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Joining of Surface Modified Carbon/Carbon Composites using a Barium–Aluminum–Boro-Silicate glass

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Abstract

Carbon/carbon composites (C/C) are known to be not wettable by most glass materials: in this paper, C/C have been joined by a barium–aluminum–boro-silicate glass (SABB) after modifying the composite surface with the formation of a silicon carbide layer. The surface modification has been obtained by heating, in an inert atmosphere, a silicon slurry deposited on the composite surface at a temperature above the silicon melting point, to achieve its transformation to β-SiC. A 'sandwich-like' joined structure (composite/glass/composite) has been made by putting a slurry of SABB glass between two β-SiC surface modified C/C samples of approximately $10 \times 12 \times 2\,mm^3$, then by heating them at a temperature above the SABB softening point, in an inert atmosphere. The obtained 'sandwich-like' joined structures were characterised by thermal analyses, X-ray diffraction, optical and scanning electron microscopy and compositional analysis. Mechanical characterisation was carried out using Vickers micro-indentation (at the glass/composite interface and in the glass joint) and with a shear stress test, performed on a compression test machine. The joined structures prepared with optimised conditions have shear strength values of up to 30 MPa at room temperature. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Carbon-fibre reinforced carbon matrix composites (C/C) are one of the most promising candidates for mechanical and structural applications,[1] because of their high specific mechanical strength and high working temperatures in an inert atmosphere. Many parts have already been produced or proposed for mechanical components (brakes, clutch plates and driving shafts), for the aeronautic industry (missiles and rockets parts, heatshields for re-entry vehicles and leading edges for trans-atmospheric aircraft), for engines (aerospatial engines, gas turbines and nozzles), for biomedical engineering (bone prosthesis and tendons), for nuclear components (for future thermo-nuclear fusion reactors) and for a wide range of industrial applications (glass-making machineries, high-temperature mechanical fasteners, hot press dies, furnace heating elements and heat exchangers).[1] There are still problems to be resolved with C/C, such as their oxidation by atmospheric oxygen[2,3] and the composite/composite joining technique; the latter is the subject of this paper.

The design of complex parts needs a fast, safe, easy and, if possible, low cost joining method. As these composites are not weldable, mechanical fastening, made by refractory metals or C/C itself, was one of the first methods attempted to join them; the strength of the obtained joints was not satisfactory however, because of the low shear and compression strength of the composites, especially for load concentrations around the bolt and rivet holes. Active brazing with filler metals such as titanium, silicon,[4] or their alloys[5] was widely studied with very good results and several patents resulted, but the low oxidation resistance of these joining materials and the thermal mismatch between them and the C/C still limit their application.

A valid alternative to brazed joints is the utilisation of glass or glass-ceramics as joining materials, which have already been successfully studied for the joining of other ceramic materials or ceramic matrix composites.[6–13] Glass materials have a

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modifiable thermal expansion coefficient and they show the unique property of being self-healing joining materials. They are mechanically reliable joining materials up to their softening point and they can be crystallised to obtain high-temperature resistant glass-ceramic joints.

However, most glass materials do not usually wet carbon or graphite surfaces and react with them producing gaseous species.[14] C. Pantano *et al.*,[15] however, demonstrated that binary B_2O_3–SiO_2 glass materials show a good wetting behaviour for carbon fibres: boron oxide itself wets graphite because of its planar structure.

Another work[16] showed that the contact angle of a barium–aluminum–boro-silicate glass (SABB) on silicon carbide was very low (about 20°). This glass was already used to join SiC/SiC composites,[13] but it was impossible to obtain joints with it on as done carbon/carbon composites.[17]

The authors decided to modify the C/C composite surface by the formation of a β-SiC layer and SABB was chosen as the joining material for C/C in this study: the β-SiC in fact, modified the C/C composite surface, allowing a good wettability and a strong interface with SABB.

