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Glass sealants for carbon–carbon composites

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SiC coatings were chemically vapour deposited (CVD) on a carbon–carbon (C/C) composite. These coatings contain thermal mismatch cracks which require sealing between 600 and 1100 °C. The volatility, wettability and moisture sensitivity of binary and multicomponent borosilicate glasses were investigated, and these glasses were found to provide sealing over some or all of this temperature range. The volatilization rate is enhanced by the presence of water vapour and results in the loss of the B_2O_3 constituent from the glass. The C/C composite surface showed poorer wetting than the CVD SiC surface, and both surfaces showed improved wetting for glasses of higher B_2O_3 content. The moisture sensitivity of the binary borosilicate glasses was proportional to the B_2O_3 content. Room-temperature moisture had little effect on the multicomponent glasses.

1. Introduction

C/C composites possess excellent mechanical properties at temperatures exceeding 2000 °C. They are, however, limited to temperatures below 500 °C in oxidizing environments unless a protective system is employed. A system that has received much attention in recent years consists of a ceramic coating (commonly SiC) with a B_2O_3 glass sealant either contained within the composite matrix or applied as an outer glaze [1]. The ceramic coating tends to crack when subjected to a temperature change. This normally occurs during cooling from its processing temperature when a process such as CVD is employed [2]. Because of the thermal expansion mismatch between the coating and the C/C substrate, tensile stresses develop causing the cracking. Due to the low melting point of B_2O_3 (450 °C) this can flow and seal cracks in the coating preventing significant oxidation of the substrate.

Using B_2O_3 as a sealant material has several serious drawbacks, the most important of these being its sensitivity to moisture at room temperature [3]. B_2O_3 absorbs moisture in humid environments, and, when heated, release of this moisture can cause spallation of the outer coating. Also, when used as an outer glaze its low viscosity causes uneven spreading which, combined with its high volatility at high temperatures, limits it use to temperatures below 1000 °C [4].

This study considered a number of glass compositions that may be more suitable for sealing cracks in the ceramic coating than pure B_2O_3. The important properties of moisture sensitivity, wettability and volatility were investigated as well as their ability to seal cracks in CVD SiC at temperatures above 500 °C.

The binary system B_2O_3–SiO_2 was selected for study since Si-based ceramics used as coatings will form SiO_2 within the cracks during oxidation, and this would be expected to flux with an inner B_2O_3 sealant. Multicomponent borosilicate glasses were also investigated as potential sealants.

2. Experimental procedure

2.1. Materials

Using starting materials of SiO_2 (particle size 0.5–10 μm; Sigma Chemical Co.) and B_2O_3 (GPR; BDH Chemicals), binary borosilicate glasses were produced by melting in a Pt crucible. The compositions and melting temperatures are given in Table I. The glasses were analysed for SiO_2 using a Camscan S4 scanning electron microscope fitted with a Link System energy-dispersive X-ray analysis (EDX) unit. The SiO_2 compositions were calculated by direct comparison with a pure SiO_2 sample using identical beam conditions.

Two multicomponent borosilicate glasses were also investigated. These were supplied in fine powder form (Bayer, UK Ltd) and the compositions of these glasses (analysis provided by BP Research) are shown in Table II. The melting range of these glasses were given as 800–850 °C for D6130 and 1000–1050 °C for 26 510.

The C/C composite material used in all experiments ("K-Karb", type A panel; BP Research, Sunbury) comprised two-dimensionally woven rayon-based fibres (fibre diameter 5 μm) within a phenolic resin matrix. This was cut into 1 cm-sided cubes using a diamond saw.

2.2. CVD SiC coatings

CVD of SiC coatings was carried out within an SiO_2 tube in a horizontal resistance-heated furnace at a constant pressure of 1700 Pa and temperature of 1100 °C. Methyltrichlorosilane (MTS, 97% purity; Aldrich Chemical Co. Ltd) was used as the precursor for SiC, with hydrogen as the carrier gas [2].

