3.4 PROCESS DEVELOPMENT AND OPTIMIZATION FOR SILICON CARBIDE JOINING AND IRRADIATION STUDIES-II —

T. Koyanagi, J. O. Kiggans, T. Cheng, Y. Katoh (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this task is to develop and optimize joining processes for silicon carbide (SiC) ceramics and composites for fusion energy applications.

SUMMARY

The candidate joining methods for SiC ceramics and composites in the ongoing work to develop and optimize performance in neutron irradiation environments include chemically vapor-deposited (CVD) SiC bonded by the NITE (nano-infiltration and transient eutectic-phase) – like processes, diffusion bonding utilizing active titanium or molybdenum inserts, and transient eutectic-phase-assisted bonding with yttria-alumina-garnet (YAG) solder. In previous work the optimal processing conditions for Ti foil joining have been established. During the present reporting period, joint specimens with high shear strength were successfully produced through the active Mo metal insert methods, and then evaluated for as-fabricated properties.

PROGRESS AND STATUS

Development of Joining Process

In the preparation of joining specimens, flat plates of chemical vapor deposition (CVD) SiC ("CVD SILICON CARBIDE," Dow Chemical, Marlborough, MA) were joined by hot pressing with inserts of molybdenum (Mo) foil (0.025 mm thick, 99.95%, 150 × 150 mm, Alfa Aesar), YAG slurry (35.1wt.% Y_2O_3-64.9wt.% Al_2O_3-7.5wt.% SiO_2) or nano-infiltrated transient eutectic-phase (NITE) SiC slurry (6wt.% Y_2O_3-Al_2O_3-SiO_2 sintering additives) [2, 3]. The CVD SiC samples were ultrasonically cleaned in acetone, and then dried in an oven. Mo diffusion bonding was carried out under a vacuum of 10^{-5} torr or Ar atmosphere with a uniaxial pressure of ~20 MPa for temperature verify from 1300 to 1700 °C. Ti powder or 5%H_2 gas were used during hot pressing in order to remove gas impurities in vacuum and Ar atmosphere, respectively. For the specimens joined by NITE and YAG, a thin layer of NITE and YAG slurry was ultrasonic-sprayed through a Sonaer Sonozap (120 KHz) ultrasonic nozzle on the face of two SiC specimens, which were then placed face to face to form a sandwich. Joining was performed in a hot-press at 1875°C in a flowing Ar atmosphere with a uniaxial pressure of 20 MPa. The holing time and the uniaxial pressure applied on the samples were 1 h and 20 MPa in all the fabrication conditions in this work. The processing conditions and the results of the testing are summarized in Table 1.

Table 1. Processing conditions, nominal shear strength, joint microstructures, and fracture behavior of CVD-SiC joined by different filler materials.

Insert materials	**Specimen ID**	**Processing Conditions**				**Joint Strength**		**As-Joined Microstructure**	**Failure Location upon Shear Test**
		Atmosphere	Temperature (°C)	Pressure (MPa)	Time (h)	Mean Shear Strength (MPa)	Standard Deviation (MPa)		
Mo foil	Mof-1300-1-Ti	Ti powder, Vacuum	1300	20	1	46.4	30.6	Porous at joint interface	Joint/base interface
Mo foil	Mof-1500-1	Vacuum	1500	20	1	55.2 [1]	15.4	No debonding [1]	Through the joint [1]
Mo foil	Mof-1500-1-Ti	Ti powder, Vacuum	1500	20	1	83.1	41.7	No debonding	Primarily at base
Mo foil	Mof-1500-1-H_2	5%H_2/Ar	1500	20	1	105.5	4.6	No debonding	Base
Mo foil	Mof-1700-1	Vacuum	1700	20	1	68.2	18.7	No debonding	Primarily at base
Mo foil	Mof-1700-1-H_2	5%H_2/Ar	1700	20	1	94	20.6	No debonding	Primarily at base
NITE slurry	NITEs-1860-1	Ar	1860	20	1	43.9 [1]	38.8	Fair/porous joint; debonding at porous joint [1]	Porous/base interface [1]
NITE coating	NITEc-1875-1	Ar	1875	20	1	67.3	33.2	Porous joint; No debonding	Joint/base interface
YAG coating	YAGc-1875-1	Ar	1875	20	1	60.3	41.6	Dense Al_2O_3 and YAG joint	Interface 75 % Base 25 %

Note: Four replicates were used in tests in order to achieve statistical accuracy.

