EFFECT OF HEAT TREATMENT ON SILICON CARBIDE BASED JOINING MATERIALS FOR FUSION ENERGY - C. A. Lewinsohn and R. H. Jones (Pacific Northwest National Laboratory)*, T. Nozawa, M. Kotani, H. Kishimoto, Y. Katoh and A. Kohyama (Kyoto University, Japan).

OBJECTIVE

Reliable and practical joining techniques are required to enable the use of silicon carbide composites (SiC/SiC) in fusion energy systems. Based on criteria relevant to fusion applications, silicon carbide (SiC) has been selected as a promising joint material [1]. The objective of this work is to evaluate the thermal stability and mechanical properties of joints consisting of silicon carbide based materials between silicon carbide substrates.

SUMMARY

Two general approaches to obtaining silicon carbide-based joint materials were used. The first method relies on reactions between silicon and carbon to form silicon carbide, or to bond silicon carbide powders together. The second method consists of pyrolysing a polycarbosilane polymer to yield an amorphous, covalently bonded material. In order to assess the long-term durability of the joint materials, various heat treatments were performed and the effects on the mechanical properties of the joints were measured. Although the joints derived from the polycarbosilane polymer were not the strongest, the value of strength measured was not affected by heat treatment. On the other hand, the value of the strength of the reaction-based joints was affected by heat treatment, indicating the presence of residual stresses or unreacted material subsequent to processing. Further investigation of reaction-based joining should consist of detailed microscopic studies; however, continued study of joints derived from polymers is also warranted.

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 [2-5], and preceramic polymer adhesives [6-13]. In this report, recent results regarding the effect of heat treatment on both types of joint will be presented. The results will be incorporated with earlier ones, for completeness.

Experimental Technique

Based upon recent promising reports [9], allyl-hydridopolycarbosilane (aHPCS) was selected as a polymeric precursor to obtain SiC based joints. To evaluate the suitability of joints formed by aHPCS, butt-joined, flexural specimens for four point bend testing were fabricated from plates of monolithic, chemically vapor deposited (CVD) silicon carbide (Morton

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Advanced Materials, Woburn, MA) and 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 850˚C. The joined materials were sent to Chand Inc. (Worcester, MA), for additional machining into mechanical test specimens.

Plates of monolithic silicon carbide (Hexoloy SA, Carborundum Co., Niagara, NY) were joined using the ARCjoinT technique at NASA Glenn Research Center [3-5]. 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. Since all of the silicon carbide in the resulting material is formed by reaction of the liquid silicon with the carbonaceous preform, this method will be referred to as reaction forming (RF).

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., Tokyo, 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 x 10^5 Pa. In this process existing silicon carbide powders are bonded to each other by silicon carbide formed by reaction of the liquid silicon with the carbon powders. Therefore, this latter technique is referred to as reaction bonding (RB). Both latter methods, however, fall into the general class referred to as reaction based.

The plates that were joined using the methods described above were cut into bars that were approximately 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 heat treated for 100 h, at 1100°C, in a vacuum furnace or in flowing, gettered argon. Some bars were heat treated, in a cyclic manner, between 200˚ and 1100˚C, for 10 cycles. The bars were heated and cooled at 20˚C/min, in vacuum or flowing argon, and held at 1100˚C for 10 h. Other bars were heat treated, in vacuum, in a cyclic manner between 250˚ and 1100˚ C. The specimens were heated at 425˚C/min and held at 1100˚C for 15 min and cooled at a rate of approximately 142˚C/min. Twenty-five cycles were performed.

Mechanical tests were performed by four-point loading of 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. Other tests were performed using asymmetrical four-point loading. This test, as described by Unal [14], 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

The room temperature strength values of all the materials have been reported earlier [15,16]. The values of strength measured varied from 50 – 200 MPa (see Table I). The strength of heat treated specimens, normalised by the average strength value of untreated specimens, is shown in Figure 1. From the data, it is seen that the effect of the 100 h heat treatment, at 1100°C, in argon, on the value of the strength of the joints derived from aHPCS was small. On the other hand, the value of the strength of joints made from reaction-bonded material increased, and that of reaction formed material decreased. These latter results indicate that either residual stresses were present in the specimens tested at room temperature, or microstructural development occurred during the heat treatments. Since the strength of reaction-bonded material was higher when measured at 1100˚C [15], it is likely that some of the increased strength may be due to the relief of residual stress. Detailed microscopic investigations are required to determine the precise mechanisms for the observed behavior.