TABLE I Compositions and melting temperatures of binary borosilicate glasses

Nominal SiO_2 content (%)	Analysed SiO_2 content (%)	Furnace temperature (°C)	Holding time (h)
75	76.3	1200	15
50	51.9	1100	15
25	22.2	1000	10
0	0.0	800	5

TABLE II Compositions of borosilicate glasses (wt %)

Glass	SiO_2	B_2O_3	CaO	Al_2O_3	Na_2O	K_2O
D6130	56	34	1.5	1.0	7.0	0.1
26 510	68	10	7.0	9.0	0.3	2.5

2.3. Glass coatings

To apply a surface glaze to the ceramic-coated samples, the multicomponent glass powders were mixed with an oil-based binder (63/84; Blythe Colours) and isopropanol solvent in the respective proportions 5 : 1 : 5, and were placed in an ultrasonic bath for 20 min. These mixtures were then sprayed on the surfaces of the samples using an air brush (model 350; Badger Air Brush Co.). This technique involved holding the spray nozzle approximately 10 cm from the sample and applying the solution in short bursts, allowing the solvent to evaporate between applications. The sample was allowed to dry for a few minutes before turning it over and coating the underside.

Firing involved holding for 1 h at 350 °C to drive off the oil-based binder, followed by 1 h at 1000 °C to melt the glass on to the surface. This was performed in an N_2 environment. Some samples were recoated with CVD SiC after glass coating to form a glass interlayer sandwiched between two SiC layers.

2.4. Thermogravimetric analysis

Measurements of the oxidation kinetics of coated C/C samples were carried out in a vertically mounted furnace in dry flowing air (21% O_2 and 79% N_2, flow rate 100 ml min^{-1}), at temperatures between 500 and 1100 °C. The specimens were supported in an Al_2O_3 basket on a Pt wire hung from a Stanton–Redcroft mass balance, and mass changes were measured as a function of time. The furnace was either held at a constant temperature for each test run or ramped at 100 °C intervals, holding for 20 min at each temperature.

For glass volatility testing a piece of the binary glass was placed in a Pt basket and the multicomponent glass was sprayed on a Pt plate. Both of these were hung on a Pt wire from the mass balance. Tests were carried out either in conditions of dry air or in wet air that contained 25% water vapour. The wet condition was created by bubbling the air through water held at a fixed temperature.

2.5. Wettability testing

For wettability testing individual pieces of each glass weighing approximately 0.05 g were placed on the upper surface of separate cubical uncoated or SiC-coated C/C samples. These were then placed in a furnace purged with N_2 and ramped at a rate of 10 °C min^{-1} to temperatures of 600, 800, 1000 and 1100 °C. For each temperature the samples were cooled to room temperature after 1 h and removed from the furnace before photographing them.

The contact angles (θ) were measured from the photographs, using

$$\tan(\theta/2) = 2h/d$$

where h is the height of the drop at the centre of d and d is the diameter of the drop.

2.6. Moisture sensitivity testing

A relative humidity chamber consisting of a fully enclosed desiccator containing a water–25% glycerol solution was used following the method of Braun and Braun [5]. Air was bubbled through the solution and circulated within the chamber using a low-power pump. A hydrometer reading of 90% relative humidity was obtained after conditions had stabilized. Pieces of glass were placed within the chamber and periodically weighed to obtain room-temperature moisture sensitivity data.

3. Results and discussion

3.1. Oxidation kinetics of SiC-coated C/C composite

The CVD of SiC coatings contained cracks after cooling from the deposition temperature (Fig. 1). SiC has a thermal expansion coefficient of 3.9×10^{-6} °C^{-1} (room temperature to 1000 °C), whereas the underlying C/C substrate has expansion coefficients of -1.3×10^{-6} °C^{-1} parallel to the fibre direction and 4.7×10^{-6} °C^{-1} perpendicular to the fibre direction (room temperature to 600 °C). Cracking of the SiC perpendicular to the fibre direction did not occur.

Oxidation of the SiC-coated C/C composite when ramped between 500 and 1100 °C commenced above

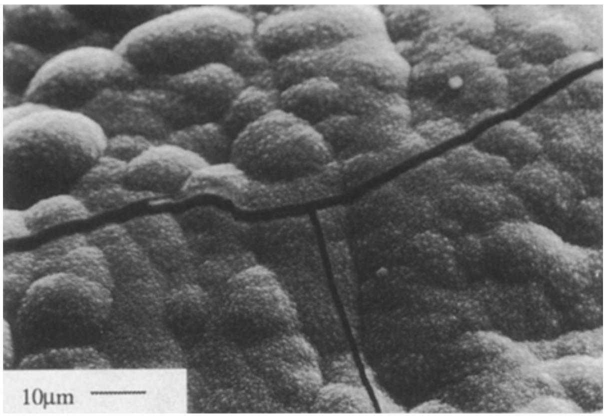

Figure 1 Cracking of the CVD SiC coating on the C/C composite substrate after cooling from the deposition temperature.

