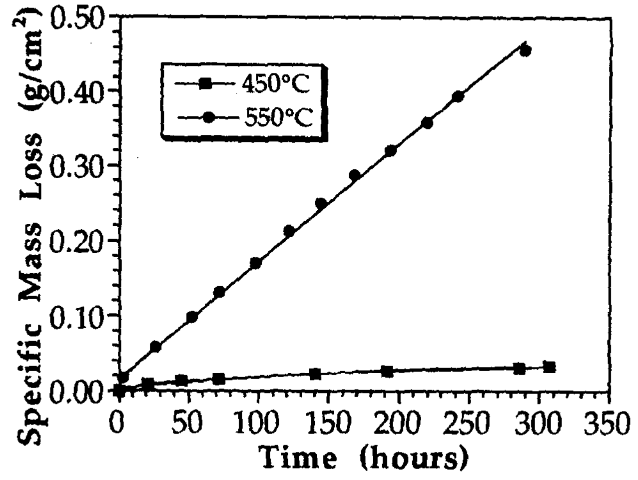

Fig. 2. A comparison of the oxidation behaviour of a 7070 glass/carbon fibre composite at 450 and 550 °C.

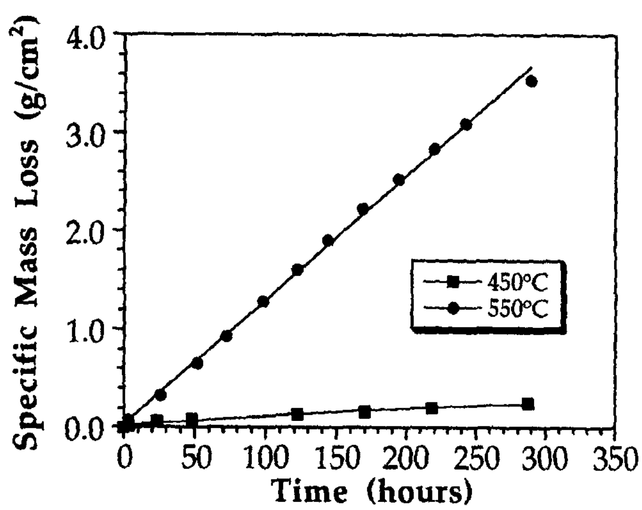

Fig. 3. Oxidation behaviour of B15 glass composite at 450 and 550 °C.

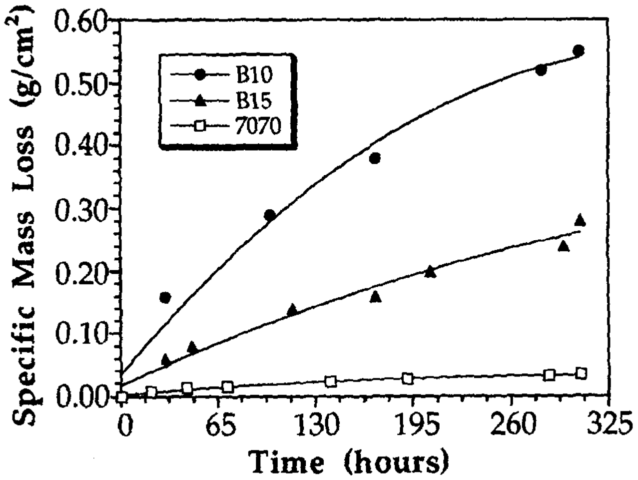

Fig. 4. Comparative oxidation behaviour for 7070, B10 and B15 glass composites at 450 °C.

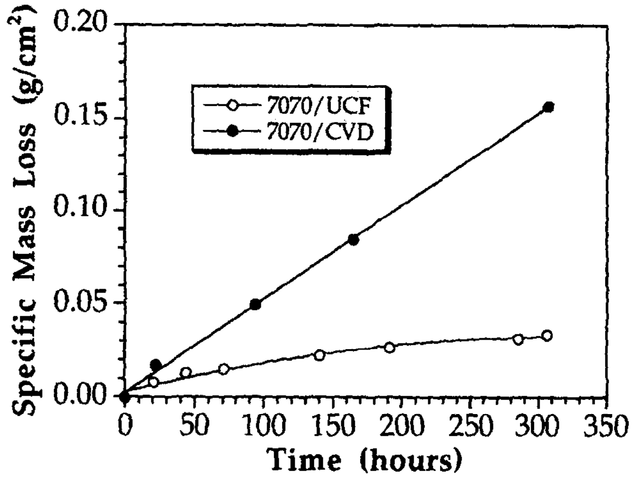

Fig. 5. Oxidation behaviour of 7070 glass composite containing CVD coated fibres at 450 °C.

that the behaviour of the B15 composite is similar to that of the 7070 glass composite, exhibiting parabolic behaviour at 450 °C and linear behaviour at 550 °C. Figure 4 compares the oxidative weight losses of the carbon in the three glass matrices at 450 °C.

