

REACTION-BASED SiC MATERIALS FOR JOINING SILICON CARBIDE COMPOSITES

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OBJECTIVE

Reliable and practical joining techniques are required to enable the use of silicon carbide composites in fusion energy systems. Based on criteria relevant to fusion applications, silicon carbide has been selected as a promising joint material. The objective of this work is to evaluate the thermal stability and mechanical properties of silicon carbide joints fabricated via reaction-based methods.

SUMMARY

The fabrication of large or complex silicon carbide-fiber-reinforced silicon carbide (SiC/SiC) components for fusion energy systems requires a method to assemble smaller components that are limited in size by manufacturing constraints. Previous analysis indicates that silicon carbide should be considered as candidate joint materials. Two methods to obtain SiC joints rely on a reaction between silicon and carbon to produce silicon carbide. This report summarizes preliminary mechanical properties of joints formed by these two methods. The methods appear to provide similar mechanical properties. Both the test methods and materials are preliminary in design and require further optimization. In an effort to determine how the mechanical test data is influenced by the test methodology and specimen size, plans for detailed finite element modeling (FEM) are presented.

PROGRESS AND STATUSIntroduction

A limitation of SiC/SiC composite materials is that they can only be produced in limited sizes and shapes. Therefore, to fabricate a complete fusion energy system a method of joining SiC/SiC components is required. In fusion energy systems utilizing silicon carbide first-wall materials it would be undesirable to use a joining technique that introduces dissimilar materials at the inner face of the first wall. In addition, to avoid poisoning the plasma the first wall must be hermetic. Therefore, two attractive methods of joining silicon carbide with other forms of silicon carbide have been developed: reaction bonding [1-4], and preceramic polymer adhesives [5-11]. In this paper, preliminary results obtained from joints formed by two reaction-based methods will be presented. Reaction bonding consists of adding molten silicon to a mixture of carbon and silicon carbide powders, which subsequently react to form silicon carbide with small amounts of residual silicon or porosity. Reaction forming consists of adding molten silicon metal to a porous carbon network, which subsequently converts to silicon carbide with minor amounts of residual silicon metal or porosity. Although design criteria for SiC/SiC and joints have not been determined there are several practical test methods for measuring the failure conditions under a variety of stress states. To obtain a better correlation between anticipated service stresses and test methods a study utilizing FEM has been initiated and will be described.

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EXPERIMENTAL TECHNIQUE

To evaluate the suitability of joints formed by the reaction-based forming approach, plates of monolithic silicon carbide (Hexoloy SA, Carborundum Co., Niagara, NY) were joined using the ARCjoinT technique at NASA Glenn Research Center [2-4]. Two plates of monolithic silicon carbide, approximately 4 mm thick, were cut into 25 mm-long by 30 mm-wide pieces. A carbonaceous mixture was applied to the ends of the plates that were to be joined and this was cured at 110-120°C for 10 to 20 minutes. Subsequently, a slurry of pure silicon powder was applied to the surface of the joint region and heated up to 1425°C for 5-10 minutes. Capillary forces drew the molten silicon into the joint region where it reacted with the carbon to form silicon carbide. The resulting joint material consisted of silicon carbide with controllable amounts of silicon and other phases as determined by the composition of the raw materials and infiltrant.

A limited number of joints between pieces of silicon carbide composite material were also fabricated. This composite was reinforced with Hi-Nicalon fibers (Nippon Carbon Co., Yokohama, Japan) that had been coated with a 1 μm -thick layer of carbon prior to matrix infiltration via chemical vapor infiltration. In addition, an approximately 2 μm -thick layer of silicon carbide was deposited on the outside of the composite to inhibit oxidation at high-temperatures.

Plates of monolithic silicon carbide (Hexoloy SA, Carborundum Co., Niagara, NY) were also joined using a reaction bonding technique. One or two layers of SiC and C powders held in tape form by organic binding agents were placed between two plates of monolithic silicon carbide that was cut into 25 mm-long by 30 mm-wide pieces. The plates were held in a proprietary fixturing and heating apparatus capable of rapid heating and cooling (Busek Co. Inc., Natick, MA). The specimens were heated to 1425°C for 10 to 30 minutes, under applied pressure ranging from 6.90 – 9.65 $\times 10^5$ Pa.

