

**POLYMER DERIVED SiC MATERIALS FOR JOINING SILICON CARBIDE COMPOSITES FOR FUSION ENERGY** - C. A. Lewinsohn and R. H. Jones (Pacific Northwest National Laboratory\*), T. Nozawa, M. Kotani, Y. Katoh and A. Kohyama (Institute of Advanced Energy, Kyoto University)

## **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 [1]. The objective of this work is to evaluate the thermal stability and mechanical properties of silicon carbide joints fabricated via preceramic polymer precursor pyrolysis.

## **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. Recently families of polymers that yield inorganic materials subsequent to pyrolysis have been a subject of extensive international research [2-9]. One such polymer, allyl-hydridopolycarbosilane (aHPCS), has been shown to have good high temperature mechanical properties as well as requiring a relatively low temperature for pyrolysis [5]. In this study the mechanical properties of joints fabricated by aHPCS were measured. Preliminary results indicate that the strength value of the aHPCS joints are slightly lower than those of reaction-based methods.

## **PROGRESS AND STATUS**

### Introduction

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 [10-13], and preceramic polymer adhesives [2-9]. In this report, preliminary results obtained from joints formed by a preceramic polymer adhesive will be presented. These results were obtained during collaborative work by Dr. Lewinsohn during a one month stay at the Institute of Advanced Energy, Kyoto University (June 15 – July 11, 2000). Plans for additional study of joining and joint testing techniques were also made and are summarized in Tables I and II (experiments already conducted are underlined).

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Table I  
Summary of Required Number of Test Specimens

Joint Material Substrate	CREST-PP		CREST-RB		Torino-CA		Starfire
	CVD-SiC	CVI SiC <sub>f</sub> /SiC <sub>m</sub>	CVD-SiC	CVI SiC <sub>f</sub> /SiC <sub>m</sub>	CVD-SiC	CVI SiC <sub>f</sub> /SiC <sub>m</sub>	CVD-SiC
F1	5	5	5	5	5	5	5
A1		5		5		5	
F2		15		15		15	5
A2		15		15		15	
D							10

Table II  
Matrix of Mechanical Test Conditions and Required Number of Specimens

Joint Material		CREST-PP		CREST-RB		Torino-CA		Starfire
Substrate		CVD-SiC	CVI SiC <sub>f</sub> /SiC <sub>m</sub>	CVD-SiC	CVI SiC <sub>f</sub> /SiC <sub>m</sub>	CVD-SiC	CVI SiC <sub>f</sub> /SiC <sub>m</sub>	CVD-SiC
Test	Treatment							
F1	N	5	5	5	5	5	5	3
A1	N		5		5		5	
F2	N		5		5		5	5
A2	N		5		5		5	
D	N		5					5
D	A							5
F1	A							3
F2	A		5		5		5	
A2	A		5		5		5	
F2	B		5		5		5	
A2	B		5		5		5	

Legend:

CREST-PP: Joint material derived from pre-ceramic polymer.

CREST-RB: Joint material consisting of reaction-bonded silicon carbide.

Torino-CA: Joint material consisting of calcium-aluminosilicate glass.

Starfire: Joint material derived from allyl-hydroxypolycarbosilane preceramic polymer.

F1 = 1/4, four-point bend test. 2 x 3 x 50 mm specimen.

F2 = 1/4, four point bend test. 2 x 2 x 25 mm specimen.

A1 = asymmetric four-point bend test. 2 x 2 x 50 mm specimen.

A2 = asymmetric four-point bend test. 2 x 2 x 25 mm specimen.

D = double notch shear test. 8 x 15 x 30 mm specimen.

N = no heat treatment.

A = 1373 K, 100 h, argon.

B = 1373 K, ten 10 h cycles, vacuum.

## Experimental Technique

### Task I – specimen preparation

To evaluate the suitability of joints formed by aHPCS, butt-joined, flexural specimens for four point bend testing [14] were fabricated from plates of monolithic, chemically vapor deposited (CVD) silicon carbide (Morton Advanced Materials, Woburn, MA) were joined by Starfire Systems, Inc. (Watervliet, NY), developers of the aHPCS polymer. Two plates of CVD silicon carbide, approximately 4 mm thick, were cut into 25 mm-long by 30 mm-wide pieces. The polymer was applied to the 30 x 4 mm faces and held in a special fixture. The material was cured and pyrolysed by Starfire Systems, Inc.. The pyrolysis temperature was 1000C. The joined materials were sent to Chand Inc. (Worcester, MA), for additional machining into mechanical test specimens.