500 °C. The rate of weight loss reached a maximum of 0.063 mg cm^{-2} min^{-1} at approximately 800 °C, then dropped considerably up to 1100 °C (Fig. 2).

Oxidation of the C/C substrate will initially be controlled by chemical reaction. As the temperature is increased, the cracks present in the SiC coating begin to close, due to the higher thermal expansion of the SiC. The closing of the cracks causes a reduction in the amount of oxygen able to diffuse down the cracks and gasify the substrate. This is balanced by the increased reactivity of the carbon at higher temperatures. Above 1100 °C the cracks will be closed and formation of SiO_2 will enhance the sealing of these cracks [2].

3.2. Effect of sealants on oxidation kinetics

Application of an outer glaze caused sealing of cracks in the SiC coating, which in turn prevented oxidation of the substrate. The temperature at which sealing occurred depended on the glass composition and on whether an SiC particulate filler was present within the glass (Fig. 3). As expected, when ramped between 500 and 1100 °C the glass with the lower melting point (D6130) produced sealing at a lower temperature, preventing any significant oxidation. It should be noted that the glaze requires a finite time to melt and flow. Hence, more-rapid heating may cause oxidation of the substrate before sealing of the surface has occurred. With the presence of an SiC filler this glass will not seal cracks until above 700 °C. The glass with the higher melting point sealed cracks above 800 °C.

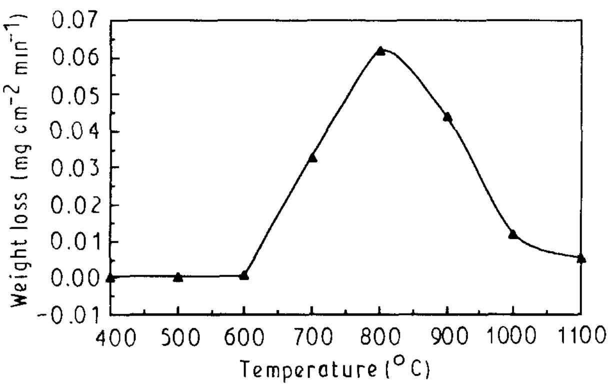

Figure 2 Effect of CVD SiC on C/C oxidation kinetics.

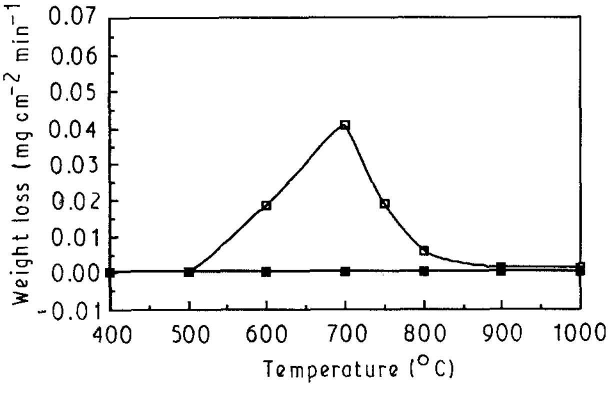

Figure 3 Effect of glass sealants on C/C oxidation kinetics: (■) D6130 and (□) 26 510.

The glass interlayer of D6130 applied between two layers of SiC did not produce sealing until 900 °C, and hence did not perform as effectively as the outer glaze of D6130 (Figs 4 and 5). Analysis of the interlayer revealed that the Na_2O component had been lost from the glass during processing. It is likely that this occurred during CVD of the outer SiC layer. The high-temperature and low-pressure conditions will cause a loss of the components with higher vapour pressure. Weight loss measurements carried out during separate experiments on samples of the glass exposed to similar conditions indicate that B_2O_3 also vaporizes during this process. Loss of these components will increase the melting point of the glass interlayer, and hence crack sealing will occur at a higher temperature. The spreading of the glass will also be restricted because it is sandwiched between two layers of SiC.

3.3. Glass volatility

The volatility of glass D6130 at 1100 °C was found to be enhanced by the presence of water vapour (Fig. 6). After approximately 30% loss there is a reduction in the rate of weight loss of the glass in wet air. The volatilization rate of glass 26510 was much lower to that of glass D6130 (Fig. 7).

