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Vitreous Joining Process of SiC_f/SiC Composites

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Abstract

The reactive joining of an SiC_f/SiC composite with a zinc borate glass was studied at various temperatures, in order to optimize the joining process and to fully understand the reactivity between glass and composite. A temperature-dependent gas-producing redox reaction between ZnO and SiC was found to give gradual disappearance of the bubbles and crystallites always present in the range from 700 to 1200°C, and to yield a highly amorphous, bubble-free joint. This study permitted us to prepare single lap shear test specimens with minimal void content in the joint, i.e. a fully reacted and amorphous joint. The shear strength value obtained for these joints was higher than 15 MPa at room temperature. Copyright © 1996 Elsevier Science Ltd

Introduction

SiC-fibre reinforced SiC composites (SiC_f/SiC) have good thermomechanical properties and chemical inertness, making them attractive structural materials for high-temperature applications.[1] However, the non-weldability and poor workability of these materials hinder the fabrication of large or complex structural parts. Assembling techniques such as mechanical fastening have limitations because of the inherent brittleness of the fibrous composite surface and the stress concentration around rivet and bolt holes. There is, therefore, a strong need for simple adhesive joining techniques, able to give thermomechanically reliable structures.

Joining of monolithic SiC has been demonstrated using various techniques including diffusion bonding,[2] brazing with alloys[3] and the utilization of a polymeric precursor.[4] These studies give useful information on chemical reactivities but the composite and monolithic SiC have different microstructural and microchemical surface properties and, hence, the joining techniques developed for monolithic SiC are not directly transferable to SiC_f/SiC composites. Yet there is only a limited amount of literature available on this subject. Rabin[5] joined SiC_f/SiC composites by hot-pressing and combustion of Ti–C–Ni joining agents, while Coon[6] studied the joining of SiC_f/SiC composites using various lithium aluminosilicate glasses.

Indeed, vitreous joining offers some distinct advantages. First, the mechanical and structural properties of the joint can be tailored by controlling the glass composition (i.e. wettability with the composite, interfacial strength and reactivity, glass infiltration into the composite porosity). Moreover, the strength of the joint can be improved by ceramisation of the glass. Finally, vitreous joining is usually performed at a temperature where the glass is already softened or even melted and, therefore, it does not require application of an external pressure. This last point may be interesting for applications involving components of large dimensions or difficult access.

In a previous paper[7] we reported on the reactivity of SiC_f/SiC composites with a zinc borate glass, chosen as joining agent. We found that the glass developed a redox reaction among SiC fibres, free carbon present in the composite and the ZnO present in the glass. In the present work we have attempted to investigate which reactions occur between ZBM glass and SiC_f/SiC composites for a wide range of temperature, and then to use the results of this study to prepare joints of maximized shear strength.

Experimental

The molar composition of the glass chosen as joining material is: 50·46% ZnO, 29·48% B_2O_3, 9·12% MgO, 4·53% SiO_2, 4·04% Al_2O_3 and 2·37% Na_2O.[7,8] Powders of the different oxides were mixed together in a platinum crucible and heated for 30 min at 1200°C. The melt was poured and cooled to room temperature. The resulting transparent glass was ground down for X-ray

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diffraction analysis (XRD; Philips PW1710), differential scanning calorimetry (DSC; Perkin–Elmer 7) and differential thermal analysis (DTA; Netzsch 4045). A heating microscope (Leitz GmbH; AII) permitted observation of the softening and melting of the glass. Cube samples of dimensions 3 × 3 × 3 mm^3 were formed with pressed glass powder, or by hard-grit paper polishing and shaping of a bulk glass sample. The cubes were positioned on a Pt-coated Al_2O_3 plate in the microscope's furnace and heated to 1200°C (10°C min^{-1}).

The SiC_f/SiC composite utilized in this study was a unidirectional reinforced material (from Dornier GmbH and German Aerospace) prepared by the liquid infiltration pyrolysis technique.

The reactions between the ZBM glass and the SiC_f/SiC composite were studied in the heating microscope on sandwiches made from two polished composites and a thin, pressed pellet of glass powder (0·3 to 0·6 mm thickness). One sandwich was heated from room temperature to 1200°C under argon flow at about 20°C min^{-1} and some photographs were taken while heating, as shown in Fig. 1 (the composite/glass interfaces were graphically superimposed).