IAE, Kyoto University procured  $\text{SiC}_f/\text{SiC}_m$  composite, fabricated by a preceramic polymer impregnation method (PIP). Initial steps to join the  $\text{SiC}_f/\text{SiC}_m$  composite with a preceramic precursor, polyvinylsilane (PVS), were made by researchers at IAE. In addition, the  $\text{SiC}_f/\text{SiC}_m$  composite will be joined, at IAE, using two other techniques: reaction sintering of silicon carbide and the use of glass ceramic materials. Mechanical test specimens will be fabricated from these materials.

### Task II – mechanical testing

The details of the experimental program were coordinated during Dr. Lewinsohn's visit to IAE. Specimens, with dimensions of 2 x 2 x 50 mm, of all joint compositions will be tested in 1/4, four point bending at room temperature to establish baseline properties. Specimens of this dimension, with  $\text{SiC}_f/\text{SiC}_m$  composite substrates only, will also be tested in asymmetric four point bending. Subsequently, the suitability of using smaller test specimens will be evaluated using  $\text{SiC}_f/\text{SiC}_m$  specimens with dimensions of 2 x 2 x 25 mm. The number and type of each specimen that will be tested are shown in Table I and II. Underlined numbers represent experiments that were performed during Dr. Lewinsohn's visit to IAE.

The high-temperature durability of joining materials will be evaluated by heat treating various specimens at 1373 K for 100 hours. The number and type of specimens that will be heat treated is shown in Table II. Numbers in bold type indicate specimens that were heat treated during the visit of Dr. Lewinsohn to IAE. The effect of thermal cycling on joint materials will be evaluated by testing materials after cycling the materials between 298 and 1373 K ten times. The number and type of specimens that will be subject to the thermal cycling treatment is shown in Table II.

## Results

The flexural strength of specimens joined with aHPCS by Starfire Systems, Inc. was tested at room temperature, before and after heat treatment at 1373 K, in argon, for 100 h. Prior to heat treatment, the value of the flexural strength was 85 MPa with a standard deviation of 11 MPa (Fig. 1). Subsequent to heat treatment the value of the flexural strength was 79 MPa with a standard deviation of 21 MPa (Fig. 2). Therefore, it appears as if the strength of the joint material was unaffected by the heat treatment that was performed. In contrast, as reported in the prior semi-annual report [14], the strength of joints made from a reaction-based silicon carbide increased from  $134 \pm 25$  MPa to  $212 \pm 108$  MPa after an identical heat treatment.

The room temperature strength of reaction-formed silicon carbide joints between Hexoloy SA silicon carbide has been reported as  $255 \pm 3.2$  MPa, by researchers at the NASA Glenn Research Center [11]. Materials fabricated at NASA Glenn were provided to PNNL and a flexural strength of 53 MPa with a standard deviation of 6 MPa (3 specimens) was measured, as reported in the prior semi-annual report [14]. Two specimens, from the same batch of materials supplied by NASA Glenn, were provided to an independent investigator (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 [14]. 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 expected strength. Additionally, the value of the strength of the joints made from the aHPCS material were in the same range as the joints made from reaction-based and reaction-formed SiC materials (Fig. 1). It must be noted that the aHPCS joints were between CVD SiC material, whereas the other joints were between sintered  $\alpha$ -SiC. Furthermore, Starfire systems claims that aHPCS containing nano-sized SiC filler material exhibits a higher strength than pure aHPCS derived material.

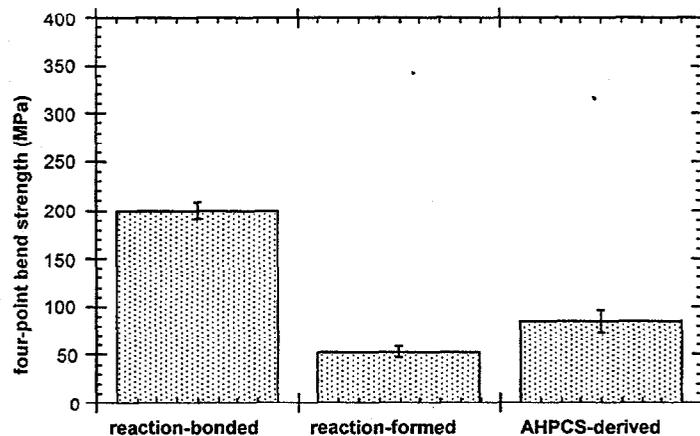


Figure 1. A comparison of strength values for joints tested at room temperature.

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were used to investigate the fracture surfaces of specimens joined by aHPCS. In all samples, both fracture surfaces were covered by aHPCS material (as determined from the presence of oxygen detected by EDX analysis) indicating that failure occurred in the aHPCS layer and not at the interfaces between the aHPCS and the SiC. In the untreated specimens there were some areas that were not covered by aHPCS. These areas appeared as continuous channels and were likely due to the evolution of gas during pyrolysis.

