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Journal of Nuclear Materials 258–263 (1998) 1546–1550

journal of nuclear materials

Glass-ceramic joining and coating of SiC/SiC for fusion applications

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Abstract

The aim of this work is the joining and the coating of SiC/SiC composites by a simple, pressureless, low cost technique. A calcia-alumina glass-ceramic was chosen as joining and coating material, because its thermal and thermo-mechanical properties can be tailored by changing the composition, it does not contain boron oxide (incompatible with fusion applications) and it has high characteristic temperatures (softening point at about 1400°C). Furthermore, the absence of silica makes this glass-ceramic compatible with ceramic breeder materials (i.e. lithium-silicates, -alluminates or -zirconates). Coatings and joints were successfully obtained with Hi-Nicalon fiber-reinforced CVI silicon carbide matrix composite. Mechanical shear strength tests were performed on joined samples and the compatibility with a ceramic breeder material was examined.

1. Introduction

Because of their excellent thermo-mechanical and low activation properties, silicon carbide fiber-reinforced silicon carbide matrix composites (SiC/SiC) are attractive structural materials for high temperature and fusion reactor applications [1]. However, the fabrication of complex structural parts is still hindered, since these composites are not weldable and are poorly workable. Also, the intrinsic porosity of these materials makes them permeable to gases. Their chemical reactivity with the ceramic breeders was reported by Sample et al. [2]. These problems might be alleviated by an innovative joining method and the use of a suitable coating [3].

Glass-ceramics can be a versatile joining or coating material with tailorable thermal and mechanical properties; they are not affected by oxidation and can be self-sealant at temperatures above the glass softening point [4]. In this work we joined and coated Hi-Nicalon fibre reinforced silicon carbide matrix composites with a calcia-alumina glass-ceramic, referred to as CA. An eutectic composition in the binary phase diagram CaO–Al_2O_3 was selected to obtain a low temperature homogeneous melt.

The CA is particularly appealing for fusion reactor applications, since it is a Low Activation Material (LAM), has high characteristic temperatures and does not contain boron, lithium and silicon oxides: the boron is incompatible with high neutron flux environment, the lithium is transformed to tritium by neutron irradiation and the silica reacts with the ceramic breeders [2].

The joints and the coatings were produced by a simple, pressureless, low-cost firing technique. The shear strength and morphology of joined “sandwich like” samples were examined. Coated samples were submitted for a preliminary compatibility test with the Li_4SiO_4 ceramic breeder.

2. Experimental

Two different bi-directional SiC (Hi-Nicalon)/SiC composites were utilized in this study: one produced by chemical vapor infiltration, referred to as SiC/SiC_{CVI}, the other by polymer infiltration pyrolysis, referred to as SiC/SiC_{PIP}. Both composites were supplied by the Kyoto University [5].

The composition (wt%) of the CA glass-ceramic was 49.77 CaO and 50.23 Al_2O_3 [6]. Powders of aluminium

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0022-3115/98/$19.00
PII: S0022-3115(98)00176-7

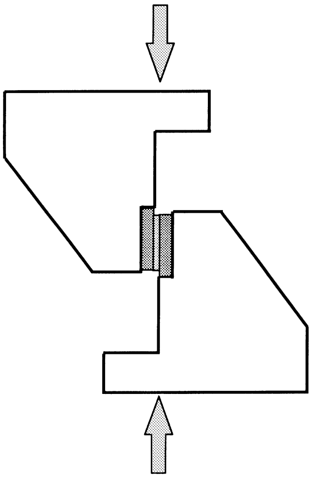

Fig. 1. Sample and grip configuration for the mechanical shear tests. The sample is glued to the grips by a bicomponent epoxydic glue.

oxide and calcium carbonate were mixed together in a platinum crucible and heated in air at 1650°C for 1 h. After cooling, the glass-ceramic was ground for X-ray diffraction analysis (XRD, Philips PW1710), Differential Scanning Calorimetry (DSC, Perkin Elmer DSC7) and Differential Thermal Analysis (DTA, Netzsch 4045).

The joined "sandwich like" samples were prepared by depositing a slurry of glass-ceramic powder and ethanol between two composite samples (about $10 \times 4 \times 2$ mm^3). Likewise, coated samples were prepared by deposition on the composite surface (15×4 mm^2). Then, these samples were heated in a tubular oven at 1500°C for 1 h under a slight Ar flow, with no external pressure being applied. The morphological analysis of the joints and the coatings was made by Scanning Electron Microscopy (SEM, Philips 525M). The mechanical shear tests on the joined samples (joint area: 10×4 mm^2) were performed at room temperature with a compression machine (SINTEC D/10), as shown in Fig. 1.