The plates that were joined using the methods described above were cut into bars that were 44 x 4 x 4 mm. The bars were cut so that the joint was at the middle of the bar and the plane of joining was aligned so that it was parallel to the applied load. Several of the bars were annealed for 100 h, at 1100°C, in a vacuum furnace or in flowing, gettered argon. Mechanical tests were performed by applying flexural loading by 1/4, four-point bending (Figure 1a) to the bars described above. This configuration subjects the specimens to a constant bending moment in the region between the two inner load points. This test, therefore, is a measure of the flexural strength of the joint. The other test uses asymmetrical four-point loading (Figure 1b). This test, as described by Unal [12], subjects the specimens to a constant, through-thickness shear stress in the middle of the specimen. This test, therefore, is a measure of the shear properties of the joint material. Flexural loading was obtained by applying a compressive force on the fixtures using a rigid, mechanical test frame.

Results

At room temperature, the maximum tensile stress obtained in flexural loading of composites and unreinforced SiC (monolithic) joined using the reaction forming method were similar (Figure 2). The room temperature strength of reaction-formed silicon carbide joints between Hexoloy SA silicon carbide has been reported as 255 ± 3.2 MPa, by researchers at the NASA Glen Research Center [2]. In this study a value of 53 MPa with a standard deviation of 6 MPa (3 specimens) was measured. Two specimens, from the same batch as used to obtain the data in Figure 2, were provided to an independent investigator

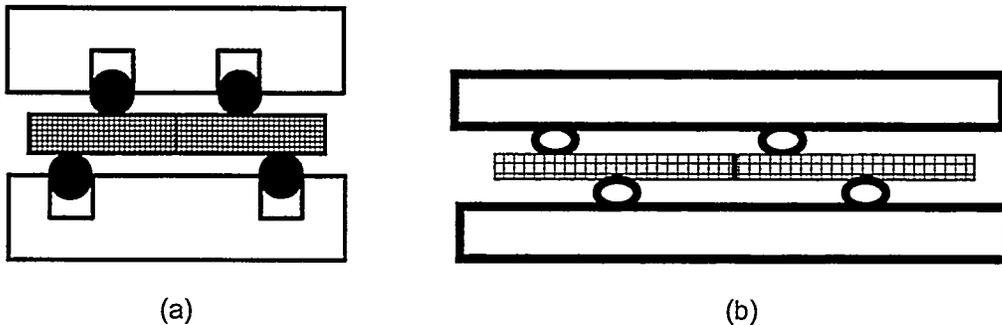


Figure 1. Schematic drawings of mechanical test configurations: (a) 1/4, four-point bending, and (b) asymmetric, four-point bending.

