

# Coatings and joining for SiC and SiC-composites for nuclear energy systems

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## Abstract

Coatings and joining materials for SiC and SiC-based composites for nuclear energy systems are being developed using preceramic polymers filled with reactive and inert powders, and using solid-state reactions. Polymer-filled joints and coatings start with a poly(hydridomethylsiloxane) precursor, such that mixtures of Al/Al<sub>2</sub>O<sub>3</sub>/polymer form a hard oxide coating, coatings made with Al/SiC mixtures form a mixed oxide–carbide coating, while coatings made with SiC/polymer form a porous, hard carbide coating. Joints made from such mixtures have shear strengths range from 15 to 50 MPa depending on the applied pressure and joint composition. The strongest joints were obtained using tape cast ribbons of Si/TiC powders such that a solid state displacement reaction at 1473 K and 1673 K using 30 MPa applied pressure resulted in shear strengths of 50 MPa, which exceeds the shear strength of SiC/SiC composite materials. However, the polymer joints are much easier to apply and could be considered for field repair.

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## 1. Introduction

It is widely considered to be a weakness of SiC-based composites that they are not fully dense and can, as yet, only be fabricated into simple shapes that require development of attachment technologies in order to achieve more complex configurations. The implication of the lack of full density is that external coatings are required, both for hermeticity considerations [1] and for corrosion protection

of the fine-grained SiC fibers and of the fiber–matrix interphase material [2]. Further, joining of simple shapes into more complex structures is also apparently required, particularly for fusion reactor first-wall vessels that cannot possibly be made as a single section [3]. Thus, a significant effort has gone into development and understanding of protective coatings and joining for SiC/SiC composites [1,2,4–12]. The Nano-powder infiltration and transient eutectoid (NITE) process, however, produces a SiC/SiC composite material with high density, low permeability, and has been used to demonstrate high-performance hot-pressed joining [13–15]. The purpose of this study is to help develop a wider range of

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coating and joining technologies for fusion. There is no single technology that can be applied uniformly as either a coating or joining technology for SiC/SiC composites and a diverse set of technologies may be advantageous at this stage of our efforts in design of fusion power plants. However, a diverse set already exists in the form of preceramic polymers, reaction bonding, glass–ceramic seals, and brazing methods [3]. In this paper we present additional coating and joining methods and technologies that have advantages, as well as disadvantages, compared to previously developed methods.

## 2. Coating and joining methods

### 2.1. Polysiloxane preceramic polymers

Preceramic polymers, such as polycarbosilanes and polysiloxanes, with inert and reactive fillers are used for SiC/SiC joining technologies [7,16–18] and have performed adequately as strong joints. Polycarbosilane, which converts to SiC, requires high-temperature processing and inert handling, while polysiloxanes, which convert to Si–O–C, can be pyrolyzed at lower temperatures and can be handled in air. Joints made from such materials exhibit strengths that range from 5 to 30 MPa when tested in shear. A known difficulty with preceramic polymers is the mass loss, which can exceed 50%, on conversion to a ceramic phase. A slightly different approach uses a linear chain of polyhydrido-methylsiloxane (PHMS) as a precursor to a highly crosslinked polysiloxane, by applying a catalytic chemistry approach developed at SRI International, that has the advantage of much lower mass loss on ceramic conversion compared to other systems [19–23] and pyrolysis occurs at temperatures as low as 873 K.

PHMS, which is a low molecular weight low viscosity liquid, is catalytically cured in-situ after its application and converts on heating in inert environments to a silicon oxycarbide phase but can be modified by side group additions to produce a more carbon-rich oxycarbide phase [23]. For the work here, however, PHMS with no side group additions is used and filled with SiC, Al, and Al<sub>2</sub>O<sub>3</sub> powders, singly and in combination. The SiC powders are 0.7 μm average diameter pure SiC, the Al powders were in the form of flakes 1–2 μm in size, and the Al<sub>2</sub>O<sub>3</sub> powders were submicron diameter. Powder loadings were in the range of 40–60% by volume and were processed in the form of liquid slurries

with approximate viscosities of less than 10 cP using cyclohexane as a solvent.

Joining was accomplished by slurry application using a dropper with a nominal weight applied during curing at 423 K in moist air. This was followed by pyrolysis with a nominal pressure of about 1 MPa in air at 1473 K. One joint was also processed at 1073 K in nitrogen without any applied pressure. Coatings were also synthesized using the same slurries by dip coating onto SiC/SiC composite coupons, as well as on 316 stainless steel coupons. Coatings were pyrolyzed at 1473 K for SiC/SiC and at 1073 K for the 316 steel. Joint strengths were tested in single-lap shear geometry at ambient temperature. Some of the coated steel coupons were exposed up to 1000 h at 1073 K in air to determine coating integrity and oxidation protection. Coated coupons were sectioned and examined using an SEM for microstructural information. Both Hexaloy SiC and SiC/SiC coupons were joined and tested in this study.