A preliminary test of compatibility between a CA-coated SiC/SiC and Li_4SiO_4 ceramic breeder (pellets) was carried out at 800°C for 140 h under a helium–hydrogen (0.1% vol. of H_2) flow: a completely coated composite (with the CA-coating on each of the six faces of the SiC/SiC) and an as-received composite (about $6 \times 4 \times 4$ mm^3) were placed in a alumina crucible containing the solid ceramic breeder (Li_4SiO_4 pellets). Then, they were heated at 800°C for 140 h under a helium–hydrogen (0.1% vol. of H_2) flow. After this treatment the samples were analysed by scanning electron microscopy and XRD.

3. Results and discussion

Table 1 presents CA characteristic temperatures as measured by the DTA, and the calculated coefficient of thermal expansion (CTE) at 25 and 350 C. The CTE's were calculated by the method proposed by Takahashi [7]. An amorphous phase and two crystalline phases, $3CaO{\cdot}Al_2O_3$ and $12CaO{\cdot}7Al_2O_3$ were detected by XRD on the CA powders. The melting points of the crystalline phases are respectively 1535°C and 1415°C according to the $CaO–Al_2O_3$ phase diagram [8].

The CA glass-ceramic did not wet the SiC/SiC$_{PIP}$ surface. In contrast, it showed good wettability on the SiC/SiC$_{CVI}$ surface. This behaviour was probably due to the difference in crystallinity of the SiC matrix. X-ray diffraction analysis on the two composites (Fig. 2) showed that the silicon carbide in the SiC/SiC$_{PIP}$ composite was almost totally amorphous, while the β-SiC phase was predominant in the SiC/SiC$_{CVI}$.

Studies are in progress examining the lack of wettability on amorphous SiC/SiC$_{PIP}$ (4).

This report will focus on coating and joining SiC/SiC$_{CVI}$. Some joined SiC/SiC$_{CVI}$ samples were prepared in Ar atmosphere at a temperature above the glass-ceramic softening point (1500°C for 1 h).

The cross-section of a SiC/SiC$_{CVI}$–CA–SiC/SiC$_{CVI}$ "sandwich" is shown in Fig. 3: the joint region was uniform with a continuous interface. The porosity of the joint was very low and no cracks were evident.

The average shear strength was 28 MPa at room temperature. The highest shear strength (up to 33 MPa) was obtained with the thinnest joint (100–200 μm thickness). The fracture always occurred in the glass-ceramic and not in the CA/composite interface. High temperature tests are under development.

Toughening of the glass-ceramic, for example with a particle dispersion, potentially could improve the mechanical properties of the CA joint.

As reported by Sample et al. [2], the Li_4SiO_4 ceramic breeder pellets react with the SiO_2 present on the SiC/SiC$_{CVI}$ composite surfaces to form Li_2SiO_3. A protective coating is needed to protect the SiC/SiC surface from this form of degradation.

Homogeneous CA-coatings could be obtained on the SiC/SiC$_{CVI}$ composite by a simple firing method which

Table 1

Glass transition (°C)	Softening point (°C)	α (25°C) (10^{-6} K^{-1})	α (350°C) (10^{-6} K^{-1})
850	1380	7.43	9.42