To determine the best joining temperature, other sandwiches were heated to the chosen temperature (700, 800, 880, 900, 930 and 1200°C) and isothermally treated for 45 min. The samples were then analysed using scanning electron microscopy and energy-dispersive spectroscopy (SEM-EDS; Philips 525M SEM and Philips 9100 EDAX); the results for the polished and cross-sectioned sandwiches (Fig. 2) are shown in Table 1. Finally, mechanical testing of the most promising joints was performed on single lap shear specimens of the ASTM 2733 type, with a SINTEC D/10 material testing machine.

Results and Discussion

The characteristic temperatures of the ZBM glass were found by DSC, DTA and heating microscopy: the glass transition (T_g) is at 536 ± 3°C; the first and second crystallizations (T_{x1} and T_{x2}) are at 676 ± 10 and 779 ± 5°C, respectively; the softening point is at 650 ± 10°C; and the melting temperature onset is at 880 ± 10°C.[7]

In order to investigate the reactivity between glass and composites, one sandwich was heated on the heating microscope from room temperature to 1200°C: Figures 1(a)–(i) show contrast photographs taken in the microscope during heating. First, softening of the glass pellet can be seen at 650°C [Fig. 1(b)]. Then, from 650 to 1200°C [Figs 1(b)–(i)], the vitreous joint expands, reacts and shows the formation of some bubbles. This bubbling is strong enough to displace the upper composite [Figs 1(g) and (h)] and seems to be at its maximum around 1100–1200°C. Above this temperature range the bubbles progressively disappeared and the joint regained its homogeneous and bubble-free appearance, with a good wetting angle with the composite ($\theta = 35°$) [Fig. 1(i)].

Zinc oxide has a well-known reactivity towards carbon to give metallic zinc and carbon monoxide [see below, reaction (1)]: the same reaction could be foreseen between zinc oxide and silicon carbide to give metallic zinc, carbon monoxide and silicon monoxide [reaction (2)]. Since free carbon is always present in the SiC_f/SiC composites in variable percentages depending on the preparation process, reaction (1) is the most probable at the glass/composite interface. At 906°C Zn is a gas and there are at least two gaseous species present above this temperature: gaseous zinc and carbon monoxide (effectively, some metallic Zn was always found at the cold bottom of the oven after the joining process). The observed swelling and displacement of the upper composite in Figs 1(g) and (h) are likely to be due to these gaseous products.

$$ZnO(s) + C(s) \rightarrow Zn(g) + CO(g) \qquad (1)$$

$$2ZnO(s) + SiC(s) \rightarrow 2Zn(g) + SiO(g) + CO(g) \qquad (2)$$

By observing Fig. 1, one could say that a heating treatment of about 45–50 min from room temperature up to 1200°C (20°C min^{-1}) can apparently give joints without bubbles, but no information is given about the kinetics of the process: i.e. it is not known how long it takes for the gaseous species to complete their reactions at a given temperature. For example, Fig. 1(d) taken at 950°C shows an evident increase of the joining material volume, but it is not clear whether this is due to the formation of bubbles and/or to a crystallization with volume increase; also, it cannot be predicted how long this reaction takes to end.

For these reasons, other sandwiches were heated from room temperature to a temperature in the range 700–1200°C and isothermally heated for 45 min at that temperature. (Longer heating times would probably be detrimental for the mechanical properties of the composites.) Furthermore, we tried to obtain sandwiches joined at the crystallization temperatures of the glass, with the aim of preparing a glass-ceramic joint that would be thermally and mechanically more stable than a vitreous one.

SEM micrographs of the cross-sections of sandwiches prepared at different temperatures are shown in Figs 2 (a)–(f). The first joined structure [Fig. 2(a)], obtained at 700°C (above the softening