2 Experimental

2.1 Materials

The C/C used in this study is a 3D composite material manufactured by the Société Européenne de Propulsion (SEP, Bordeaux, France) and produced by Chemical Vapour Infiltration (C.V.I.);[18] reinforcement fibres were produced by polyacrylonitrile (PAN) polymeric precursor. The surface modification of the C/C is carried out by using a slurry of silicon powders (Si grain size $< 150 \mu m$, Merck) dispersed in ethanol. The composition of the glass chosen as joining material (SABB) is: 70·4 SiO_2–2·1 Al_2O_3–17·5 B_2O_3–10·0 BaO wt%.[13,14]

The powders of the starting materials (oxides or carbonates) are mixed together in a platinum crucible and heated in air for 5 h at 1650°C; the melt was then cooled at room temperature and ground for X-ray powder diffraction analysis (XRD, Philips PW1710), Differential Scanning Calorimetry (DSC, Perkin Elmer DSC 7 with Thermal Analysis Controller TAC 7/DX), Differential Thermal Analysis (TG-DTA, Setaram 92) and heating microscopy (Leitz GmbH AII).

The glass transition (T_g), measured by DSC and DTA, is about 650 ± 5°C; the softening point, measured by heating microscopy, is 970 ± 5°C, no crystallisation peaks were observed and the melting point is about 1120 ± 10°C. The SABB powders resulted amorphous to XRD analysis.

2.2 C/C surface modification and joining procedure

The C/C composite was cut out with a diamond rotary blade, to form approximately $10 \times 12 \times 2\,mm^3$ samples and then cleaned in an ultrasonic bath in acetone or ethanol. A silicon slurry (silicon powders dispersed in ethanol) was placed on the composite surface to form a homogeneous thin layer and then dried at room temperature. The heating treatment was performed in a tubular oven (Bicasa) under a slight argon flow (< 50 mbar); the samples were heated to 1550°C for 1 h (temperature rate $30°C\,min^{-1}$) and cooled. Some specimens were prepared for electron microscopy (SEM: Philips 525M with EDS SW9100 EDAX) and XRD.

The glass powder was put in ethanol to make a second slurry, which was applied between two modified composite plates (as previously described) to form a sandwich structure [Fig. 1(a)]. The specimens were heat treated at 1200°C for 60 min, at 1300°C for 5 min or 1 h (temperature rate $50°C\,min^{-1}$) in argon flow. The process temperatures were chosen according to previous studies on SiC/SiC composites joining.[13] Some of the joined

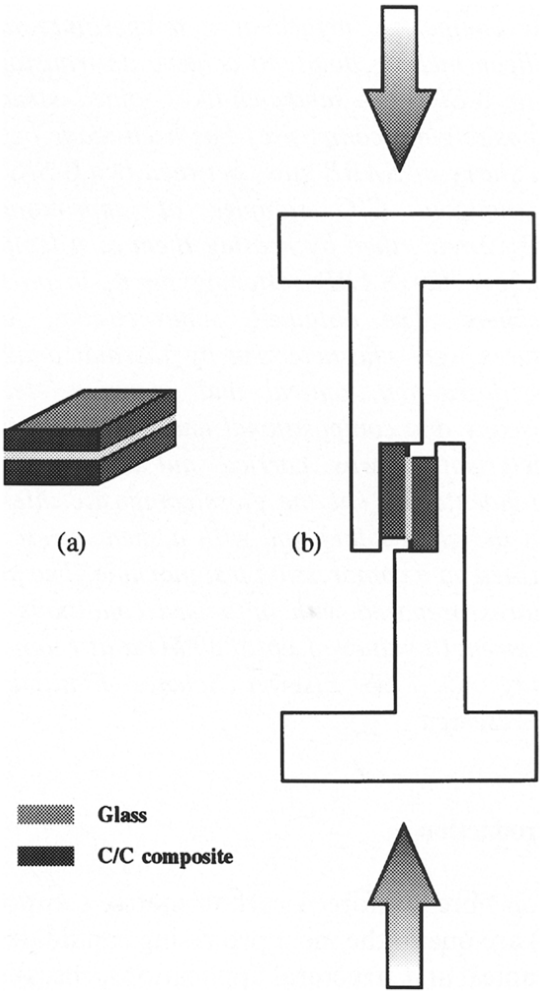

Fig. 1. Mechanical characterization of the joined structures: (a) sandwich-like joined structure; (b) grips for shear stress measure with a compression test machine.

samples were characterised with SEM, EDS, XRD and mechanical tests, according to the procedure described below.

