

COATINGS AND JOINING FOR SiC/SiC COMPOSITES FOR NUCLEAR ENERGY SYSTEMS—C. H. Henager, Jr., and Y. Shin (Pacific Northwest National Laboratory^{*}), Y. Blum (SRI), L. A. Giannuzzi (FEI Company), and S. M. Schwarz (University of Central Florida and NanoSpective, Inc.)

OBJECTIVE

It is widely considered a weakness of SiC-SiC 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 purpose of this study is to help develop a wider range of coating and joining technologies for fusion.

SUMMARY

Coatings and joining materials for SiC/SiC composites for nuclear energy systems are being developed using preceramic polymers filled with reactive and inert powders, and using solid-state reactions with no polymers. Polymer-filled joints and coatings start with a poly(hydridomethylsiloxane) precursor, such that mixtures of Al/Al₂O₃/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 1473K using 30 MPa applied pressure resulted in shear strengths of 200 MPa, which exceeds the shear strength of SiC/SiC composite materials.

Preceramic polymers with inert and reactive fillers are being considered for SiC-SiC joining technologies [7, 13–15] and have performed adequately if not spectacularly as strong joints. A known difficulty with preceramic polymers is the mass loss, which can exceed 50%, on conversion to a ceramic phase. A slightly different approach has been considered here using a poly-hydridomethylsiloxane (PHMS) as a precursor to a polysiloxane that has the advantage of much lower mass loss on ceramic conversion compared to other systems [16, 17]. In addition, pyrolysis can be achieved at temperatures as low as 873K. PHMS, which is a low viscosity liquid, converts on heating to a Si-O-C phase but can be modified by side group additions to produce a more carbon-rich oxycarbide phase [18]. For the work here, however, we used PHMS with no side group additions but filled the polymer with SiC, Al, and Al₂O₃ powders, singly and in combination. The SiC powders are 0.7- μ m average diameter pure SiC, the Al powders were in the form of flakes 1–2 μ m in size, and the Al₂O₃ powders were submicron diameter. Powder loadings were in the range of 40% to 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 423K in moist air. Figure 1 shows a batch of joints made in this manner. This was followed by pyrolysis with a nominal pressure of about 1 MPa in air at 1473K. One joint was also processed at 1073K 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 1473K for SiC-SiC and at 1073K for the 316 steel. Joint strengths were tested in single-lap shear geometry at ambient temperature and results are shown in Fig. 1.

^{*} Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO-1830.

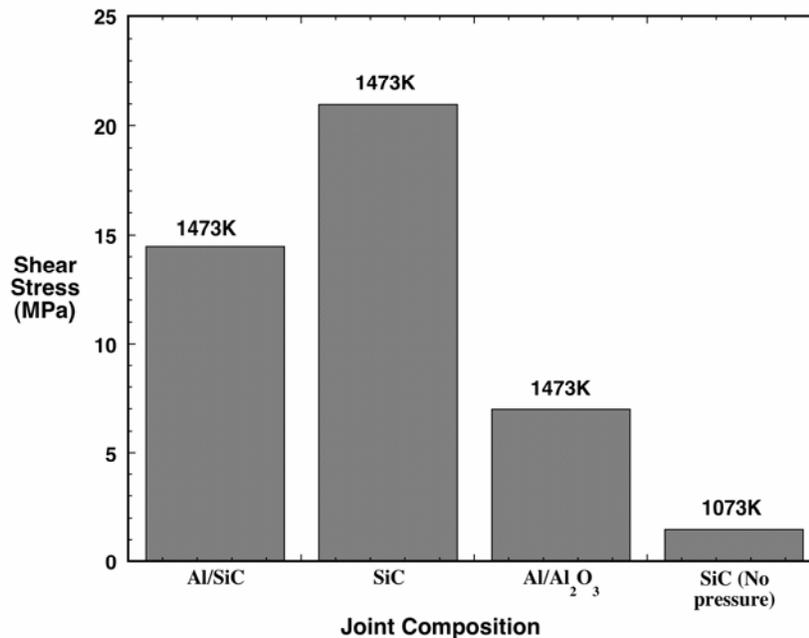


Fig. 1. Single-lap shear strength of PHMS joints processed in air at 1473K using 1 MPa pressure or in nitrogen with no applied pressure at 1073K.

