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Silicon carbide-based materials for joining silicon carbide composites for fusion energy applications

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Abstract

This paper describes issues related to using silicon carbide derived from inorganic polymer precursors for joining silicon carbide composites for fusion energy applications. Evolution of gases and shrinkage during processing are identified as critical processes that may control the presence of strength limiting flaws and residual stresses. Precursor composition and structure effect the amount of gaseous species evolved during processing, chemical compatibility with substrates, and processing environments. Results from the literature and from the authors' investigations are used to illustrate the use of polymer derived material for joining.

1. Introduction

To enable the use of silicon carbide fiber reinforced silicon carbide matrix composites (SiC_f/SiC_m) in fusion energy applications, a method of joining SiC_f/SiC_m components that satisfies the requirements of radiation resistance, mechanical integrity, desirable thermal properties, safety during operation and maintenance or accident, and acceptable waste management characteristics is required. Joints made from silicon carbide (SiC) satisfy the above criteria, but practical and reliable methods of their production must be developed. The use of pre-ceramic polymers for joining offers a number of attractive features, such as easy application and low processing temperatures (<1200 °C for obtaining a dense ceramic layer) that inhibit fiber damage during joining, but several issues remain to be addressed. The purpose of this paper is to illustrate the issues associated with using polymer pre-ceramic precursors to obtain silicon carbide-based joints.

2. Experimental methods

To evaluate the effect of high-temperature heat treatments on joints derived from hydridopolycarbosilane (HPCS, Starfire Systems, Inc., Watervliet, NY), butt-joined, flexural specimens for four-point bend testing were fabricated from plates of chemically vapor deposited (CVD) SiC (Morton Advanced Materials, Woburn, MA). The HPCS contained ≈ 3 vol.% allyl groups attached to promote cross-linking and contained 42 wt% SiC powders (F800 powder from UK Abrasives. Lot No. SZ0802A7). Joining was performed by Starfire Systems, Inc. Two plates of CVD SiC, ≈ 4 mm thick, were cut into 25 mm long by 30 mm wide pieces. The 30×4 mm^2 faces were cleaned using hexane, polymer paste was applied by hand, and then the pieces were held together in a special fixture. The material was cured and pyrolysed at 850 °C for 1 h in inert gas, using a heating and cooling rate of 1 °C/min. After pyrolysis the joint was re-impregnated with polymer and pyrolysed again. The flexural strength of specimens was measured before

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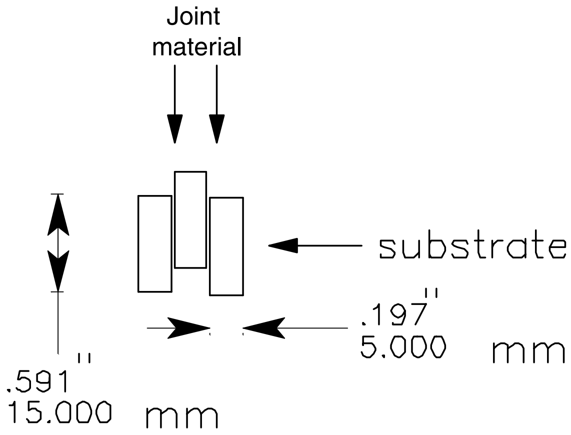

Fig. 1. Schematic diagram of double-lap shear test specimen. The specimen is loaded in compression.

and after annealing at 1100 °C, for 100 h, in flowing, gettered argon (<20 ppm O_2).