Mechanical testing and characterization

As mentioned in the earlier report [1], the joint strength was estimated by loading a double-notched test specimen of uniform width in compression, which is the standard test method ASTM C1292 for inter-laminar shear strength of continuous fiber-reinforced advanced ceramics at ambient temperatures. This test method, often referred to as double-notch shear (DNS) test, is in principle a variation of the offset single lap shear test as defined in ASTM D905 with an improved alignment capability due to the presence of the extended end sections. The bonded plates were machined into DNS specimens according to the dimension scheme shown in Fig. 1. The actual dimensions adopted were L = 20.0 mm, W = 6.0 mm, t = 7.6 mm, h = 1.3 mm, and d = 3.0 mm. Figures 2 (a) and (b) show a schematic and a photograph of the test setup and a specimen. Failure of the test specimen occurs by shear between two centrally located notches machined halfway through the thickness and spaced a fixed distance apart on opposing faces (ASTM C1292). The test fixture has been slightly modified, shown in Fig. 2, based on the initial one used previously [1].

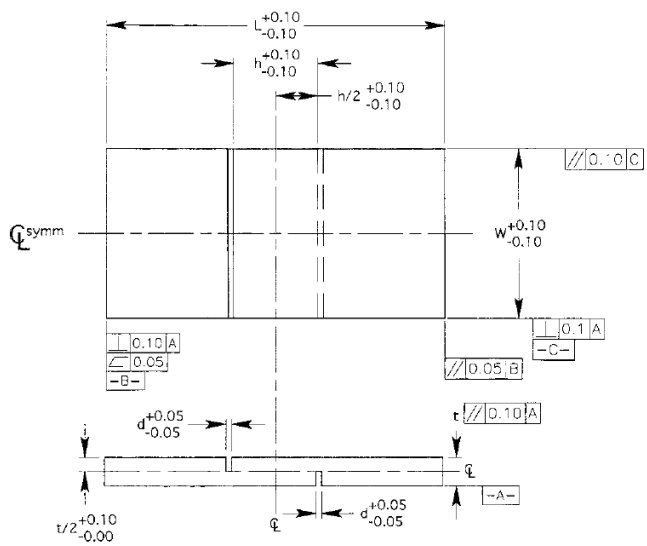

Fig. 1. Schematic of the double-notched compression test specimen.
Note: All dimensions are in millimeters [1].

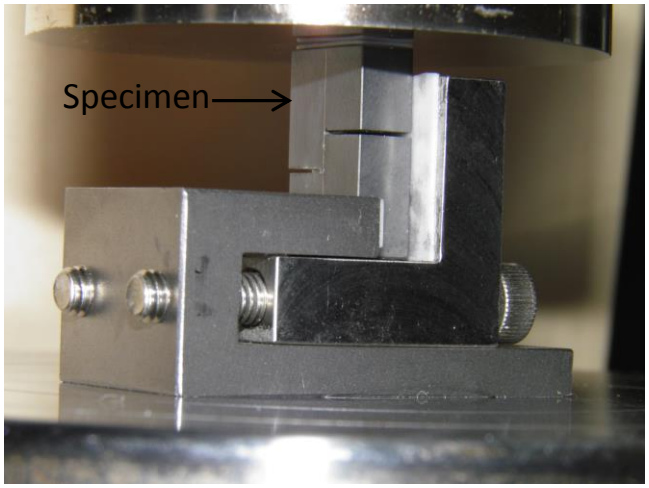

Fig. 2. An image of test fixture for the double-notched compression test specimen.

Polished cross-sections of the tested specimens were characterized using field-emission-gun scanning electron microscopy (FEG-SEM) in a Hitachi Model S4800, equipped with energy dispersive spectroscopy (EDS). The surface phases formed and their relative amounts were determined by X-ray diffraction (XRD) analysis (Model Scinatag Pad V, Thermo ARL). (NOTE: all SEM images shown below were taken on specimens after shear testing.)

Results of As-fabricated Characterization

Multiple joining conditions were attempted for each joining material in order to determine their optimal processing conditions, which will be used for fabricating the joint specimens for irradiation behavior study. Table 1 lists processing conditions, nominal shear strengths, joint microstructures, and fracture behaviors of CVD-SiC joined by Mo foil, NITE slurry, and YAG slurry.