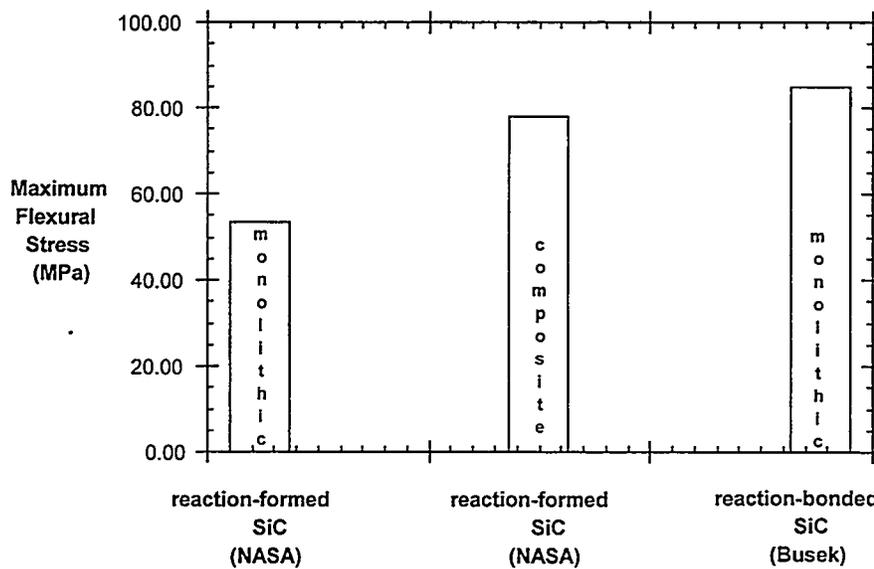


Figure 2. Comparison of room-temperature flexural strength

(Dr. O. Unal, Ames Laboratory, Ames, IA) who had earlier measured values similar to those that had been reported by investigators at NASA Glenn Research Center. These specimens exhibited 1/4, four-point flexural loading of 72 MPa and 122 MPa. These results indicate that although there may be some experimental error in the measurements made at PNNL, the material provided by NASA Glenn Research Center had a lower than average strength. The reasons for the lower than anticipated flexural stress values are not fully understood. The initial microstructural investigation [13], however, revealed that the untreated joints contained excess carbon and silicon that is indicative of an incomplete reaction. Therefore, it is likely that the joints were weaker than expected because the reaction to silicon carbide had not been completed.

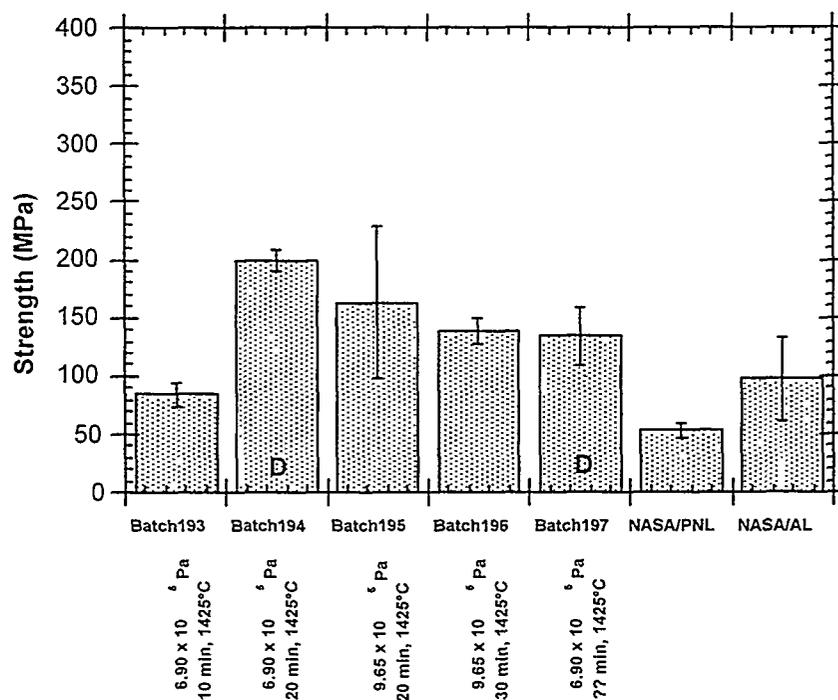


Figure 3. Room-temperature flexural strength of reaction bonded and reaction formed joints

Several batches of joints consisting of reaction bonded SiC were also tested in 1/4, four-point bending (Fig. 3). The processing temperature and applied pressure are indicated underneath the graph abscissa. Data for joints consisting of reaction formed SiC, labeled as "NASA", are also shown in Figure 3. The results obtained at PNNL and by Dr. Ozer Unal, at Ames Laboratory, are further identified by the designation "PNL" or "AL", respectively. There was no clear trend in the value of the joint strength and the processing conditions, although the joints that were formed by using a double layer of precursor tape (indicated by the symbol "D" in Figure 3) showed a slightly higher strength than those processed under identical conditions using only a single layer. The strength of the reaction bonded joints was slightly higher than that of the reaction formed joints, but it has already been mentioned that the reaction formed joints were from a batch with lower than average strength values.