To investigate the effect of surface roughness on joint strength, coupons of a three-dimensionally reinforced SiC_f/CVI-SiC_m with ≈40 vol.% Ceramic-grade Nicalon and a 100 nm thick carbon coating (SNECMA, SEP Division, St.-Medard-en-Jalles, France) were joined with a slurry of ≈50 vol.% liquid HPCS (Starfire Systems, Watervliet, NY) and β-silicon carbide (SiC) powders (nominal diameter <1 μm; B10, H.C. Starck GmbH & Co. KG, Goslar, Germany) that was pyrolysed at 1200 °C for 1 h (heating/cooling rate = 2 °C/min). The samples were prepared by lightly polishing one of the 10×10 mm^2 faces of each $10 \times 10 \times 3$ mm^3 coupon of composite with 400 grit SiC paper. The slurry was applied to the faces to be joined by hand, using a spatula. After pyrolysis in nitrogen (99.99% purity) the joint thickness was about 30–50 μm. The shear strength of the joints was tested using a slightly modified version of ASTM D905-89 (see Fig. 1). Since failure always occurred in the joint material, following testing the surfaces that had been joined were subsequently polished using the same procedure described above, and the specimens were joined and tested again. Ten replicate specimens were tested for each condition. After each testing and joining cycle the surface morphology of the surface to be joined was measured using a stylus profilometer (Surfcom 1400A, TSK, J, Tokyo, Japan).

3. Results and discussion

3.1. Processing issues

Numerous small cracks were observed in the microstructure of joints derived from HPCS (Fig. 2). These cracks are likely to limit the strength and permit environmental degradation of the joints. Cracks throughout the bulk of the joint, such as those observed in Fig. 2, may be due to gas evolution, volumetric shrinkage, or thermal expansion mismatch stresses arising during processing.

Improperly controlled gas evolution leads to the formation of strength limiting defects [1–4], such as pores and cracks, in joints. To minimize the evolution of volatile species during joint processing a relatively slow heating schedule should be adopted, especially in the 400–800 °C range, where most of the decomposition takes place. Additionally, gas evolution may be reduced by using precursors with a lack of side chains that can be lost during pyrolysis or bulky side groups that inhibit cross-linking. Thermal cross-linking at low to intermediate temperatures (200–600 °C, depending on precursor composition) decreases the concentration of volatile species containing metal cations and long-chain moieties. Moreover, the transformation of linear polymer-precursor chains into branched structures (by cross-linking) prevents the loss of low molecular weight compounds during pyrolysis, and thus increases the ceramic yield.

Weight loss during conversion and pyrolysis can vary from as much as 80 wt% to as little as 28 wt% and causes volumetric shrinkage [4–6]. Typically the linear shrinkage is >30% [4]. Therefore, the development of precursors with high yield and low shrinkage would allow for improvement in the strength of joints derived from preceramic precursors.

If shrinkage during conversion of the polymer precursor is constrained during joining, such as shown in Fig. 3, shrinkage stresses are generated. A recent analysis [7] suggested the following expression for the in-plane stress, σ_P, at the fabrication temperature in a joint due to constrained shrinkage,

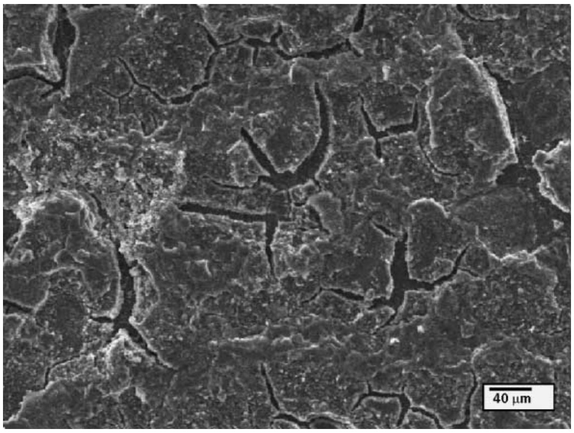

Fig. 2. Microstructure of a joint derived from aHPCS showing cracks resulting from gas evolution during processing.