<u>Mo foil joints</u>

Previously reported results indicated: (1) short-time (1 h) hot pressing is sufficient to obtain good quality joints; (2) Mo foil is favored over Mo powder slurry as the insert material because it experiences much less volume shrinkage during hot pressing; and (3) oxygen is suspected to have caused the low strength observed in certain joining condition because a detectable amount of oxygen was observed in the EDS spectrum of the joint [1]. Therefore, an oxygen getter (e.g., Ti) or a hydrogen gas flow were used in the present Mo foil joining processes, performed at temperatures of 1300, 1500, and 1700 °C and pressures of 20 MPa for 1 h (Table 1). The nominal shear strength of joints produced under the above conditions was plotted in Fig. 3. Compared with other Mo joints, the one formed at 1500°C for 1 h in 5%H_2/Ar gas exhibits the maximum strength of 106 MPa and minimum data deviation of 4.6 MPa. In contrast, the Mo joint formed in vacuum shows a significantly lower strength of 55 MPa. Using Ti powder to absorb O_2 also improves the Mo joint strength to a moderate extent. However, Ti powder tends to aggregate due to sintering at high temperatures, gradually losing its reactivity

during hot pressing, which is also the reason of using H_2 instead of Ti at 1700°C. As expected, applying H_2 gas increases strength of the Mo joint formed at 1700°C from 68 to 94 MPa on average, as shown in Table 1 and Fig. 3.

The low strength of the Mo joint produced at 1300°C for 1 h is likely caused by the large number of pores formed along the joint interface (Fig. 4 (a)), because the fracture location was mainly at joint/base interface as shown in Fig.4 (b). The Mo_5Si_3 phase was formed adjacent to the bond layer /SiC interface. While some Si was detected in the middle of the joint due to atom diffusion, extensive amount of Mo foil still remains intact in this joining condition.

The Mo joints formed at 1500 and 1700 °C with and without oxygen eliminator show similar microstructure to each other as shown in Fig 5 and 6. These joint layers mainly consisted of Mo_2C at the center of the joint layer and Mo_5Si_3 sandwiched by Mo_2C and SiC, based on XRD and SEM-EDS analysis. Note that vertical cracks to the joint interface were observed in all the specimens. A phase containing Mo and Si is lying between CVD SiC and Mo_5Si_3 (arrowed in Fig. 6), the thickness of which is similar among those joints. This thin layer was also observed and identified as Mo_5Si_3C by Martinelli using XRD and EDS [4]. A few µm pores located at the joint interface formed at 1500°C using H_2, despite its highest nominal shear strength. This result indicates that this kind of small pore was not critical flaw for the Mo joint in this work. The similar microstructure with the different strength may be caused by the difference of the quality of the joint layer. The impurities oxygen is one of the causes affecting that. Differential amount and distribution of carbon and/or Mo_5Si_3C phase formed in Mo_5Si_3 phase [4] also potentially affect the mechanical properties of the Mo_5Si_3 phase.

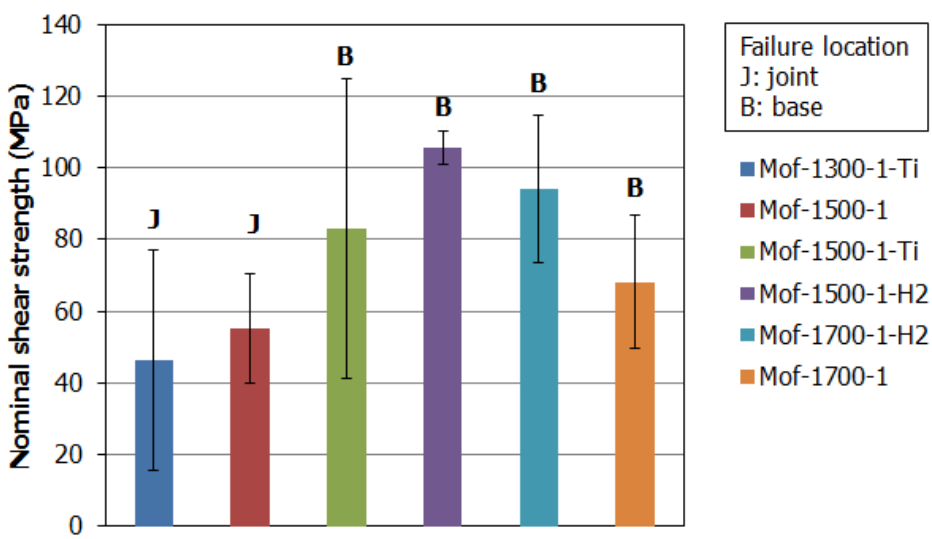

Fig. 3. Shear strength of joint formed between SiC plate and Mo foil filler hot pressed at various conditions.