2.3 Mechanical tests

Some of the joint structures were embedded in a polymeric resin, cut and polished to a 1 μm finish. At least 10 Vickers micro-indentations were performed on the composite/glass interface and on the joined zone, to qualitatively determine the relative strength of the interface and the presence of any residual stress in the joint.

The mechanical shear stress tests of joints were carried out with the grips shown in Fig. 1(b), using a compression testing machine (SINTEC D/10). The samples were glued to the grips using a bicomponent epoxy glue, which can be dissolved in acetone to recover specimens and analyse their fracture surfaces by SEM, EDS and XRD. At least five joined samples were tested for each thermal treatment: the most significative values are reported in Table 1, as will be discussed in Section 4.3.

3 Results

3.1 Glass/composite interface

After the silicon slurry deposition and the heat treatment of up to 1550°C, XRD analysis was carried out on the modified surface of the C/C composite: this shows the presence of β-SiC. The SEM observation of the cross-section reveals that the thickness of the layer formed on the C/C is about 5–10 μm.

The carbon fibers on the modified C/C surface appeared to be covered by a thin layer of β-SiC crystals, as can be seen in Fig. 2, and also according to Refs 19 and 20.

Figure 3 shows a particular of the interface of a joined structure prepared by heating at 1300°C for 60 min: a thin β-SiC interlayer with a mean thickness of about 5 μm is evident at the glass/composite interface. In this case, the interface is continuous and homogeneous, while for the samples treated at 1300°C for 5 min there are some discontinuities and the glass and composite are not apparently joined in some places. For the heating at 1200°C for 60 min, the morphology of the interface is similar to that of the sample heated at 1300°C for the same time. Where the surface porosity of the composite is large enough, C/C appears to be impregnated with glass as can be seen in Fig. 4; glass adheres only where β-SiC is present. Figure 5 shows a particular of a carbon/carbon modified surface partially coated with SABB: the contact angle is very low and in some cases near to zero degrees. The glass perfectly adheres to the modified substrate without cracks or bubbles.

Table 1. Mechanical shear strength of the C/C joined structures

Heat treatment		*Experimental shear strengths (MPa)*
Temperature (°C)	*Time (min)*	
1300	60	21·0–29·8–**25·4**–22·8
1300	5	22·4–27·4–19·5
1200	60	22·9–**20·6**–20·8–**22·5**

A partial oxidation of β-SiC coated C/C composite occurred in some cases: the thin β-SiC layer was to some extent transformed (likely in some amorphous species), while the carbon fibres were consumed and a thin void between the transformed layer and the carbon fibre is observable in Fig. 6 (see arrow). The XRD analysis, in this case, only revealed peaks due to the not oxydised β-SiC and to the C/C.

When trying to coat this surface with a SABB slurry, as before, it was not possible to obtain a

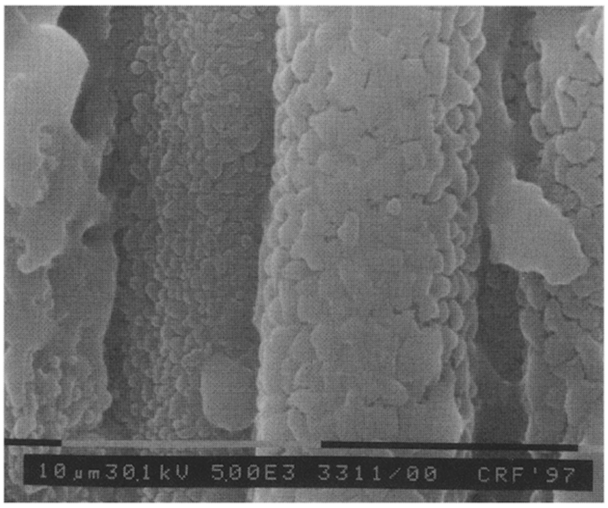

Fig. 2. β-SiC crystals on the carbon fibers of the C/C surface, obtained by heating a silicon slurry at 1550°C for 1 h.