The volatility of the SiO_2–B_2O_3 binary glass increased in the presence of water vapour (Fig. 8) and

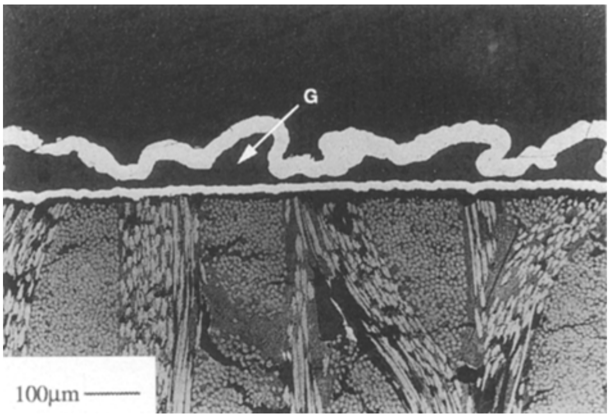

Figure 4 D6130 glass interlayer (G) between two layers of CVD SiC.

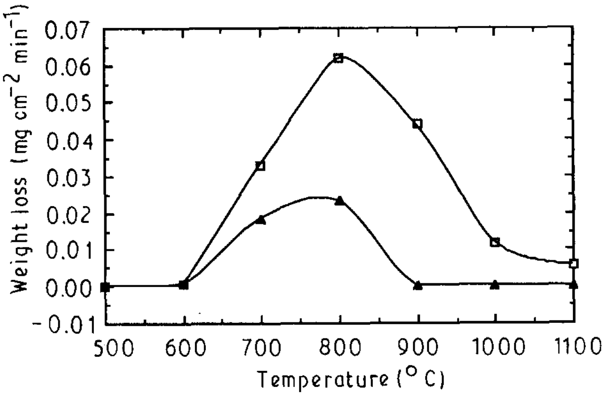

Figure 5 Influence of layers within CVD SiC: (□) MTS, 1100 °C and (▲) glass interlayer.

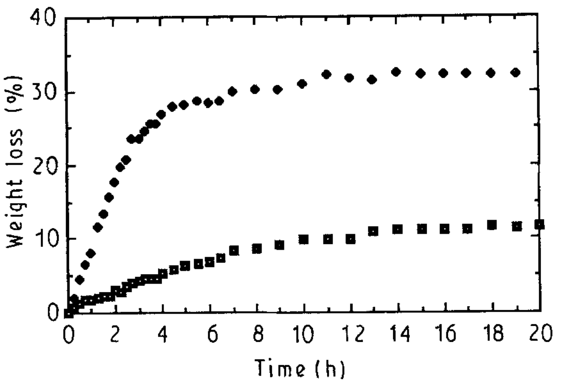

Figure 6 D6130 glass volatility in (■) dry and (◆) wet air at 1100 °C.

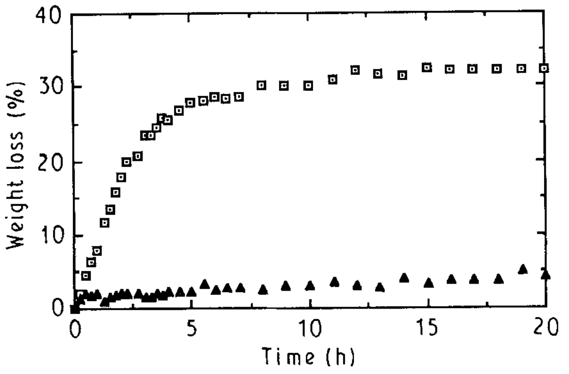

Figure 7 Glass volatility in wet air at 1100 °C: (□) D6130 and (▲) 26 510.

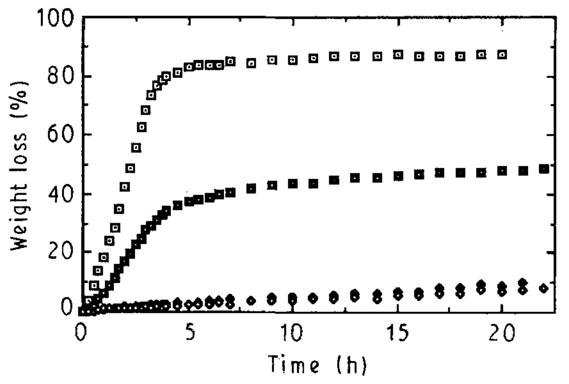

Figure 8 Binary glass volatility in (□, ■) wet and (◇, ◆) dry air at 1100 °C: B_2O_3 content (wt %) : (□, ◆) 100 and (■, ◇) 75.

for greater proportions of B_2O_3 (Fig. 9). The increase was most notable between the B_2O_3 compositions of 50 and 75%.