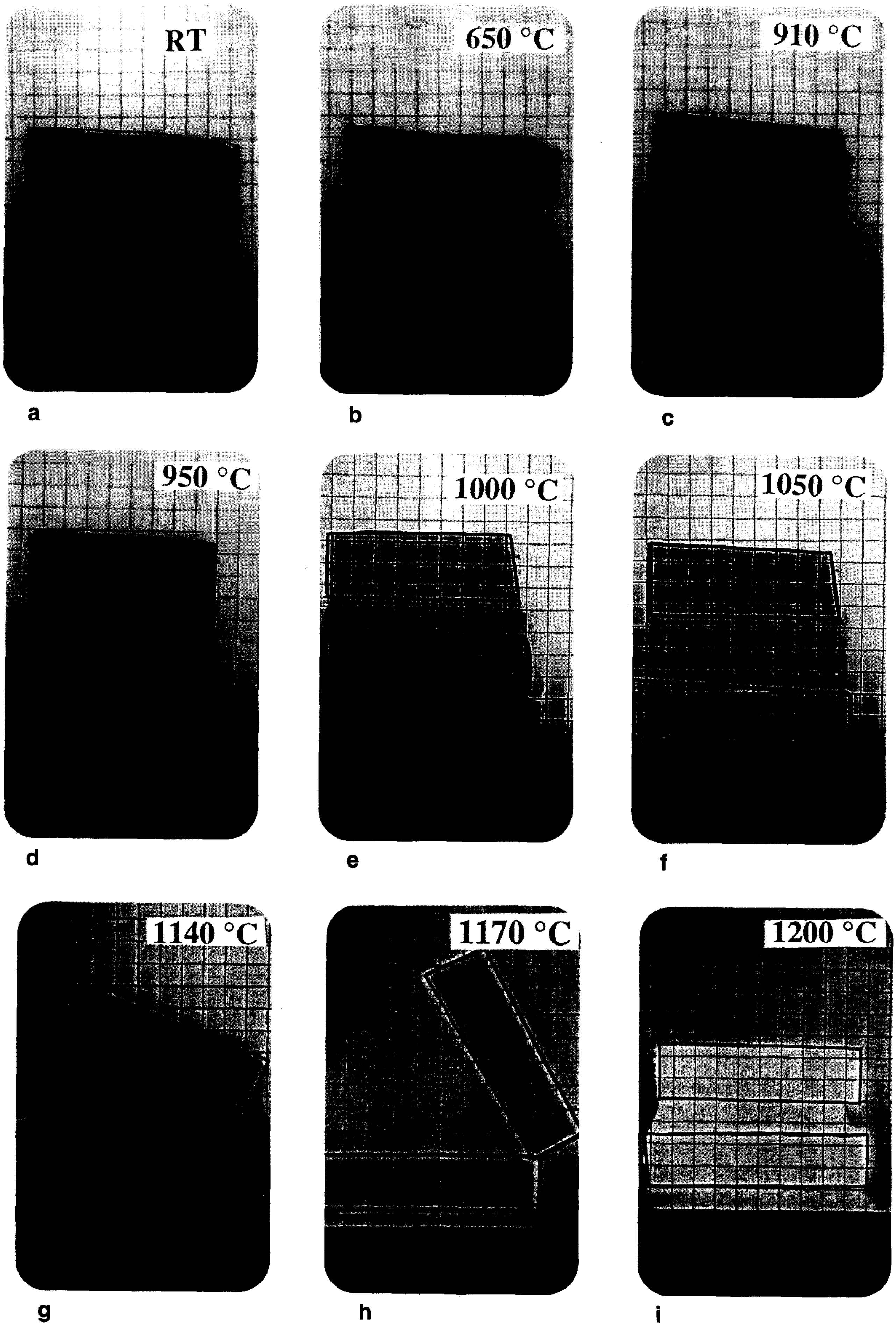


Fig. 1. Contrast photographs of an $SiC_f/SiC/ZBM/SiC_f/SiC$ sandwich (magnification: 3×) taken in the heating microscope during heating. The temperatures at which the photographs were taken are indicated. The composite/glass interfaces have been graphically superimposed.