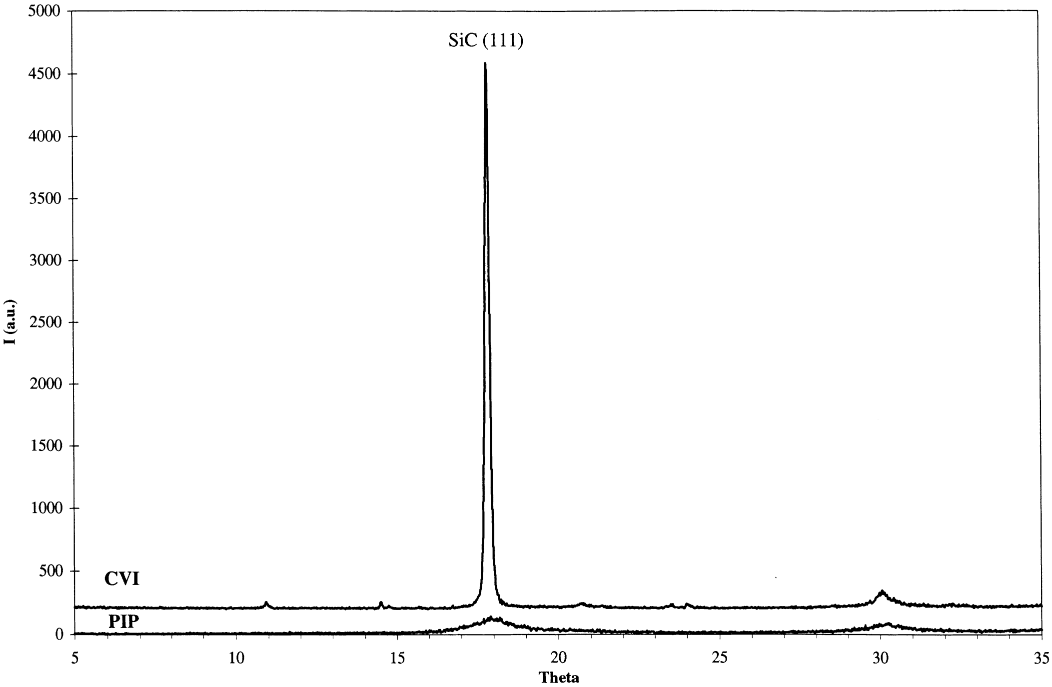

Fig. 2. X-ray diffraction patterns of the SiC/SiC_{CVI} and the SiC/SiC_{PIP}.

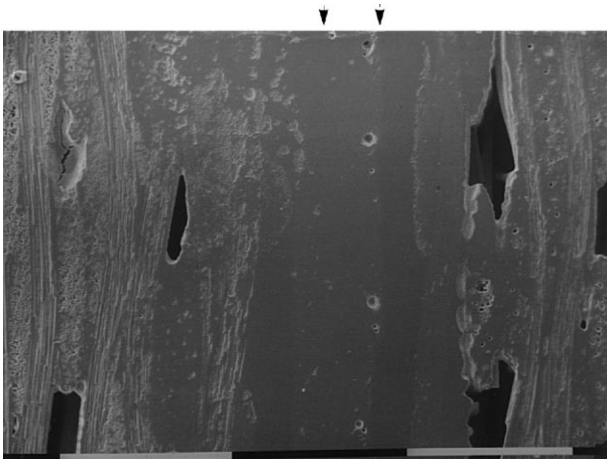

Fig. 3. Scanning electron micrograph of the cross-section of a sandwich SiC/SiC_{CVI}–CA–SiC/SiC_{CVI} prepared at 1500°C for 1 h. The joint region is indicated by the arrows.

consisted of the deposition of a CA powder plus ethanol slurry on the composite surface and heating 1 h at 1500°C in Ar flow.

Fig. 4 shows the surface of the as-received SiC/SiC_{CVI} before the compatibility test, while Fig. 5(a) and (b) correspond to the unprotected composite surface after the compatibility test. The modification of the unprotected composite surface was evident (compare Figs. 4 and 5(a)): several crystalline growths (nodules) were observed after only 140 h (see Fig. 5(a) and the same surface at higher magnification, Fig. 5(b)). The X-ray diffraction analysis on this surface confirmed the presence of a new crystalline phase, Li_2SiO_3 (the nodule shown in Fig. 5(b)) and Li_4SiO_4.

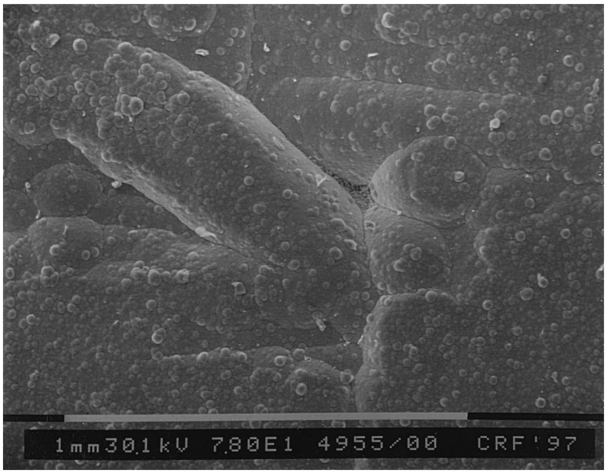

Fig. 4. Scanning electron micrograph of the as-received SiC/SiC$_{CVI}$ surface.