To evaluate the effect of high temperature exposure on the properties of joints consisting of reaction bonded silicon carbide, the strength of specimens was measured at 1100°C (Figure 4). The specimen was held at 1100°C for 15-30 minutes, prior to testing, to allow the temperature to equilibrate. The strength of specimens measured at 1100°C was higher, 247 ± 85 MPa, than that measured at room temperature, 134 ± 25 MPa. In addition, specimens that were annealed at 1100°C for 100 h, in flowing gettered argon (<20 ppm O_2) had a strength of 212 ± 108 MPa. These results suggest that high temperature annealing improves the strength of the joints. Additional microscopy will be conducted to determine if microstructural changes are responsible for the improved strength after heat treatment. It was assumed earlier that the strength of reaction formed joints improved after heat treatment due

to additional reaction between free silicon and carbon. Due to the rapid processing times of the reaction

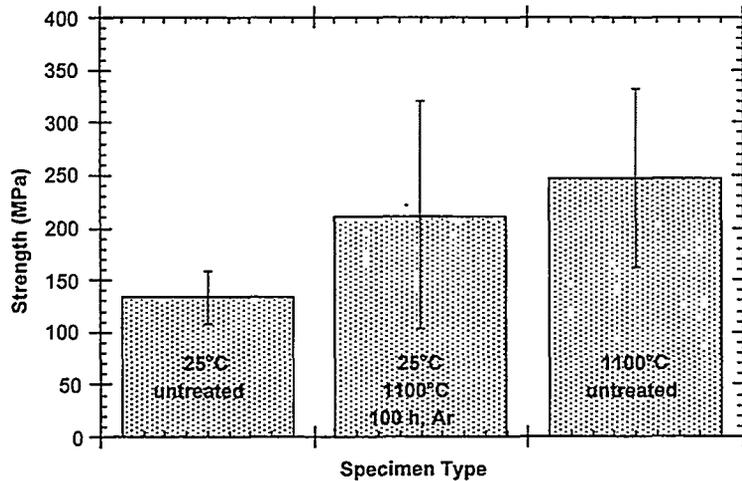
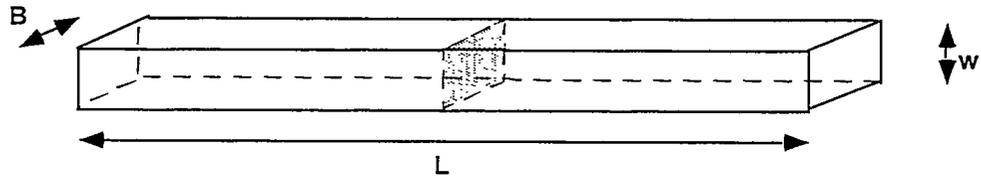


Figure 4. 1/4, four-point flexural strength of monolithic SiC joined by reaction bonded SiC, before and after heat treatment.

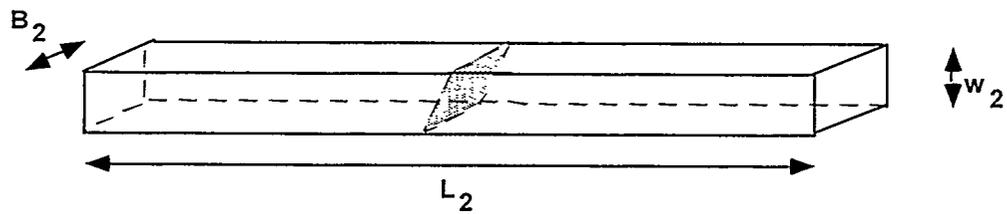
bonded joints a similar effect may have occurred. It is possible that deleterious residual stresses, remaining after processing, may be relieved during heat treatment, thus explaining the improved strength after heat treatment. Without further testing, it cannot be determined if there was also an increase in strength of the joints measured at 1100°C due to the temperature dependence of the material properties.

All of the strength results described above were obtained by using 1/4, four-point flexural loading. This test methodology subjects the test specimens to a constant bending moment between the inner loading points. The stress state of a joint within a reactor, however, will experience a generalized stress state. In addition, the stress state in the joint will be influenced by its geometry. To analyze the implications of these two issues, and to evaluate test methods for determine likely failure modes within realistic joints a plan to conduct analysis by the finite element method (FEM) of several joint geometries and test methods was made. The test configurations that will be evaluated are shown in Figure 5. The dimensions of the specimens that will be analyzed are given in Table I, and relevant material property values are given in Table II.