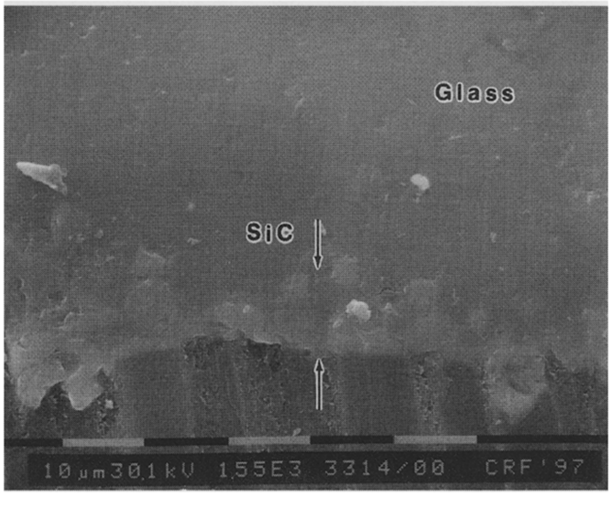

Fig. 3. Particular of the interface between β-SiC modified C/C and SABB glass.

continuous thin layer, as shown in Fig. 7, where some glass drops show that the wettability is greatly reduced. Sandwich-like joined structures, with a joint thickness of about 120–160 μm, were prepared and can be observed in Fig. 8 (back-scattered electrons SEM micrograph). The glass joint is continuous, with few bubbles; the XRD analysis in the joint region does not show the presence of new crystalline phase after the heat treatments. An evident infiltration of silicon, which is suddenly transformed into β-SiC, is noticeable through the composite section (bright in the back-scattered electrons SEM micrograph).

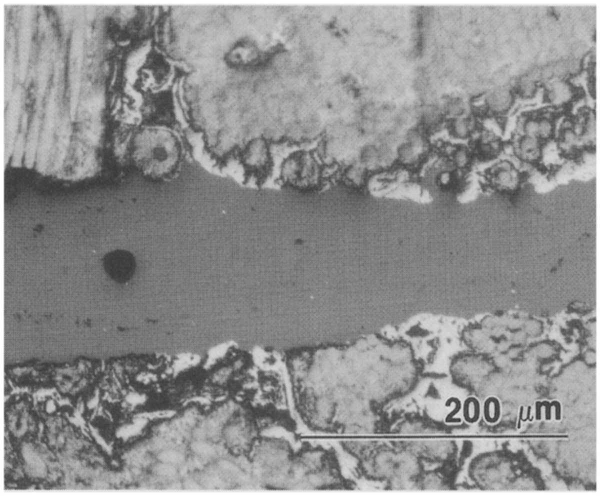

Fig. 4. Sandwich-like joined structure :β-SiC modified C/C joined using SABB glass (optical microscopy; bar = 200 microns).

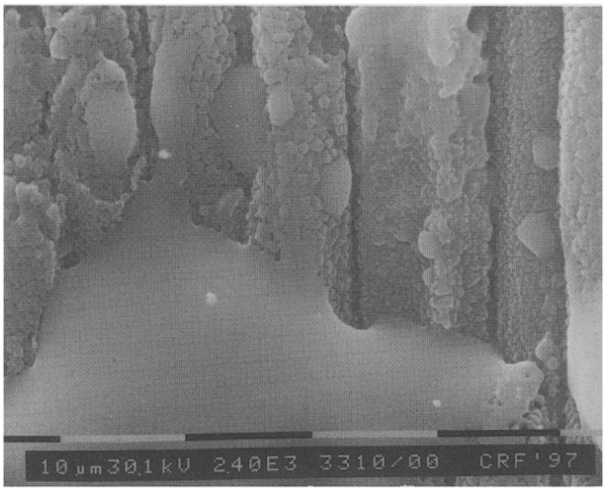

Fig. 5. High wetting of the SABB glass on the β-SiC modified carbon fibers of the C/C surface.