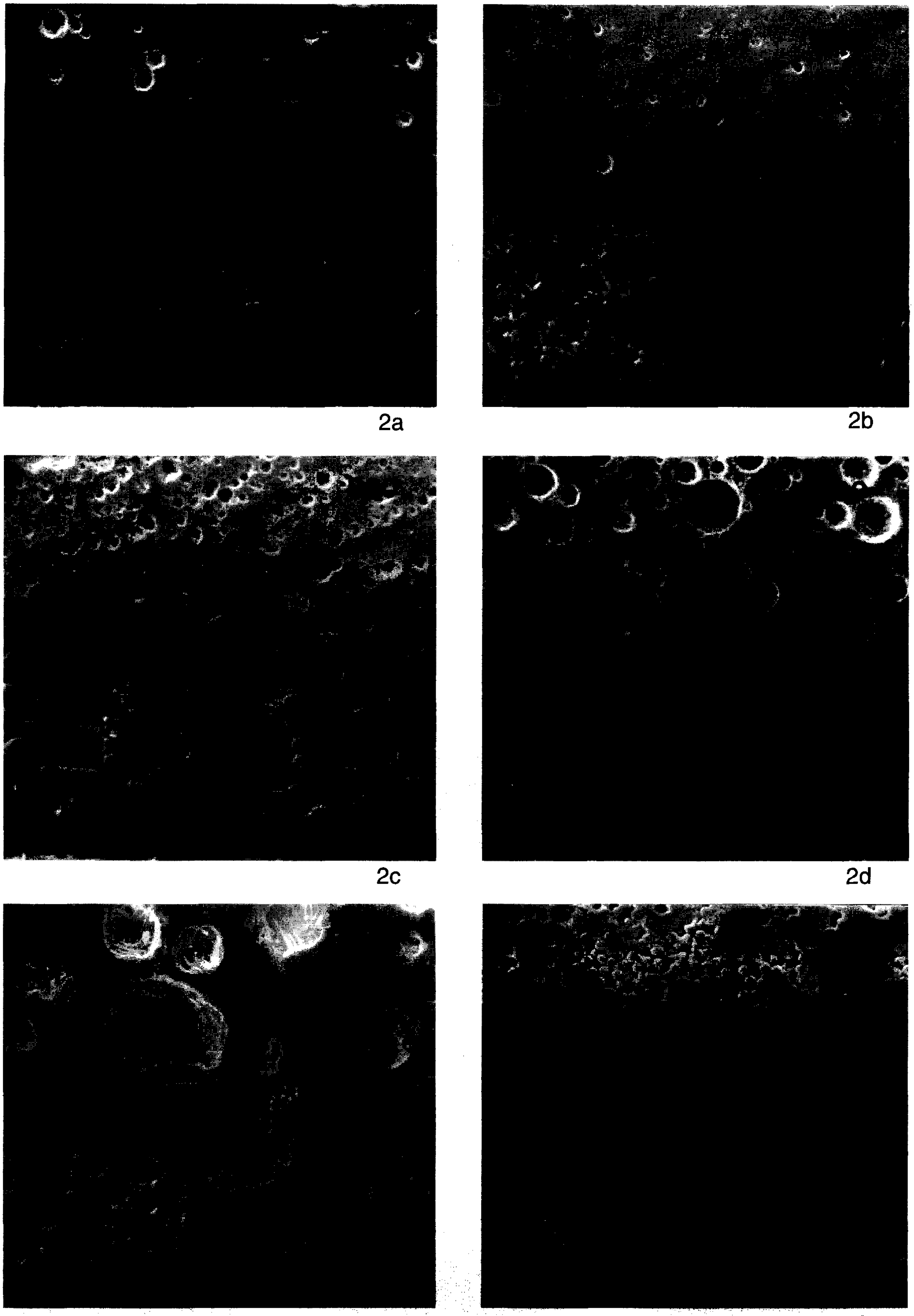

2a
2b
2c
2d
2e
2f

Fig. 2. SEM micrographs of cross-sectioned $SiC_f/SiC/ZBM/SiC_f/SiC$ sandwiches heat-treated for 45 min at different temperatures, as indicated on the micrographs.

Table 1. Effect of heat treatment on morphology and structure of the joints. The first column indicates the temperature at which the sandwiches were heated for 45 min and in which micrograph the sandwich is shown (in parentheses); Na, Mg, Al, Si and Zn reported are wt% measured by EDS (the values obtained for bulk ZBM are included for comparison)