### 2.2. Solid-state displacement reactions

Previous research at PNNL on solid-state displacement reactions demonstrated that the reaction between TiC and Si produced an interwoven structure of Ti<sub>3</sub>SiC<sub>2</sub>, TiSi<sub>2</sub>, and SiC, with the majority phases being the ternary Ti<sub>3</sub>SiC<sub>2</sub> and SiC [24–27]. This reaction was used to make joints from tape cast powder mixtures of TiC and Si powders, which were 99.99% purity having average diameters less than 45 μm with a TiC:Si ratio of 3:2. Tapes were about 200 μm thick and were cut to shape and applied between either Hexaloy SiC coupons or CVI SiC composite coupons.<sup>1</sup> Joints were formed by heating in argon to 573 K at 5 K/min and holding for 2 h for binder burnout with a nominal applied pressure followed by heating to 1473 K or 1673 K at 10 K/min and holding for 1 h at 30 MPa applied pressure. Joints were tested in shear using a double-notch shear and sectioned for SEM examination.

## 3. Results and discussion

### 3.1. Joining

Polymer slurry joints between Hexaloy SiC coupons made with PHMS filled with SiC, Al/SiC,

<sup>1</sup> Hi-Nicalon Type-S fibers from GE Power Systems with a 2D 5-harness satin weave architecture.

and Al/Al<sub>2</sub>O<sub>3</sub> at 1473 K using 1 MPa applied pressure exhibited reasonable strengths in single-lap shear testing at ambient temperatures of 21 MPa, 14.5 MPa, and 7 MPa, respectively, as shown in Fig. 1. SEM micrographs of a SiC-filled PHMS Hexaloy joint processed at 1473 K in air is shown in Fig. 2. These joints possess reasonable shear strength values and are thin and dense after only 1 MPa applied pressure. Compared to similar joints prepared by others, these have the distinction of being slightly stronger and easier to process. Polycarbosilane requires inert handling and higher conversion temperatures; however, it does convert to SiC whereas this polymer converts to a silicon oxy-carbide, which may be a disadvantage in terms of

creep strength and corrosion resistance depending on the structure and amount of free carbon [28,29]. The low strength of the joint processed at 1073 K in nitrogen suggests that a small amount of pressure and higher temperatures are required for adequate bonding.

The solid-state reaction joints for Hexaloy SiC between TiC and Si resulted in high strength joints,

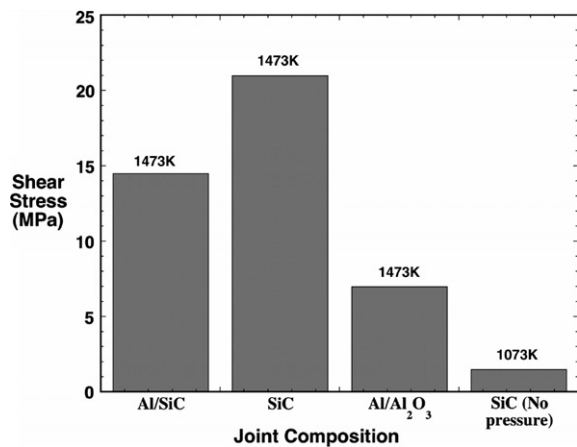


Fig. 1. Single-lap shear strength of PHMS joints between Hexaloy SiC coupons processed in air at 1473 K using 1 MPa pressure or in nitrogen with no applied pressure at 1073 K.

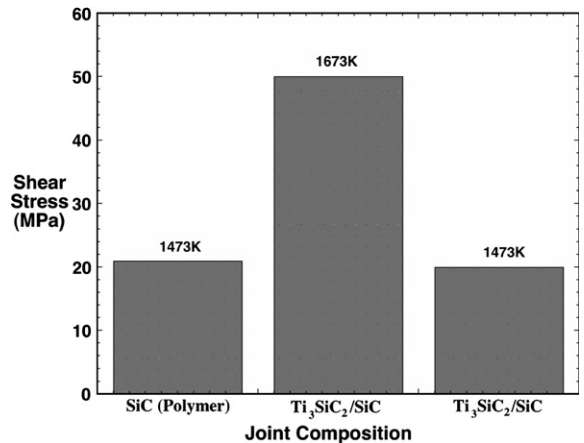


Fig. 3. Comparisons of joint shear strengths for SiC-filled PHMS (single-lap) with solid-state reaction joints of TiC + Si to form Ti<sub>3</sub>SiC<sub>2</sub>/SiC joints (double-notch). Solid-state reaction joints are significantly stronger when processed at high temperatures and 30 MPa applied pressure.