It is known that the volatilization rate of B_2O_3 is greatly enhanced by the presence of water vapour, due predominantly to the formation of volatile HBO_2 [4, 6]. As the glass D6130 contains approximately 30% B_2O_3, it seems likely that, in the presence of moisture, this component had diffused to the surface and totally volatilized. The lower weight loss of glass 26 510 would seem to be due to its lower B_2O_3 content.

The large increase in volatility of the binary borosilicate glass above 50 wt% B_2O_3 indicates non-ideal thermodynamic behaviour. Deviations from ideality have been observed elsewhere, with the partial molar volume of B_2O_3 being found to decrease by 6.5–7.5% with the addition of 50 wt % SiO_2 at 1300 °C [7]. The Si^{4+} ions are effective at altering and/or cross-linking the relatively fluid B_2O_3 in the intermediate-to-low B_2O_3 composition region, leading to departures from ideality.

3.4. Glass wettability

The contact angle of the various glasses tended to decrease as the temperature was increased. The binary SiO_2–B_2O_3 glass showed an increase in contact angle with increasing SiO_2 content. The multicomponent glasses D6130 and 26 510 showed large contact angles at all temperatures (Fig. 10).

Glass on the CVD SiC surface showed superior wettability, i.e. smaller contact angle, than the surface of the C/C composite (Figs 11–13). The wetting of the glasses with the SiC substrate depends on the surface tension of the glass and whether this is reduced by being in contact with the SiC. The lowering of the contact angle with increasing temperature is expected due to the weakening of the glass structure causing a decrease in the surface tension [8]. It should be noted that the glass compositions with higher melting points will take longer to attain an equilibrium condition [9], and this may not have been reached during the time-span of the test. However, it is felt that this is a valid

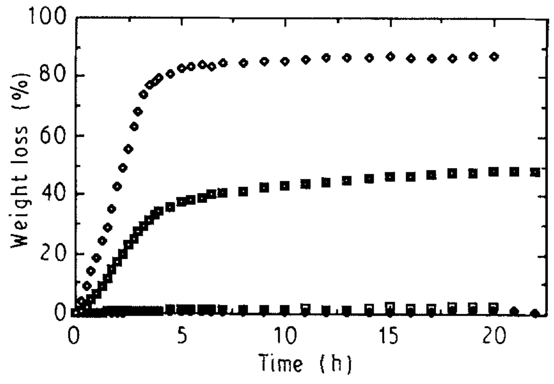

Figure 9 Binary glass volatility in wet air at 1100 °C: B_2O_3 content (wt %) : (◆) 25, (□) 50, (■) 75 and (◇) 100.

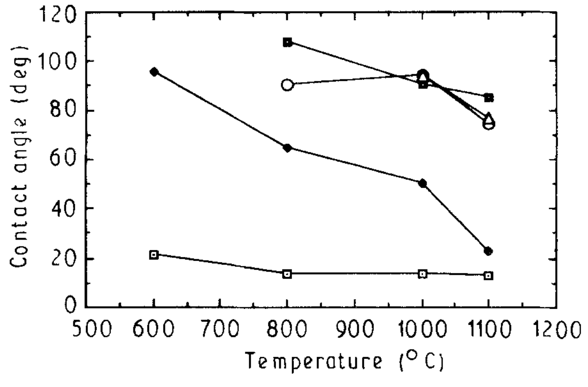

Figure 10 Wettability of borosilicate glass on CVD SiC: B_2O_3 content (wt %) : (■) 50, (◆) 75 and (□) 100; glass type : (○) D6130 and (△) 26 510.

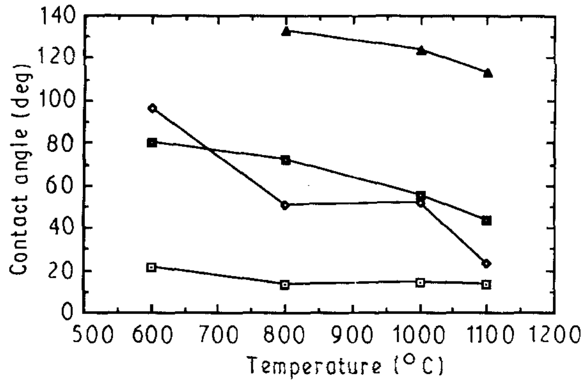

Figure 11 Wettability of (■, ▲) C/C composite and (⊡, ◆) SiC : B_2O_3 content (wt %) : (■, ⊡) 100 and (▲, ◆) 75.