Temperature (°C)	*Composition (wt%)*					*Pores*	*Morphology*
	Na	*Mg*	*Al*	*Si*	*Zn*		
ZBM bulk	7·16	0·59	3·12	2·41	86·7	—	amorphous
700 (2a)	5·94	0·56	3·88	3·73	85·88	yes	crystalline
800 (2b)	9·16	0·52	2·49	3·77	84·03	yes	crystalline
880 (2c)	5·82	—	5·52	4·5	84·14	yes	crystalline
900 (2d)	6·29	—	3·63	6·07	83·99	yes	crystalline
1200 (2f)	—	—	1·29	97·84	0·87	no	amorphous

point and T_{x1}, but below T_{x2}), presents a joined layer that is slightly bubbled and partially crystallized [$Zn_3(BO_3)_2$, as detected by XRD and EDS]. The interface between glass and composite is partially discontinuous. The samples shown in Figs 2(b) and (c), obtained by heating at temperatures above T_{x2} (800 and 880°C, respectively), gave bubbled and crystallized joints with partially discontinuous interfaces; when the joining temperature was above the melting temperature [Figs 2(d) and (e)] the interface between glass and composite was improved with respect to that produced at lower temperature [Figs 2(a)–(c)] but the amount of gaseous product becomes predominant, as already observed by heating microscopy [see Figs 1(d) and (e)]. Clearly the glass matrix is reacting with the composite and drastically changing its composition, with the production of gaseous species.

One can also note that the joint shown in Fig. 2(e) does not show any crystalline phase or porosity, in contrast to the samples of Figs 2(b)–(d). As the crystalline phase has been found to be $Zn_3(BO_3)_2$, its disappearance could be explained by zinc removal from the ZBM glass matrix, as discussed above [reaction (1)] and shown in Table 1. The reaction between the ZBM glass and the SiC_f/SiC composite appears to be complete after 45 min at a temperature of about 1200°C, leaving a continuous, bubble-free and amorphous joint region [Figs 1(i) and 2(f)].

The Zn content (wt%), measured by EDS analysis in the joint region of the above-described sandwiches, gives information about the onset and completion temperature for the reaction between glass and composite (Table 1: only the Zn percentages are reliable and significant, as the others are too low for the detection limits of this instrument). As can be seen, the Zn content decreases from the starting concentration to a few wt% when the temperature increases towards 1200°C. The vitreous and bubble-free joint obtained at 1200°C *no longer contains zinc oxide*: the reactive joining process gave rise to a glass of different composition with respect to the starting ZBM one.

To understand the influence of ZnO in these reactions, we performed identical joining experiments with a borate glass containing all oxides present in the ZBM glass except ZnO. The new glass composition was adjusted to keep the relative molar percentages of the other oxides identical to those of the ZBM glass: i.e. 59·5% B_2O_3, 18·4% MgO, 9·1% SiO_2, 8·2% Al_2O_3 and 4·8% Na_2O. Its preparation and characterization were identical to those of the ZBM glass. This glass (called BMA) had T_g = 565 ± 3°C (30°C higher than that of the ZBM), one crystallization peak at 810 ± 10°C and T_m = 1050 ± 10°C. First attempts at obtaining bubble-free sandwiches with the BMA glass failed: a sandwich $SiC_f/SiC/BMA/SiC_f/SiC$ heat-treated for 45 min at 880°C is shown in Fig. 3 as a typical example. Here again the glass wetted and reacted with the composite, but the joint contains many bubbles. We can therefore conclude that ZnO is not the only reacting oxide in ZBM glass; some new glass compositions will be tested to understand this feature.

In the case of ZBM joints, the data showed that all reactions producing gases are completed after