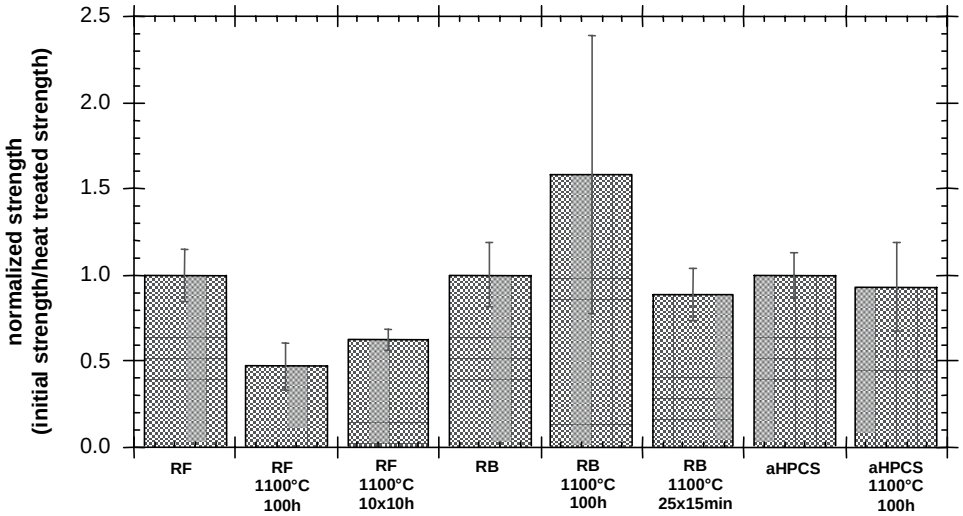

Figure 1. A comparison of room temperature strength after heat treatment, normalised by the strength, for reaction formed (RF), reaction bonded (RB), and polymer derived (aHPCS) joints.

Although the strength values for joints derived from aHPCS were not strongly affected by heat treatment, there is concern that the amorphous nanostructure of these materials is not stable under irradiation. Microcracking was observed on the fracture surfaces of tested specimens. It is well known that silicon carbide based fibers, derived from preceramic polymer materials, undergo shrinkage during irradiation. The material, however, can be processed at relatively low temperatures, which minimizes the potential for degradation of the fibers in composites. Reaction-based joining, however, requires processing above the melting temperature of the particular silicon alloy chosen. Pure silicon melts at 1410˚C. In

addition, the influence of excess silicon, prevalent in all reaction-based SiC materials, during irradiation is unknown. Therefore, joints derived from polymer materials deserve further study.

Table I Experimental Results

Joint Material	Substrate	Treatment	Test Method*	Average Strength (MPa)	Std. Deviation (MPa)
Reaction-formed SiC	Sintered SiC	untreated	4PBS	53.4	6.0
Reaction-formed SiC	SiC_f/SiC_m	untreated	4PBS	78.0	8.0
Reaction-formed SiC	SiC_f/SiC_m	untreated	AFPB	32.0	4.9
Reaction-formed SiC	SiC_f/SiC_m	1100˚C,100 h, inert gas	AFPB	15.0	4.4
Reaction-formed SiC	SiC_f/SiC_m	RT-1100˚C, 10 x, 10 h hold	AFPB	20.0	1.9
Reaction-bonded#	Sintered SiC	untreated	4PBS	134	25.4
Reaction-bonded#	Sintered SiC	untreated, tested at 1100˚C, air	4PBS	247	85
Reaction-bonded#	Sintered SiC	1100˚C,100 h, inert gas	4PBS	212	108
Reaction-bonded#	Sintered SiC	250-1100˚C, 25 x, 15 min hold	4PBS	119	20
aHPCS	CVD SiC	untreated	4PBS	85.0	11.0
aHPCS	CVD SiC	1100˚C,100 h, inert gas	4PBS	79.0	21.0

All tests conducted at room temperature, unless otherwise noted.
*4PBS = 1/4, four-point bend strength; AFPB = asymmetric four point bend strength.
derived from the tape cast material.

Conclusions

The effects of heat treatments on the strength of silicon carbide-based joints obtained from two general methods were investigated. The strength of joints derived from a polymer precursor were unaffected by heat treatment. On the other hand, heat treatment degraded the strength of reaction formed joints and enhanced that of reaction bonded joints. Polymer derived joints can be fabricated at temperatures that are not expected to degrade the properties of SiC/SiC, yet issues of microcracking must be addressed. On the other hand, reaction-based joining is also an attractive method, but the effect of irradiation on residual silicon must be investigated.

FUTURE WORK

Efforts will be made to optimize processing conditions used for obtaining joints via polymer based methods, such that bending strengths greater than 150 MPa will be obtained. Furthermore, attempts will be made to obtain specimens of reaction-based material with controlled amounts of excess silicon, in order to study the effect of residual silicon on

mechanical properties. In addition, efforts will be made to measure the strength of promising joint materials at elevated temperatures.

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