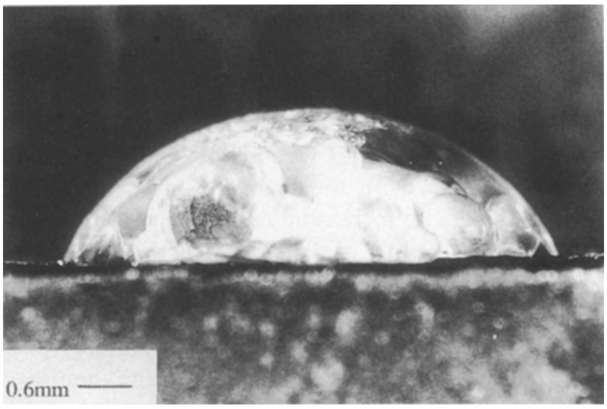

Figure 12 Wettability of binary glass (75% B_2O_3) on the CVD SiC surface (cooled from 1000 °C).

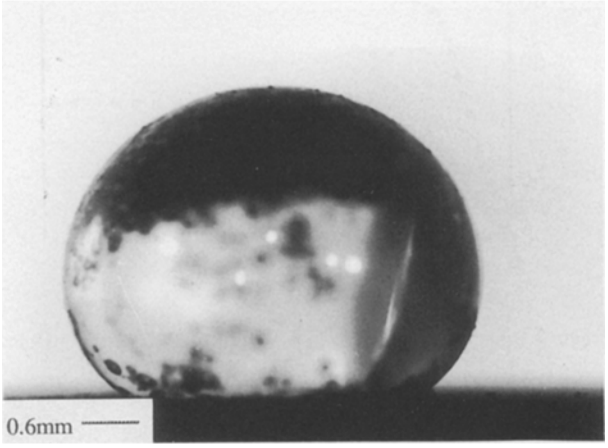

Figure 13 Wettability of binary glass (75% B_2O_3) on the C/C composite surface (cooled from 1000 °C).

technique to gauge the spread of the glass to spread over a limited period.

When melted, glasses tend to form ionic groups and the charges produced on the surface of the glasses influence their wetting characteristics. Auto-ionization in SiO_2 and B_2O_3 produces cationic and anionic groups [10] :

$$2SiO_2 \rightleftharpoons SiO^{+}_{3/2} + SiO^{-}_{5/2}$$

$$B_2O_3 \rightleftharpoons BO^{+} + BO_2^{-}$$

In a multicomponent glass the ions of the various oxides present will influence the surface tension of the glass. The value of r/Z (radius of the ion per unit charge) influences the surface tension, which increases with r/Z for network formers and decreases with r/Z for network modifiers [8]. In the case of network modifiers, if Na^+ is replaced by Ca^{2+}, for example, the greater ionic field strength of the Ca^{2+} reduces the negativity of the anionic group, and thus with Ca^{2+} present poorer wetting occurs [10].

Due to the high value of electronegativity of Si (1.90), the ionicity of SiC is relatively low [11]. Therefore, the ionic interaction is not expected to have a strong influence on the wettability of SiC.

The glass–SiC interface will be thermodynamically stable up to high temperatures, and therefore interfacial chemical reactions will be minimal [12]. At high temperatures gaseous reaction products may form:

$$2SiO_2 + SiC \rightleftharpoons 3SiO(g) + CO(g)$$

$$\Delta G^\circ = 622.3\ \text{kJ mol}^{-1} (1200\ \text{K})$$

$$\text{Log[total pressure(Pa)]} = -1.8$$

This will produce a weak boundary layer with the rate of reaction being kinetically limited by the transport of reaction products away from the interface [13]. The low pressure of the reaction products indicates that this layer will disrupt the interface and lead to poorer wetting only at very high temperatures.

The chemical compatibility of the glass with the substrate may also be significant and will depend on the surface chemistry. In the case of B_2O_3 this is known to be highly compatible with carbon surfaces, and for this reason is used to inhibit the reaction with oxygen [14]. Above the melting point of B_2O_3 (450 °C) a glassy residue of polymeric oxide is formed which blocks the active sites on the carbon surface. Carbon sites on the $\{1\ 0\ \bar{1}\ 1\}$ faces are preferentially poisoned by the strongly bonded adsorbant (Fig. 14). In B_2O_3 liquid the preferred orientation of planar $[BO_3]$ triangles and $[B_3O_6]$ boroxyl rings at surfaces and interfaces is energetically favourable. In this orientation they can more readily wet the carbon surface [13]. This improved wetting with increasing B_2O_3 content was observed experimentally. The presence of Na_2O within the glass will create $[BO_4]$ tetrahedra [15] and hence increase the contact angle of the glass in contact with carbon, i.e. decrease the wetting.