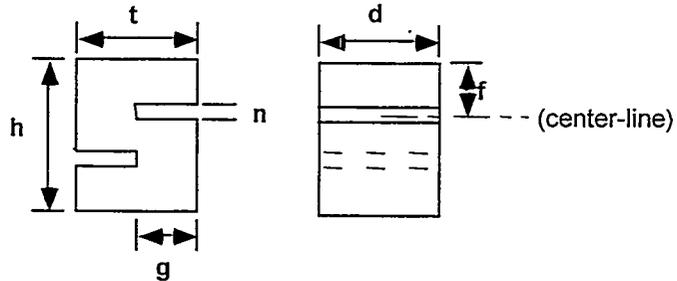
Butt-joined flexural test specimen



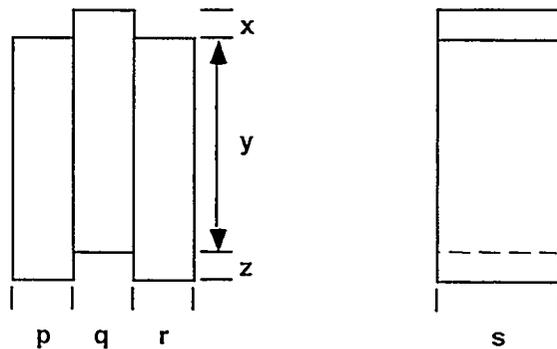
45° Butt-joined flexural test specimen



Double-notch-shear specimen



Offset sandwich specimen



not drawn to scale.

Figure 5. Test specimen geometries to be analyzed by FEM.

Table I
Physical Dimensions (in mm) of Specimens to be Analyzed by FEM

Butt-joined flexural test specimen	Size 1	Size 2
B	4.00	2
w	3.00	1.5
L	50.00	30.00
45° Butt-joined flexural test specimen		
B ₂	4.00	2
w ₂	3.00	1.55
L ₂	50.00	25.00
Double-notch shear specimen		
t	8.00	4.00
d	15.00	7.5
h	30.00	15.00
f	11.5	5.75
n	0.50	0.25
g	4.00	2.00
Offset sandwich specimen		
p	3.00	1.50
q	3.00	1.50
r	3.00	1.50
s	10.8	5.0
x	4.00	2.00
y	12.4	6.00
z	4.00	2.00

TABLE II
Material Property Values for FEM Modeling

	Monolithic SiC (SA)	SiC _f /SiC _m	Joint (RB SiC)
Young's Modulus (GPa)	408 ^M	300 ^H	393 ^C
Poisson's Ratio	0.14 ^M	0.3 ^H	0.19 ^C
Coefficient of Thermal Expansion (10 ⁻⁶ °C ⁻¹)	5.8 (25 – 1 000°C) ^K	3.0 ^H	4.3 (25 – 1 000°C) ^C
Thermal Conductivity (W/m·K)	125.6 ^S	10 ^Y	125 ^C

M= McHenry & Tressler, J. Am. Ceram. Soc., vol. 63[3-4], pp.152-156 (1980).

K = Kern et al., Mat. Res. Bull., vol. 4, pp. S25 – S32 (1969).

C = "Materials Properties Standard 2000, Coors Ceramics Company, Golden, Colorado, 1999.

H = K. Kageyama, and I. Kimpara, Key Engineering Materials, vols. 164-165, pp. 127-132 (1999).

Y = Youngblood et al. Fusion Materials semiannual report.

S = "Physical Properties of Hexoloy® SA Silicon Carbide"
(<http://www.carbo.com/hexoloy/properties/index.html>), Carborundum Corporation, Niagara Falls, NY.

CONCLUSIONS

Preliminary studies have shown that joints between silicon carbide and silicon carbide composites can be fabricated by both reaction forming and reaction bonding methods. Both methods result in similar flexural strength values measured by 1/4, four-point bending. The specimens joined by reaction formed silicon carbide had lower than average strength values, probably due to insufficient reaction time during processing. Efforts to analyze the stress state in practical joints and joint test methodologies via finite element analysis have begun.

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