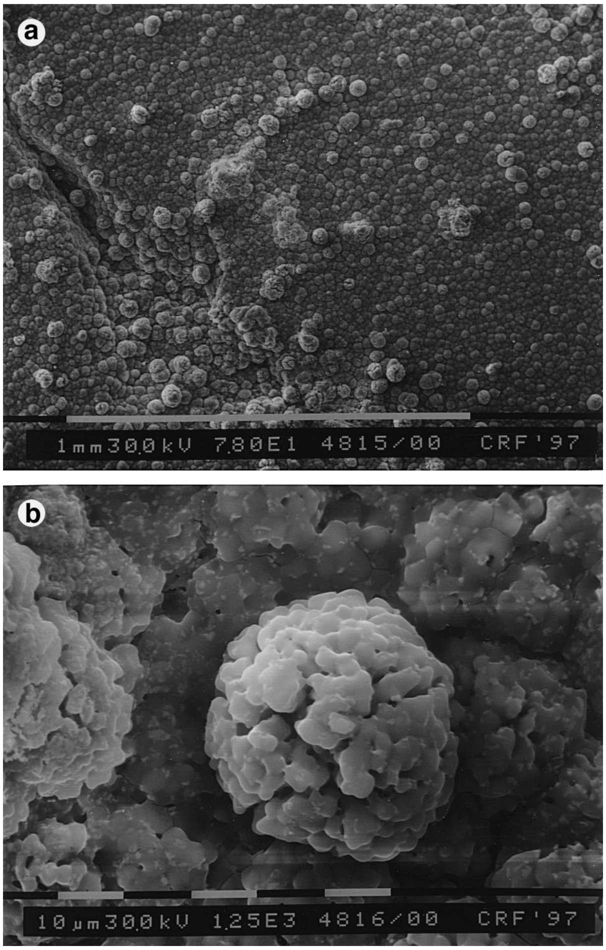

Fig. 5. (a) Scanning electron micrograph of the uncoated SiC/SiC$_{CVI}$ surface after the compatibility test with Li_4SiO_4 at 800°C for 140 h. (b) Magnification of one of the crystalline growths on the SiC/SiC surface of Fig. 5(a).

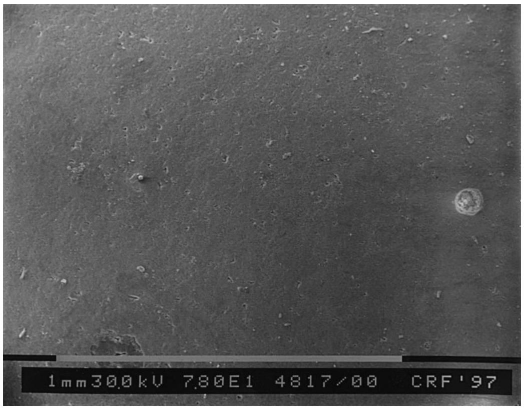

Fig. 6. Scanning electron micrograph of the CA coated SiC/SiC$_{CVI}$ surface after the compatibility test with Li_4SiO_4 at 800°C for 140 h.

In contrast, the CA glass-ceramic coating does not react with Li_4SiO_4. No cracks were produced on the CA-coating during the test: Fig. 6 shows the SEM micrograph of the surface of the CA-coated SiC/SiC$_{CVI}$ after the compatibility test. The CA-coated SiC/SiC$_{CVI}$ before the test (not reported) is identical.

Since the treatment temperature of 800°C is below its glass transition temperature (Table 1), the CA is thermomechanically stable at 800°C.

In conclusion, the proposed calcium–alumina glass-ceramic coating could find effective application both as Li_4SiO_4 breeder protection and as joining material in the thermonuclear fusion reactor.

4. Conclusion

The joining and the coating of SiC/SiC composites was obtained by a simple, pressureless, low-cost technique. Initial results indicated that CA glass-ceramic could be employed either as a joining or as a coating material for SiC/SiC. The average shear strength of the joined structures was of 28 MPa at room temperature and the CA-coated composites did not seem to be affected after 140 h at 800°C in contact with a ceramic breeder.

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