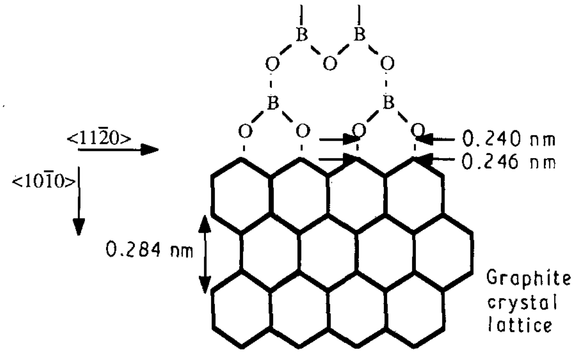

Figure 14 Bonding of a $(BO_3)_n$ polymeric residue on the $\{1\ 0\ \bar{1}\ 1\}$ face of graphite [14].

The two multicomponent glasses investigated (D6130 and 26 510) were found to have similar wetting characteristics. Both showed rather large contact angles over the range of test temperatures. It would seem that the variation in composition was not sufficient to cause a significant variation in the wetting characteristics. Although the D6130 glass has a high B_2O_3 content, the presence of Na_2O will restrict the influence of this on the wetting behaviour. Glass 26 510 contains significant CaO, which decreases wetting, but the low levels of Na_2O and K_2O mean that the wetting influence of B_2O_3 will be less restricted. This balance of glass components leads to a situation in which similar wetting behaviour occurs.

The results show that glass will not wet the C/C composite surface as readily as it will wet the SiC surface. Wetting is affected both by surface morphology and by surface chemistry. Although the surface morphologies were dissimilar, it is known that surface chemistry is the predominant factor affecting wettability for carbon materials, and superior wettability can be correlated with a higher coverage of oxygen-containing surface groups [16].

Reaction of the glass with the carbon substrate will produce gaseous products (primarily CO), producing a weak interface and reducing the wetting [13], e.g.

$$SiO_2 + 3C \rightleftharpoons SiC + 2CO(g)$$

$$\Delta G^\circ = 192.4\,\mathrm{kJ\,mol^{-1}}(1200\,\mathrm{K})$$

$$\mathrm{Log[total\ pressure\ (Pa)]} = 1.2$$

The pressure of the reaction products is higher than for the reaction with SiC, indicating that the gaseous product will have a greater influence on the wetting behaviour.

3.5. Glass moisture sensitivity

Under conditions of 90% relative humidity all binary SiO_2–B_2O_3 glasses were found to absorb water. The lower the SiO_2 content, the greater the amount of water absorbed (Figs 15 and 16). The glasses rapidly became frosty in appearance and gradually began to flake and crumble as the test proceeded. Glasses D6130 and 26 510 showed no significant weight change after 200 h under conditions of 90% relative humidity.

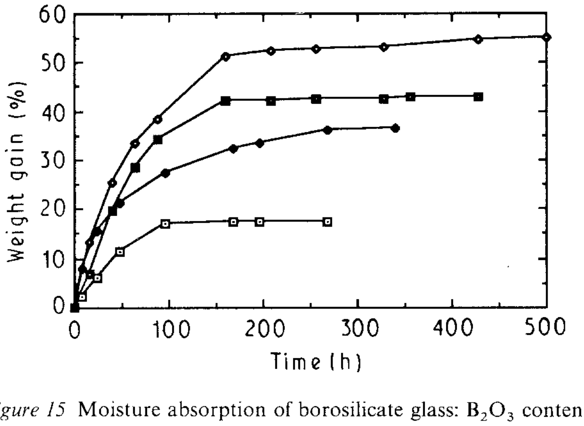

Figure 15 Moisture absorption of borosilicate glass: B_2O_3 content (wt %) : (□) 25, (◆) 50, (■) 75 and (◇) 100.