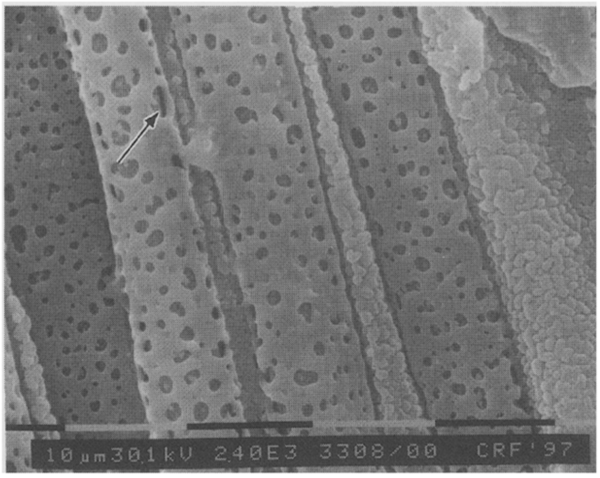

Fig. 6. Partial oxidation of the β-SiC modified carbon fibers on the C/C surface: the carbon fibres were consumed and a thin void between the transformed layer and the carbon fibre is indicated by the arrow.

3.2 Indentation and mechanical shear stress testing

Vickers micro-indentation test were performed with a load of 4·9 N at the glass/composite interface (Fig. 9); the cracks propagate in the composite and partially in the glass, but not at the interface between them (see arrows). The joint region was also indented: the first Vickers tip (left corner in Fig. 10) is due to a load of 2·94 N, while the second (right corner in Fig. 10) to 4·9 N. The cracks propagate in the glass from 4·9 N onwards, parallel to the composite surfaces, while no transversal propagation can be observed.

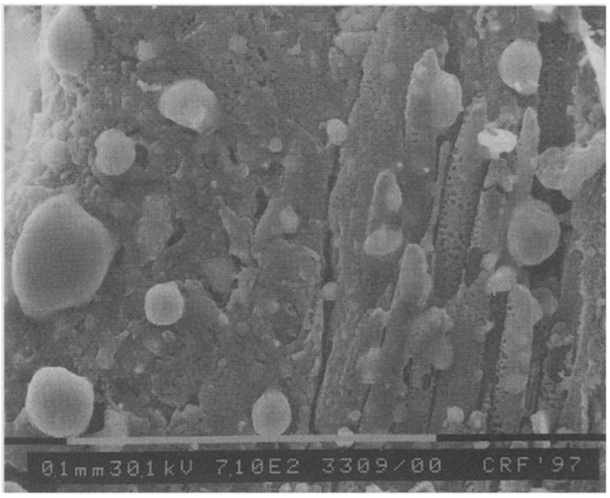

Fig. 7. Poor wetting of the SABB glass on the partially oxidised β-SiC modified carbon fibers on the C/C surface.

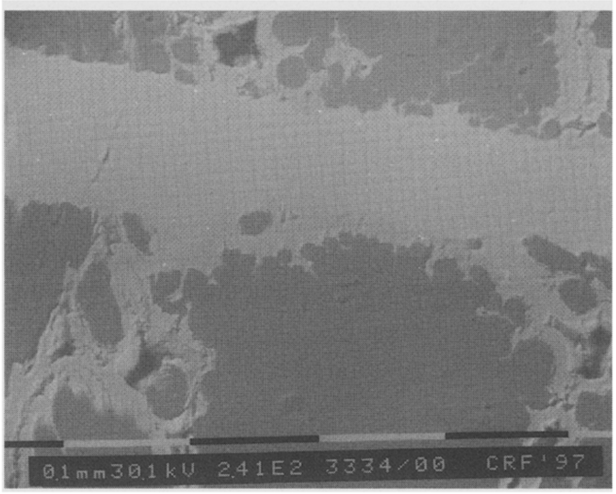

Fig. 8. Sandwich-like joined structure :β-SiC modified C/C joined using SABB glass (SEM-Back scattered electrons).

Shear stress tests were performed on joined structures obtained according to the indicated conditions of time and temperature, as shown in Table 1. The C/C composites sometimes failed in compression, before the joint fracture (bold values in Table 1).

The failure of the joints can take place in the glass, at the interface or in the composite; when the value of the shear strength is high, as in the case of heat treatment at 1300°C for 60 min, the cracks propagate only in the joining glass, as shown in Fig. 11 (the cross-section of the specimen broken at 29 MPa) and in Fig. 12 (plan view of the same sample).