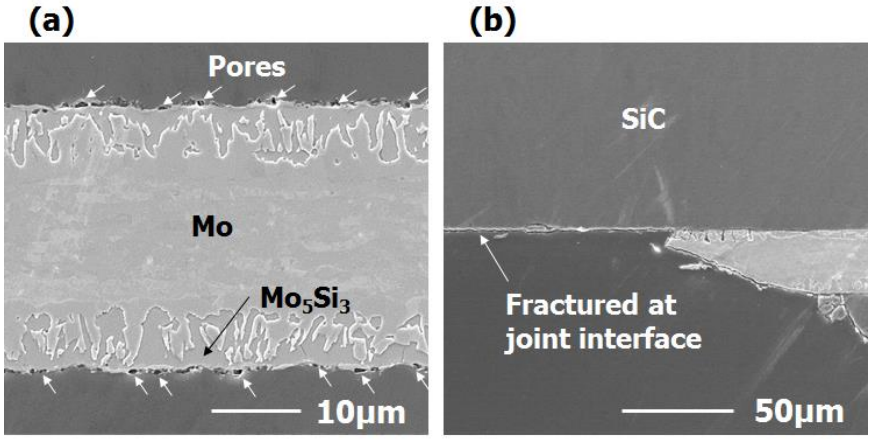

Fig. 4. Secondary electron images of Mo foil joint hot pressed at 1300°C for 1 h: (a) Joint interface before DNS test, (b) Joint interface after DNS test.

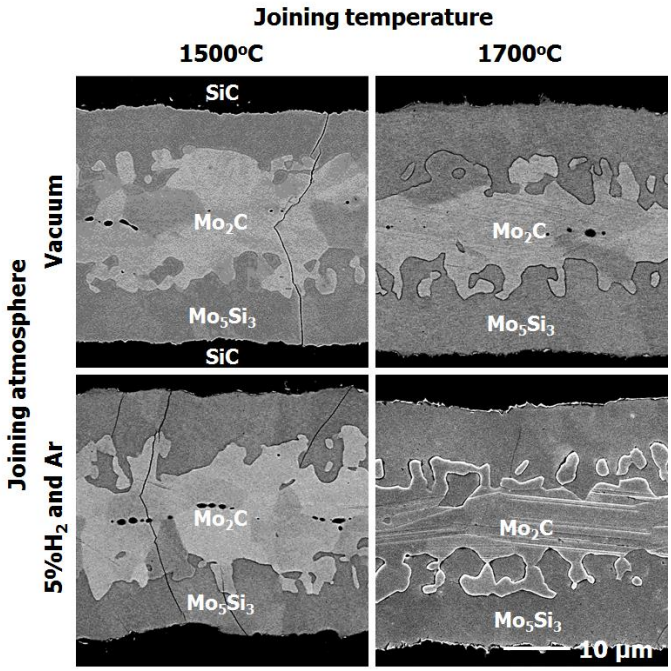

Fig. 5. Back scattering electron images of the Mo joints formed at 1500 and 1700 °C with and without oxygen eliminator.

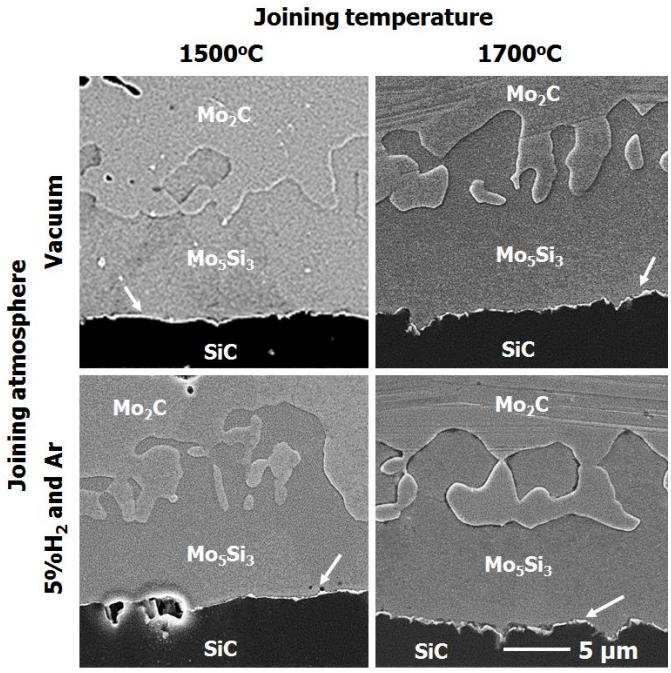

Fig. 6. Secondary electron images of the Mo joints formed at 1500 and 1700 °C with and without oxygen eliminator. The thin layers between SiC and Mo_5Si_3 are indicated by arrows.