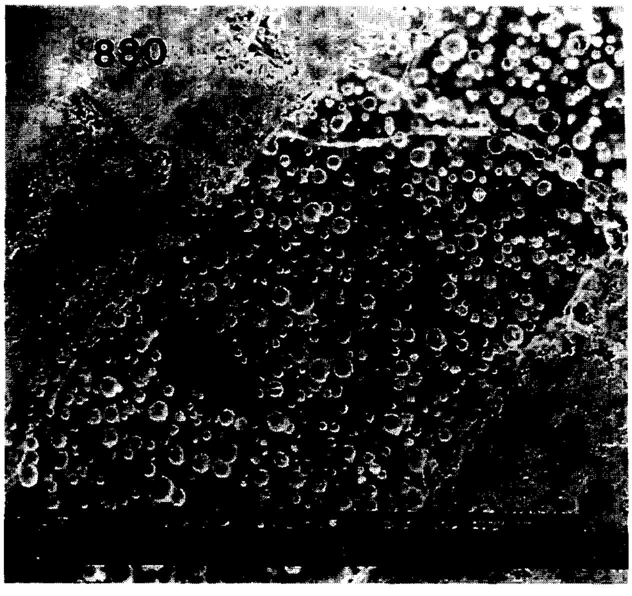
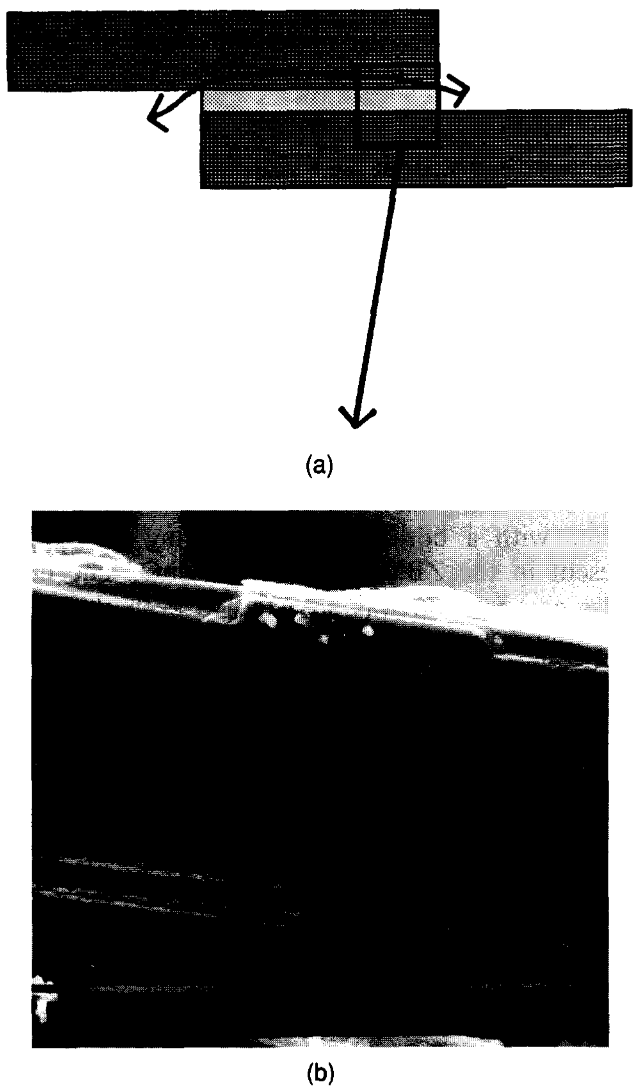


Fig. 3. SEM micrographs of cross-sectioned $SiC_f/SiC/BMA/SiC_f/SiC$ sandwich heat-treated for 45 mins at 880°C.



(a)

(b)

Fig. 4. (a)View of lap joint and fracture mode after shear tests and (b) cross-sectioned view of the fractured region indicated in Fig. 4(a), for a joined $SiC_f/SiC/BM/SiC_f/SiC$ structure prepared at 1200°C for 45 min.

45 min at 1200°C. Therefore, it being impossible to obtain bubble-free joints at lower temperatures even by changing the glass composition, we followed the route of a reactive joining, by heating the $SiC_f/SiC/ZBM/SiC_f/SiC$ sandwiches for 45 min at 1200°C. We prepared completely reacted and continuous joined structures and tested them in single lap shear experiments.

Failure always occurred in the composite by peeling stress with minimal bending of the adherends, for an average shear stress of 15 MPa on the joint. A cross-sectioned view of the fracture region shows that the specimen broke in the composite region nearest the joint [Figs 4(a) and (b)], the composite probably having been weakened by the heat treatment and/or because of the interfacial strength of the glassy joint. We can therefore state that the joint shear strength τ is superior to 15 MPa. This result compares well to the shear strength value found for a partially reacted joined structure (1000°C, 45 min: $\tau = 2{\cdot}6$ MPa in Ref. 7). The authors' belief is that the better surface coverage obtained for the 1200°C heat treatment is responsible for this significant improvement of the joint strength.

This lower limit of 15 MPa for the joint shear strength is an encouraging result for a vitreous, oxidation-resistant joint.

Conclusions

We have studied the temperature dependence of the reactions between a zinc-borate joining glass and an SiC_f/SiC composite. The results show that all gas-producing reactions are complete after 45 min at 1200°C; the composition of the joining glass changes during the process and the new glass wets the composite well, giving a continuous and stable interface. This study permitted the preparation of oxidation-resistant joints having acceptable shear strength.

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