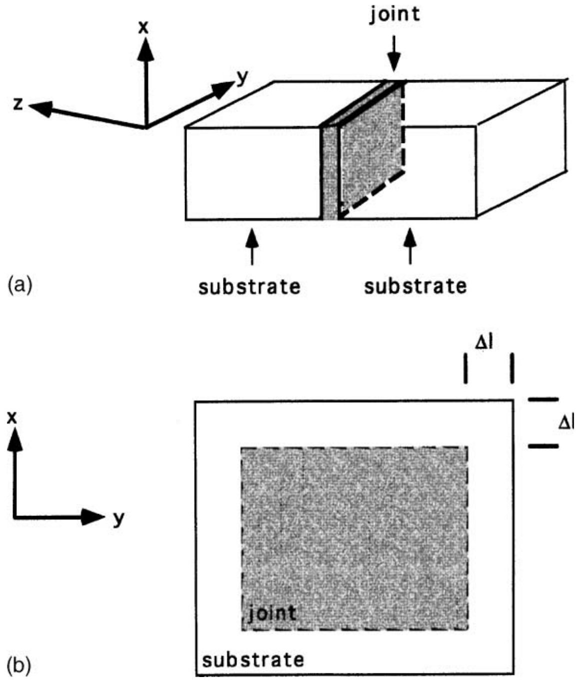

Fig. 3. Effect of low-temperature melting, reactive filler powder composition on the strength of joints, between a fiber reinforced ceramic composite, derived from a silicon–acetylene polymer.

$$\sigma_{\mathrm{P}} = \frac{3\eta_{\mathrm{f}}[\rho/(3-2\rho)]\dot{\varepsilon}}{[1-1/2[\rho/(3-2\rho)]^{1/2}]} = \frac{3\eta_{\mathrm{f}}[\rho/(3-2\rho)][1-(Y\rho_{\mathrm{i}}/\rho_{\mathrm{f}})^{1/3}]}{\Delta t_{\mathrm{p}}[1-1/2[\rho/(3-2\rho)]^{1/2}]},$$

where η_{f} represents the viscosity of the densified material, ρ is the relative density of the pre-ceramic precursor (the volume fraction of solids, or the density of the pyrolysed material normalised by the final density), $\dot{\varepsilon}$ is the rate of viscous densification, Y is the yield of the precursor, and Δt_{p} is the processing time. Following this analysis, the in-plane stresses for typical values of the shrinkage rate and viscosity of silicon carbide precursor materials are shown in Fig. 4. It can be seen that shrinkage rates greater than 1×10^{-5} s^{-1} and values of viscosity above 1×10^{11} Pa s are required to generate values of stress that are likely to cause cracking (>10 MPa). Since cracking may not occur until higher stresses arise, the values of shrinkage rate and viscosity can be considered as upper limits for obtaining joints without cracks.

The development of thermal residual stresses in joints has been extensively described in the literature [8–10] and is not reviewed here. Generally, silicon carbide-based materials derived from pre-ceramic polymer precursors have a coefficient of thermal expansion (CTE) similar to that of SiC (e.g., 3×10^{-6} °C^{-1}). An estimate of the net residual stresses is obtained by superposing the stresses predicted by CTE mismatch and differential shrinkage. If the mismatch in CTE is 1×10^{-7} °C^{-1} then stresses that can arise during cooling from 1000 °C can be ≈10 MPa, assuming no stress relaxation during cooling and an elastic modulus of 100 GPa for the polymer derived material. It is important to note that these stresses, if they occur, increase as the temperature cools from the processing temperatures and do not reach their maximum value until the joint is fully cooled.