When the heat treatment is performed at 1300°C for a time of 5 min, the plan view of the fracture surface reveals the presence of some zones where the failure takes place at the interface glass/SiC: a composite zone covered by SiC crystals, surrounded by broken glass, is observable in the middle of Fig. 13. The fracture surfaces of the samples prepared at 1200°C for 60 min, are similar to those of samples prepared at 1300°C for the same time.

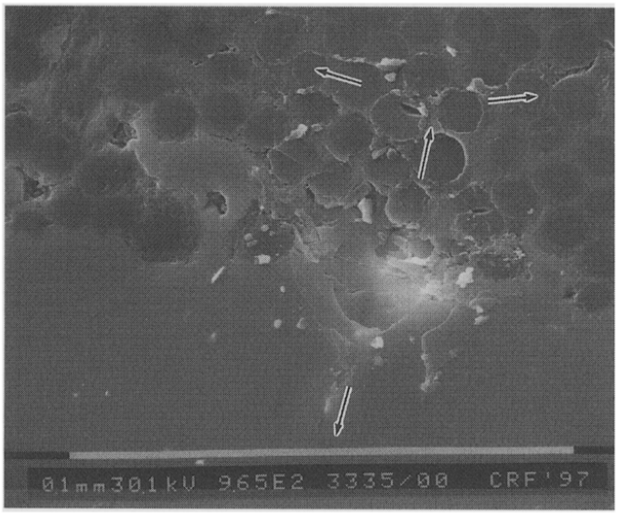

Fig. 9. Vickers micro-indentation at the interface between β-SiC modified C/C and SABB glass: note the crack propagation in the composite and in the glass, but not at the interface.

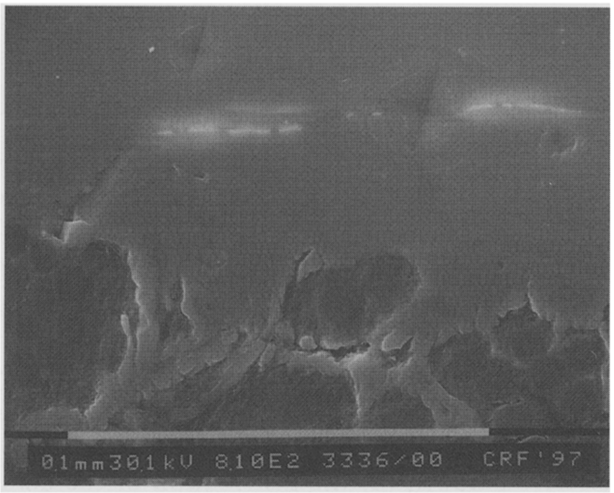

Fig. 10. Vickers micro-indentation on the SABB joining zone of the β-SiC modified C/C: note the crack propagation parallel to the interface.

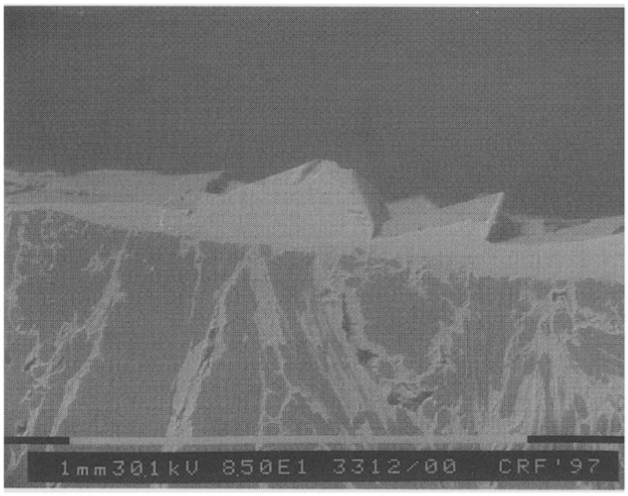

Fig. 11. Cross-section of a fracture surface after mechanical test (sample prepared at 1300°C, 60 min, $\tau = 29$ MPa).