In contrast to the assumptions that Na_2O would catalyse the carbon oxidation reaction, it appears that B_2O_3 inhibits oxidation. This behaviour can be understood from examinations of the microstructures of the composites. The B10 and B15 glasses, which exhibit a higher glass transition temperature, are less viscous during fabrication by pressing (although different pressing temperatures were utilized for each glass to account for the differences in viscosity). Accordingly, the glasses that contain less B_2O_3 as a vitrifier tend to be more porous and show poorer adherence to the carbon fibres. Both phenomena lead to short circuit diffusion paths for oxygen, as well as for the gaseous oxidation products. Thus the B10 glass shows the least oxidation resistance, the B15 glass is intermediate, and the 7070 glass, with the largest amount of B_2O_3, exhibits the best oxidation resistance.

Since the 7070 glass matrix composite exhibited the best oxidation behaviour of the three glass matrices examined, composites with either CVD or dip coated fibres were fabricated. CVD coating of the fibres increases the oxidation rates of the composites, as shown in Fig. 5, for a 7070 glass matrix composite. Dip coating of the fibres, on the other hand, results in significant decrease in the oxidative weight loss of the 7070 glass matrix composites. Figure 6 shows the oxidative weight loss behaviour of the 7070 glass matrix composite, and shows that at 550 °C the oxidation behaviour of the composite containing coated fibres changes to a parabolic rate in contrast to the linear oxidation rate exhibited by the composite containing uncoated fibres. Some benefit of dip coating the fibres is also observed at 450 °C.

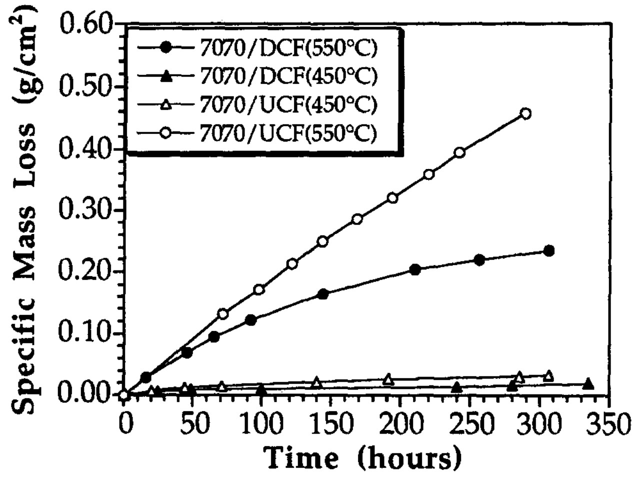

Fig. 6. Oxidation behaviour of 7070 glass composite containing dip coated fibres (DCF) and uncoated fibres (UCF).

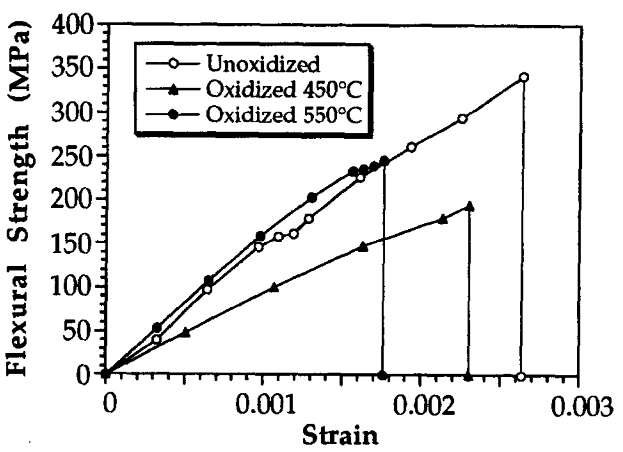

Fig. 7. Mechanical properties of 7070 glass composite before and after oxidation at 450 and 550 °C for 300 h.

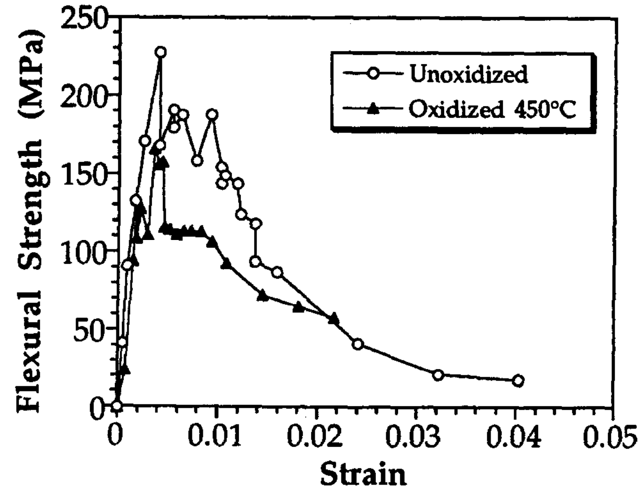

Fig. 8. Mechanical properties of B10 glass composite before and after oxidation at 450 °C.