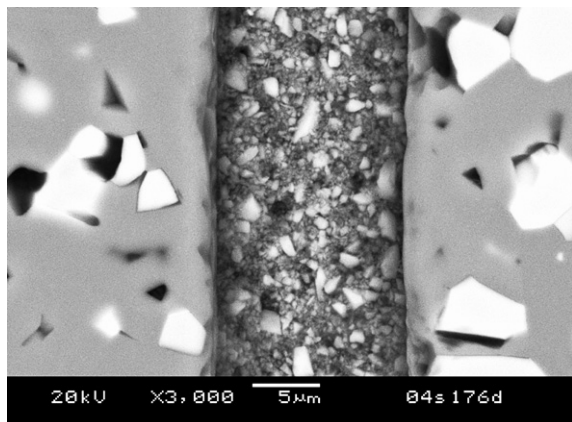


Fig. 2. SiC-filled PHMS joints in polished cross-sections showing clean joint/coupon interfaces and good joint densities for Hexaloy SiC coupons.

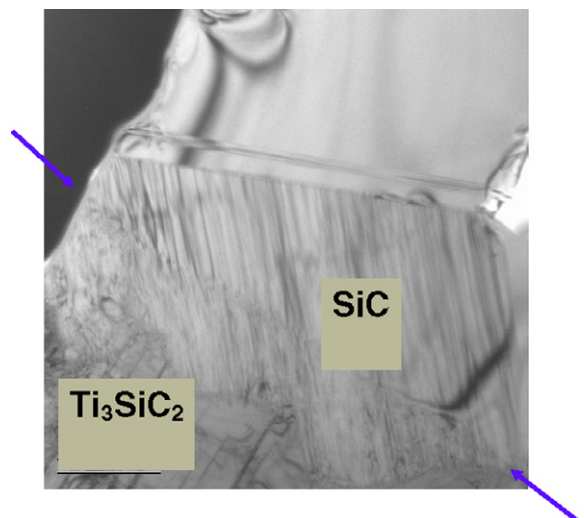


Fig. 4. TEM micrograph of joint region of Hexaloy coupon using the TiC–Si solid-state joining method. The original SiC surface is marked with the arrows and epitaxy is observed across this interface into the Ti<sub>3</sub>SiC<sub>2</sub>/SiC joint region.

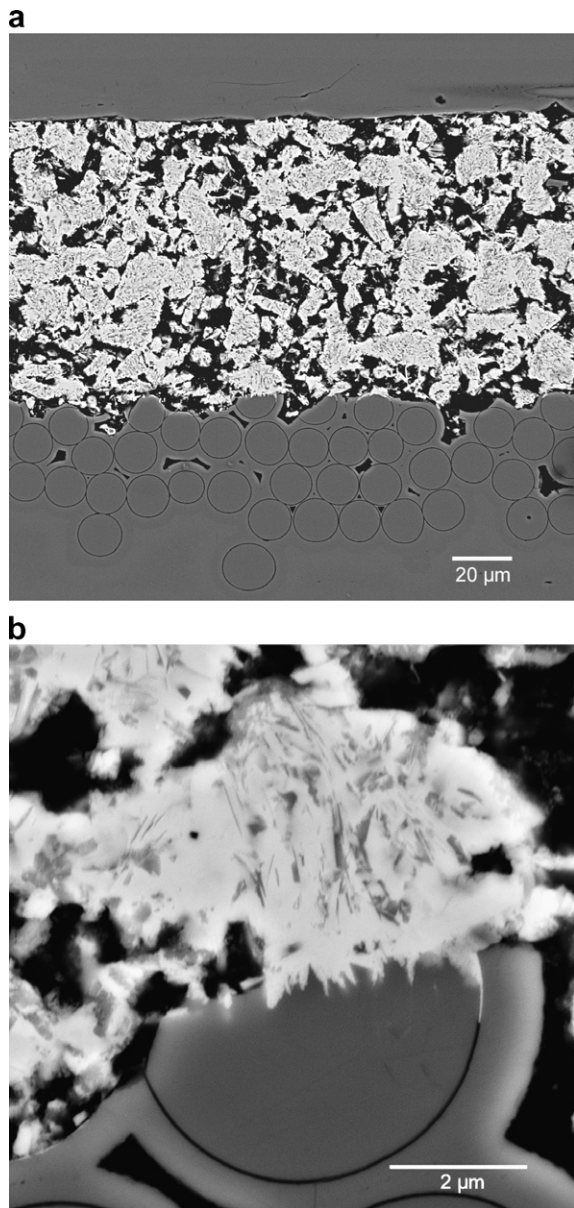


Fig. 5. SEM micrographs of polished cross-sections of TiC–Si solid-state joining of SiC/SiC composite coupons. This joint is not fully dense but exhibits strong bonding at the interface.