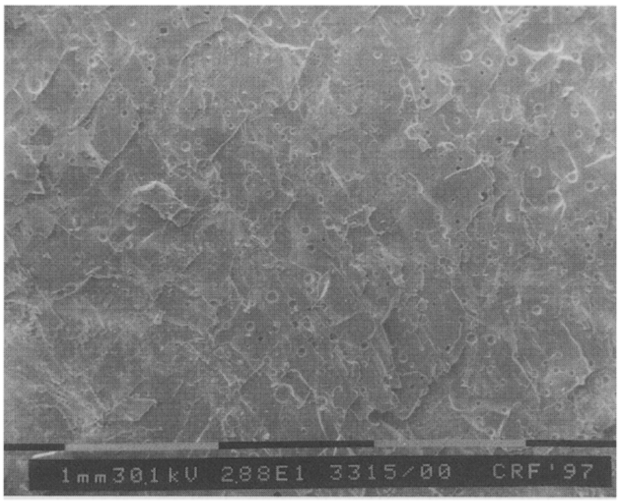

Fig. 12. Plan view of a fracture surface after mechanical test (sample prepared at 1300°C, 60 min, $\tau = 29$ MPa).

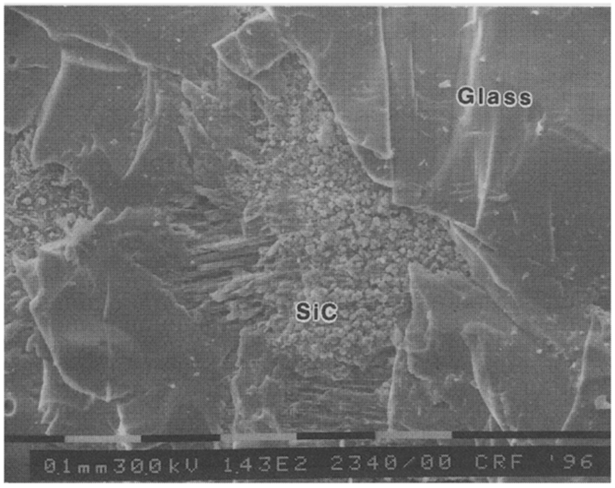

Fig. 13. Plan view of a fracture surface after mechanical test (sample prepared at 1300°C for 5 min): as the time was not enough for a complete reaction between β-SiC and SABB, the interface resulted not continuous in some places and the fracture surface shows some β-SiC crystals.

4 Discussion

4.1 C/C surface modification

Liquid silicon has been utilised to form SiC composites since 1974, when Hillig[20] produced a SiC/Si composite with silicon impregnation of carbon fibers. It is well known that the contact angle of liquid silicon on carbon is near 0°; complete wetting allows silicon to penetrate into the pores of carbon matrix; molten silicon quickly reacts with carbon to form β-SiC.[21,22]

Silicon infiltration also occurs in this work and it is followed by a complete reaction of silicon to give β-SiC: it is evident even at a distance of 1 mm or more from the treated C/C surface (Fig. 8, bright zones in the SEM micrograph). More important, the C/C surface is successfully and easily modified by the formation of a thin β-SiC layer (Figs 2 and 3).

The thinness of the silicon slurry layer and the process time and temperature (1550°C for 60 min) causes the complete transformation of silicon to β-SiC, as confirmed by the XRD analysis, which was carried out on the unpolished modified composite surface. Only the peaks, due to the carbon/carbon composite and to the β-SiC, were detected, without any signal due to pure Si.

4.2 SiC/glass interface

The reactivity between SiC and glass materials was widely studied particularly in the field of SiC fibre/glass or /glass ceramic matrix composites: carbon, silica and gaseous SiO, CO and CO_2 were the main products of these complex reactions.[23,24] Particularly, L. Yurkov *et al.* studied the wetting between SABB glass and SiC: it was found that monocrystals of silicon carbide dissolve in the glass melt, without giving carbon layer or gaseous products at the interface between glass and silicon carbide: as a consequence, the glass darkens.[16,25]

This is in agreement with the authors observations on β-SiC modified C/C joined with SABB, because: (1) the SABB bulk glass is colourless and transparent, while the joint zone between the two β-SiC modified carbon/carbon is blue and it darkens as the heat treatment proceeds, (2) the β-SiC/glass interfaces have a high shear strength (incompatible with the presence of any C layer, not observed in the authors samples) and (3) gas bubbles were not found at the β-SiC /glass interface (Fig. 3).