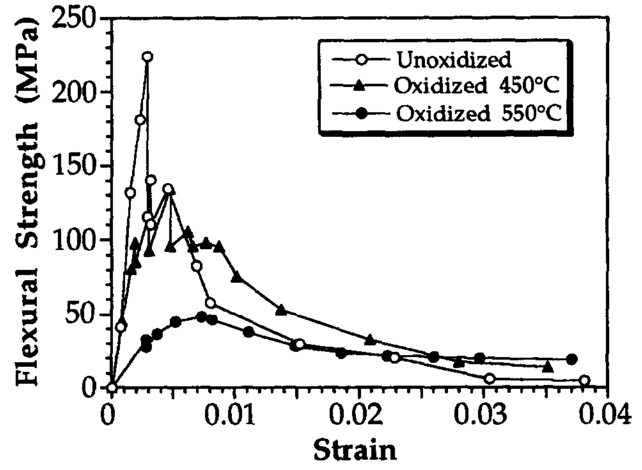

Fig. 9. Mechanical properties of B15 glass composite before and after oxidation at 450 and 550 °C.

The increased oxidation rate of the CVD coated fibres can be directly correlated to the structure and properties of the coating. The CVD coatings tended to crack and pull away from the fibres during fabrication. This resulted in short circuit paths for oxygen, and the conversion of the oxidation rate from diffusion control (parabolic kinetics) to reaction rate control (linear kinetics). The dip coatings, on the other hand, were adherent to the carbon, provided a diffusion barrier to gas transport, and retained diffusion controlled kinetics to 550 °C.

Figure 7 compares the flexural strength of the 7070 glass oxidized at 450 and 550 °C for 300 h. In each case the mechanical response of the composites indicates a strong bond between the fibres and the matrix. The flexural strength of the 7070 glass composite is also the highest of the three glasses, also indicative of a strong bond between the fibres and the matrix. In each case, however, the flexural strength and the strain to failure of the 7070 glass matrix composite is degraded by oxidation; the degree of degradation being controlled by the amount of oxidation.

The mechanical properties of the B10 and B15 glass composites are shown in Figs 8 and 9, respectively. Both composites exhibit lower flexural strengths than the 7070 glass composites. However, both composites exhibit "graceful" failure, with strains to failure in the 4% range (in contrast to the 7070 glass composite which exhibited a maximum strain of 0.25%). Also, the 7070 glass composite exhibited a completely brittle failure, while the B10 and B15 glass composites did not exhibit a clean break. Finally, although the flexural strength of the B10 and B15 glass composites was markedly reduced, the strains to failure for these composites were virtually unaffected by prior oxidation. Oxidation attacks the fibres closest to the surfaces of the composite samples, reducing their flexural strength. Fibres removed from the surface, however, provide the crack bridging mechanism required to provide toughness and "graceful" failures. The results of the mechanical property studies, combined with the oxidation results, confirm the microstructural observations that the 7070 glasses exhibit a strong bond with the carbon fibres, while the B10 and B15 glasses do not. The result of the nature of the glass to fibre bonding is that the 7070 glasses exhibit better intrinsic oxidation resistance. However, the weaker bonding in the B10 and B15 glasses results in superior composite properties, although the flexural strengths are lower and the reductions in flexural strength as a result of oxidation of the carbon fibres are greater.

4 CONCLUSIONS

The following conclusions can be drawn:

1. The oxidation kinetics of glass matrix/carbon fibre composites with ~40% carbon fibres is parabolic at 450 °C, but becomes linear at 550 °C.
2. Reducing the amount of B_2O_3 in the glass matrix of the composite, which increases the glass transition temperature, increases the oxidation rate of the carbon fibres. The increase in oxidation rate is associated with greater porosity in the glass and poorer adhesion of the glass to the carbon fibres. Both phenomena provide short circuit gas diffusion paths.
3. CVD coating of the carbon fibres with SiC prior to fabrication results in increases of oxidation rates for 7070 glass matrix composites. The increase in oxidation rates is associated with cracking and debonding of the coating during fabrication, providing short circuit diffusion paths between the coating and the carbon fibres.
4. Dip coating of carbon fibres with a CVD precursor prior to fabrication increases the oxidation resistance of the fibres in a 7070 glass matrix composite.
5. Composites fabricated with 7070 glass show high flexural strength but poor toughness. Pre-oxidation of the composites reduces the flexural strength and the strain to failure.
6. Reducing the amount of B_2O_3 in the glass matrix of the composites results in a reduction in flexural strength, but the reduction in interfacial adhesion provides for "graceful" failures. Pre-oxidation of these composites also reduces the flexural strength, but the failure mode remains "graceful".

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