Previous research at PNNL on solid state displacement reactions demonstrated that the reaction between TiC and Si produced an interwoven structure of Ti_3SiC_2 , $TiSi_2$, and SiC, with the majority phases being the ternary Ti_3SiC_2 and SiC [19–22]. 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 coupons or CVI SiC composite coupons[†]. Joints were formed by heating to 573K at 5K/min and holding for 2 hours for binder burnout with a nominal applied pressure followed by heating to 1573K at 10K/min and holding for 1 hour at 30 MPa applied pressure. Joints were tested in shear using a double-notch shear and sectioned for SEM examination.

Polymer slurry joints made with PHMS filled with SiC, Al/SiC, and Al/Al₂O₃ at 1473K 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. These joints possess reasonable shear strength values and are thin and dense after only 1 MPa applied pressure. No irradiation or other fusion relevant data exist for these joints, but they should be low activation based on their constituents. 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 oxycarbide, which may be a disadvantage in terms of creep strength and corrosion resistance. The high-temperature fracture and creep strength of these materials remains to be determined, but their ease of processing may make them amenable to field repair applications. The low strength of the joint processed at 1073K in nitrogen reveals that a small amount of pressure and temperatures in the 1400K range are required.

[†]Hi-Nicalon Type-S fibers from GE Power Systems with a 2D 8-harness satin weave architecture.

The solid-state reaction joints between TiC and Si resulted in high strength joints, with shear strengths in excess of 50 MPa[‡] as shown in Fig. 2. Almost more importantly, this shear fracture was observed to include some of the Hexaloy SiC and was not restricted to the joint material indicating 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 and we are currently exploring this effect with regard to SiC-SiC composite joints. A further consideration is that Ti₃SiC₂ and SiC are low-activation materials and there is some evidence of pseudo plasticity in the Ti₃SiC₂ phase that might give these joints a measure of fracture resistance that a pure SiC joint would lack. Although, with this system care must be taken to prevent the formation of the brittle TiSi₂ phase if possible.

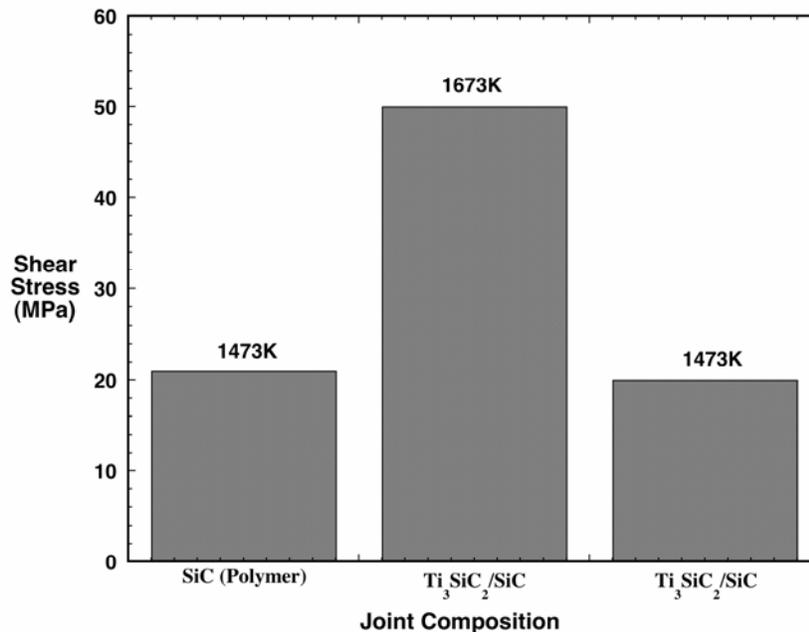


Fig. 2. Comparison of joint shear strengths for SiC-filled PHMS (single-lap) with solid-state reaction joints of TiC+Si to form Ti₃SiC₂/SiC joints (double-notch). Solid-state reaction joints are significantly stronger when processed at high temperatures and 30 MPa applied pressure.

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 ITER and other fusion projects. Solid-state joints appear to be very strong and, in comparison to reaction bonded joints, may have an advantage of no glassy phases or residual Si.

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[‡]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.

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