The failure origin was located at a corner of the fracture surface of each specimen joined by aHPCS. Although this means that the true strength of the joint was not obtained (due to the stress intensification by the corners and free surfaces), this also indicates that there were no large strength limiting defects in the microstructure. The entire surface of the aHPCS material contained cracks (Fig. 3), but the crack opening in the area around the failure origin was greater than that observed at other locations on the fracture surface (Fig. 4). The cracks

were likely due to shrinkage during curing and pyrolysis. It could not be determined whether the cracks were the cause of failure, or caused by it. Either hypothesis can be justified, but since the regions of larger crack opening were located at the corners, rather than along an entire surface, it is more likely that the fracture was initially more tortuous and then became

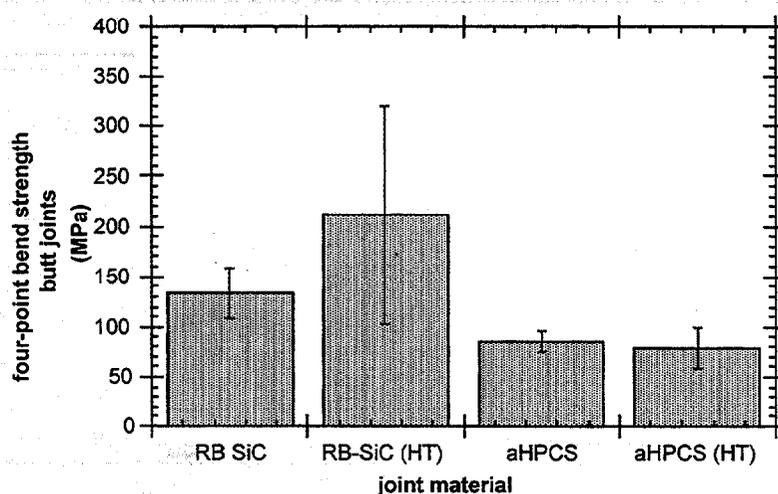


Figure 2. A comparison of the strength, before and after heat treatment at 1373 K for 100 h, of sintered SiC (Hexalloy™, Carborundum Co.) joined by reaction-bonded SiC (Busek, Inc.) with CVD SiC (Morton Advanced Materials, Inc.) joined by aHPCS derived SiC.

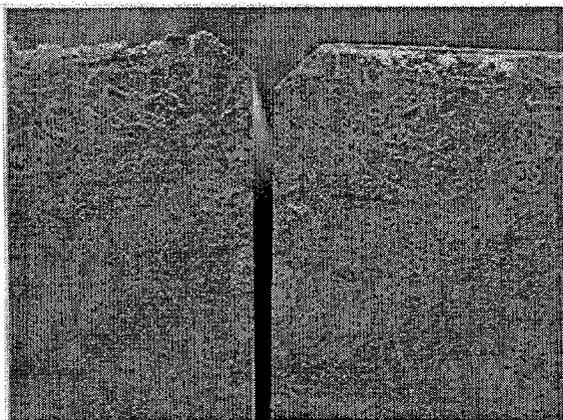


Figure 3. A micrograph (50 x) of the matching surfaces of a typical fractured specimen joined by aHPCS derived material.

more planar as the crack velocity increased. If an entire side of the specimen had contained cracks with a larger opening than the rest of the specimen this may have been due to asymmetrical heat loss or transport of product gases during pyrolysis.

### Conclusions

Initial studies have shown that joints between silicon carbide can be fabricated from preceramic polymer precursors. The strength of joints made from aHPCS were within the range of values obtained for joints made from reaction based methods. Preliminary results

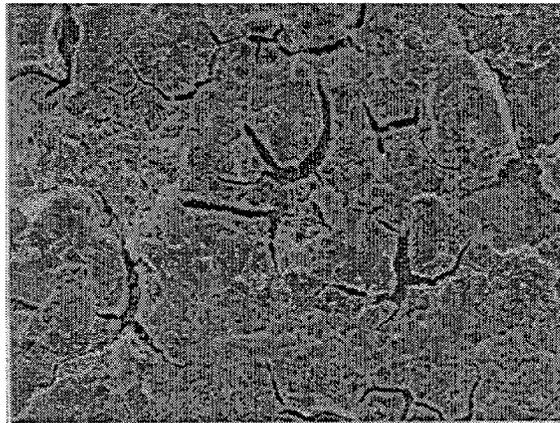


Figure 4. Higher magnification (500 x) view of a typical fracture surface showing cracks in aHPCS material.

indicate that failure occurs in the aHPCS layer and that the bonding between the aHPCS and SiC is relatively strong.

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