with shear strengths<sup>2</sup> in excess of 50 MPa, as shown in Fig. 3. Almost more importantly, this shear fracture was observed to include some of the Hexaloy SiC and was not restricted to the joint material indi-

<sup>2</sup> Since the double-notch shear test involves some measure of stress concentration at the notches, it is reasonable to expect that these measure values for the solid-state joints are an underestimate of the actual strength.

cating very strong bonding. The reason for such strong bonding is that the SiC formed during the solid-state reaction between TiC and Si preferentially forms at the existing SiC interface, either the Hexaloy or SiC/SiC composite. This reaction formed SiC is epitaxial with the Hexaloy SiC as shown in Fig. 4. A further consideration is that  $Ti_3SiC_2$  and SiC are reduced-activation materials and there is some evidence of pseudoplasticity in the  $Ti_3SiC_2$  phase that might give these joints a measure of fracture resistance that a pure SiC joint would lack. The SEM micrograph of a solid-state TiC–Si joint between SiC/SiC coupons (Hi-Nicalon Type-S fibers) is shown in Fig. 5. Apparent strong bonding at the joint–coupon interface can be seen in this micrograph although the joint does not appear to be fully dense.

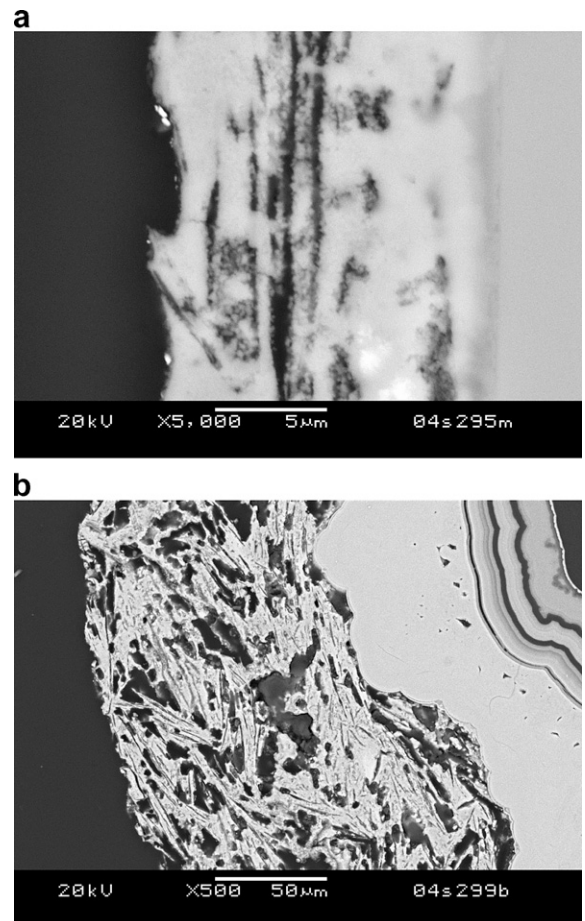


Fig. 6. PHMS-based coatings pyrolyzed at 1073 K in air for 2 h on various materials including (a) Al/Al<sub>2</sub>O<sub>3</sub> coatings on SiC/SiC and (b) Al/SiC on SiC/SiC.



### 3.2. Coating microstructures

Polymer coatings are made with the same simple processing as for the polymer joints. The liquid slurry is prepared and the coating is applied using dip-coating techniques. Pyrolysis is carried out in air, nitrogen, or argon at 973–1473 K depending on the substrate. Fig. 6 shows coatings in polished cross-sections after pyrolysis on SiC/SiC coupons. The coatings have varying degrees of porosities that are due in part to the mass loss during pyrolysis. The Al/Al<sub>2</sub>O<sub>3</sub> coating is fairly dense but the Al/SiC coating is porous. Although such coatings have yet to be studied under fusion relevant conditions it is apparent that simple processing using PHMS filled with ceramic particles can be used to synthesize protective coatings for SiC/SiC composites. These coatings are compliant and slightly porous but are strongly bonded to the ceramic surface and can act as thermal barriers. The processing is extremely simple and robust.

### 4. Conclusions

New developments in preceramic polymers have been introduced to show that simple joints and coatings may be produced using simple materials and processing. Since fusion engineering is in its infancy and no single coating or joining technology is the clear favorite at this point, new technologies should continue to be developed to allow as much diversity in synthesis and processing as possible. This will ensure that many choices are available as required to meet the needs of fusion projects, such as test blanket modules or future uses of SiC-based materials. Solid-state joints appear to be very strong and, in comparison to reaction bonded joints, may have an advantage of reduced glassy phases or residual Si.

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