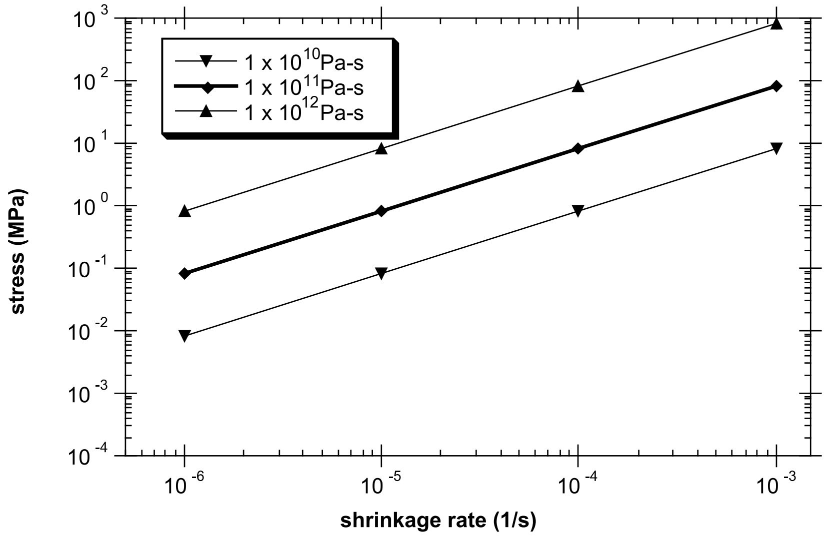

Fig. 4. Fractography of the joints made with the (a) Al–12at.%Si and (b) Al–50at.%Si filler powders. The upper micrograph illustrates the formation of low volume fraction of Al_2O_3 grains with high aluminum filler alloy while the lower micrograph shows a higher volume fraction of Al_2O_3 with a network structure with low aluminum filler alloy. Both test specimens were cured at 1200 °C and tested at 800 °C.

3.2. Thermal stability

The four-point bend strength (≈80 MPa) of the joints, between CVD SiC, derived from HPCS was unaffected by heat treatment at 1100 °C, in flowing argon, for 100 h. This indicates that the initial microstructure of the joint was stable after processing. The same effect has been observed in other systems [2]. In general, however, increasing the maximum processing temperature or the processing time at a given temperature increases the strength of the joints, due to more extensive crystallization, additional reaction with filler powders or the substrates, or increased density from structural relaxation.

3.3. The effect of surface roughness

The shear strength of the 3D SiC/SiC$_f$ ceramic composite joined with a slurry of liquid HPCS and SiC powders increased with decreasing substrate surface roughness (Fig. 5). Microscopy and profilometry data show that each iteration of the polishing and testing procedure produced a smoother surface (Fig. 5(a)). Since the surfaces were polished prior to each joining step, the change in surface morphology is due to the filling of the large inter-bundle pores in the composite substrates. As a result of this procedure the joint strength increased considerably (Fig. 5(b)). Since strength is generally determined by flaw size, these results imply that each joining cycle reduces the flaw size or number of flaws. It is also possible, however, that the surface treatment increased the contact area between the joint and the substrate and decreased the effective stress in the joining material. The increase of scatter in the measured strength values with decreasing surface roughness is likely to be associated with decreasing the uniformity of the size and shape of the inter-bundle pores. A controlled study of the influence of surface treatment and contact area is recommended.

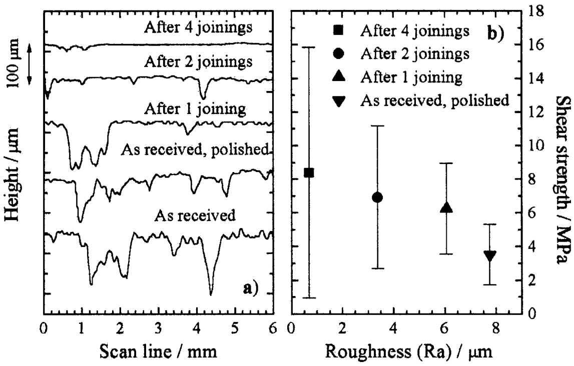

Fig. 5. Surface profiles (a), and values of shear strength (b), for composite specimens joined using HPCS in an iterative testing and surface grinding procedure.

4. Summary

The primary requirements for inorganic polymer, pre-ceramic precursors to be suitable for joining in fusion energy applications is that they must have high ceramic yield, minimal evolution of volatile decomposition products, optimal rheological properties, and practical curing characteristics. Precursor compositions with minimal evolution of gaseous species and low shrinkage, that can be handled and processed in ambient conditions, are highly desirable. Conditions where high shrinkage rates and viscosity occur at the same time must be avoided to prevent stresses occurring due to constraints. The role of surface roughness, particularly in woven ceramic matrix composites, and the contact area between the joint and substrate requires further investigation. Although intrinsic and extrinsic variables influence the value of strength reported for polymer derived joints, many studies indicate that the use of pre-ceramic polymers is an attractive method for obtaining silicon carbide-based joints for fusion energy applications.

Acknowledgements

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