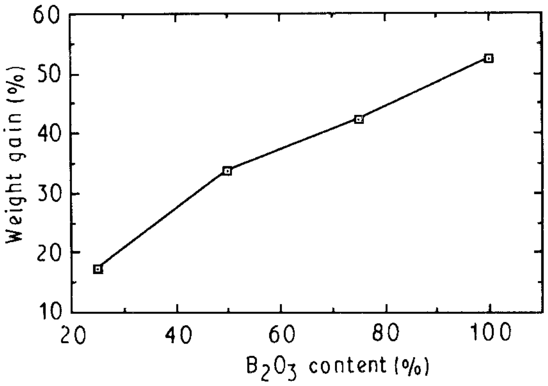

Figure 16 Moisture absorption of borosilicate glass after 200 h.

The curves for the moisture absorption of the binary borosilicate glasses (Fig. 15) suggest that a saturation level is reached at which point no further water is absorbed. The saturation level is proportional to the B_2O_3 content. Considering the weight changes involved, it would seem that boric acid (H_3BO_3) is the main reaction product, in agreement with other results [3]. Moisture absorption is initially rapid for all compositions, and as the surface of the glass deteriorates this allows further access of water until the saturation point is reached.

Adams and Evans [15] also observed a deterioration in the chemical durability of binary borosilicate glass in water. The addition of small quantities of Na_2O was found to improve the durability of the glass greatly. This was explained in terms of the structural changes within the glass. Na_2O will increase the tetrahedral connectivity of the three-dimensional network, due to the formation of BO_4 units analogous to the SO_4 tetrahedra. The presence of such oxides within the multicomponent glasses investigated explains their resistance to moisture. It should be noted that higher concentrations of Na_2O will reduce the water durability of the glass, due to the introduction of non-bridging oxygens [15].

4. Conclusions

Although SiC coatings crack due to thermal mismatch with the C/C substrate, this study has shown that a surface glaze can provide sealing over the necessary temperature range to prevent oxidation of the substrate. The glaze is also resistant to room-temperature moisture, indicating a significant advantage over the use of pure B_2O_3. The volatility of the glaze at high temperatures is a major disadvantage, but may be improved by using the glass as an interlayer.

The wetting of carbon surfaces by glass is inferior to that of SiC surfaces. Improvement in the wettability of these surfaces can be achieved by increasing the B_2O_3 content of the glass.

The moisture sensitivity of B_2O_3 is not improved by mixing with SiO_2. To produce a moisture-durable glass, a third component such as Na_2O is required to increase the overall connectivity of the three-dimensional network.

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References

1. J. R. STRIFE and J. E. SHEEHAN, *Ceram. Bull.* **67** (1988) 369.
2. F. J. BUCHANAN and J. A. LITTLE, *Surf. Coatings Technol.* **46** (1991) 217.
3. C. E. CHANG and W. R. WILCOX, *Mater. Res. Bull.* **6** (1971) 1297.
4. D. W. McKEE, *Carbon* **24** (1986) 733.
5. J. V. BRAUN and J. D. BRAUN, *Corrosion* **14** (1958) 117.
6. J. T. WENZEL and D. M. SANDERS, *Phys. Chem. Glasses* **23** (1982) 47.
7. E. F. RIEBLING, *J. Amer. Ceram. Soc.* **47** (1964) 478.
8. W. VOGEL, "Chemistry of Glass" (American Ceramic Society, Columbus, Ohio, 1985).
9. G. J. COPLEY and A. D. RIVERS, *J. Mater. Sci.* **10** (1975) 1291.
10. R. G. SIMHAN, L. L. MOORE and P. R. VAN GUNTEN, *J. Mater. Sci.* **20** (1985) 1748.
11. S.-Y. OH, J. A. CORNIE and K. C. RUSSEL, *Ceram. Engng Sci. Proc.* **8** (1987) 912.
12. J. E. SHEEHAN, in Proceedings of the 4th Annual Conference on Materials Technology: Recent Research into CCCs, Illinois University, 1987, p. 56.
13. C. G. PANTANO, G. CHEN and D. QI, *Mater. Sci. Engng* **A126** (1990) 191.
14. D. W. McKEE, C. L. SPIRO and E. J. LAMBY, *Carbon* **22** (1984) 507.
15. P. B. ADAMS and D. L. EVANS, *Mater. Sci. Res.* **12** (1978) 525.
16. H. H. STRECKERT and F. C. MONTGOMERY, in Proceedings of the 3rd International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, San Diego, California, 1987, Vol. 79, edited by J. D. Mackenzie and F. C. Montgomery.

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