It must be underlined that the foreseen diffusion of a small quantity of the thin β-SiC layer in the SABB glass is a very limited phenomenon, not sufficient to affect the starting glass properties (i.e. viscosity, Tg, coefficient of thermal expansion,...); it was also observed that the β-SiC layer is stable after 50 h at 1100°C.[26]

However, the presence of β-SiC on the C/C surface is extremely important for SABB glass wettability and adhesion: the glass adheres to C/C only where a SiC coating is present; moreover, where the C/C pores are coated with β-SiC they are filled by the glass (Fig. 4). It was also verified that SABB glass does not wet the as-received C/C composites at all. Furthermore, the accidental formation of a thin amorphous oxidised layer, during the reaction between C/C and silicon (Fig. 6), probably reduces or totally inhibits the possibility of any reactions: SABB does not wet the partially oxidised surface, as shown in Fig. 7. As a consequence, the adherence of the glass to the partially oxidised surface is poor and the process control during the formation of the β-SiC layer on C/C is particularly important for the success of the joining process.

4.3 Mechanical test configuration

The set up for shear tests (Fig. 1) was chosen according to considerations on stress distribution in composites and joining and on different models of mechanical tests described elsewhere.[4] This testing method should partially eliminate bending and peeling effects, which considerably alter the results, as with other configurations[4] designed for a tensile testing machine.

The stiffening of the system, obtained by the thickening of lateral supports, has the purpose of keeping the two sides of the joint parallel; the joining region is stressed in shear or in compression, and only a little in bending or peeling.

It was however evident during this work, that the main factors that affect the reproducibility of the mechanical results are: (1) sometimes the two loaded sides of the grips (Fig. 1) are not perfectly parallel, (2) the distribution of the composite porosity is not uniform, (3) in some of the specimens the C/C composite fails under compression (and the joining region remains intact) and (4) the quality of the β-SiC layer is not homogeneous.

4.4 Mechanical properties

The best results in shear strength for the joints are obtained when the failure totally occurs in the glass and not at the interface; Figs 11 and 12 show the specimen prepared at 1300°C, for 60 min, which broke at 30 MPa and it is evident that only the glass failed, while the interface and the composite seem to be intact. When the interface is discontinuous, it could induce cracks; furthermore, some zones actually do not participate in the load transfer, because the β-SiC and glass are not joined in some places. This situation is shown in Fig. 13, where β-SiC crystals, which are not covered by SABB, are visible on the fracture surface.

From the mechanical tests and particularly from observation of the fracture surface morphology, the temperature range 1200–1300°C seems to be suitable to obtain good results. Moreover, the 5 min process seems to give less continuous interfaces, probably because this time is not sufficient for the glass to react and to join with β-SiC (Fig. 13). It is well known that the four cracks originating from a Vickers tip have the same length if the material is not under stress condition; if a residual stress is present, the crack length varies according to the stress type (compression or traction).[27] In our case (Fig. 10), it is evident that the joining zone is under compression; in fact cracks propagate in the joining material parallel to the composite surfaces with no transversal failure. If the joining material was under traction stress, the cracks would propagate perpendicularly to the composite surface. The compression of the joint zone derives from the different coefficients of thermal expansion between C/C and SABB ($\alpha_{SABB} < \alpha_{C/C}$); this phenomenon could probably increase the strength of the joints, preventing the formation of glass cracks during the cooling process.

The Vickers indentation at the interface glass/composite (Fig. 9) also shows that the induced cracks did not propagate along this interface, but in the composite and in the glass: thus, the interface fracture energy could be assumed to be higher than those of SABB and C/C.

5 Summary and Conclusions

The wettability and the adhesion of a glass on C/C can easily be obtained by the modification of the composite surface with a thin β-SiC layer. Samples of a β-SiC surface modified C/C composite can be joined by a SABB glass as joining material, even though it is not possible with the as received C/C composite. The shear strength results are very promising: about 30 MPa at room temperature in the optimised conditions. The whole process is easy, fast and at a low cost.

Acknowledgements

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