Ultrasonically spray-coated (USC) NITE slurry joint

In an earlier effort, the NITE joints fabricated through a hand painting of the precursor slurry appeared to involve inhomogeneous microstructure with relatively dense regions and relatively porous regions spatially separated. While a good physical contact between the bonding layer and the SiC base was achieved at the dense regions, the porous joint apparently resulted in insufficient bonding. In order to achieve a uniform and dense NITE joint with good contact with the SiC base, multiple approaches have been implemented, including increasing viscosity of the NITE slurry or the sintering aids concentration, improving the uniformity of the NITE slurry layer by ultrasonic spray coating (USC), screen printing, or grinding CVD SiC to minimize bonding interface unevenness, etc. Figure 7 shows an example of microstructure of the USC NITE slurry joint hot pressed at 1875°C for 1 h at 20 MPa (slight temperature difference from the earlier work shall not lead to significant joint quality evolution). Unlike the NITE joint applied by manually painting onto the CVD SiC [1], the USC NITE joint appears to be much denser, whereas significant big pores observed within the joint (Fig. 7 (a) and (b)). However, fairly porous locations were also found, shown in Fig. 7 (c) and (d), implying limited sintering at some localized regions. The fracture occurred at the joint/base interface due to less base contact at the fairly porous joint. The average shear strength of the USC NITE joint, shown in Table 1, increased to 67.3 MPa from 43.9 MPa for the manual painted slurry joints. However, strength of the USC NITE joint is still significantly lower than those reported previously. The large standard deviation of 33.2 MPa indicates that a significant improvement in the spatially uniformity for this joint is achievable.

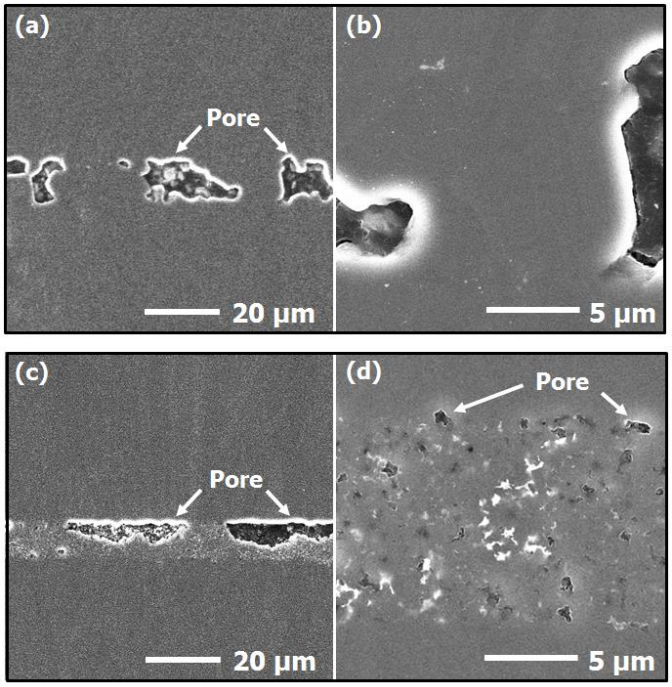

Fig. 7. SE images of ultrasonic-spray coated NITE slurry joint hot pressed at 1875°C for 1 h. (a), (b): well-sintered region with large pores. (c), (d): Fairly porous region.

Ultrasonic-spray coated (USC) YAG slurry joint

The same USC technique was used to apply the YAG slurry onto the CVD SiC substrates. The four replicates exhibited considerable variance in shear strength: 32, 48, 39 and 122 MPa. A representative cross sectional image for the first three specimens of low strength was shown in Fig. 9 (a) and (b). While the joint appears to be dense without debonding from the SiC base, it is primarily composed of Al_2O_3 in lieu of the YAG phase, resulting to the unacceptably low strength. These specimens fractured at the Al_2O_3 joint/SiC base interface, summarized in Table 1, possibly due to few micron pores at the joint interface and/or weak bonding between SiC and Al_2O_3, and/or the effect of the secondary phases along the joint interface as shown in Fig. 9 (b). In contrast, microstructure of the YAG joint with much higher strength (122 MPa) is also shown in Fig. 9 (c). While Al_2O_3 joint was still observed in this specimen, two pieces of CVD SiC substrates are joined together by Y-Al oxides in some region. This specimen, which fractured at the SiC base, shows the adequate strength, despite the non-uniform microstructure. This result shows that the YAG joining process has high potential for achieving robust SiC joint. Further improvement of this technique will focus on achieving homogenously mixing the yttria, alumina and silica powder to obtain uniform microstructure.

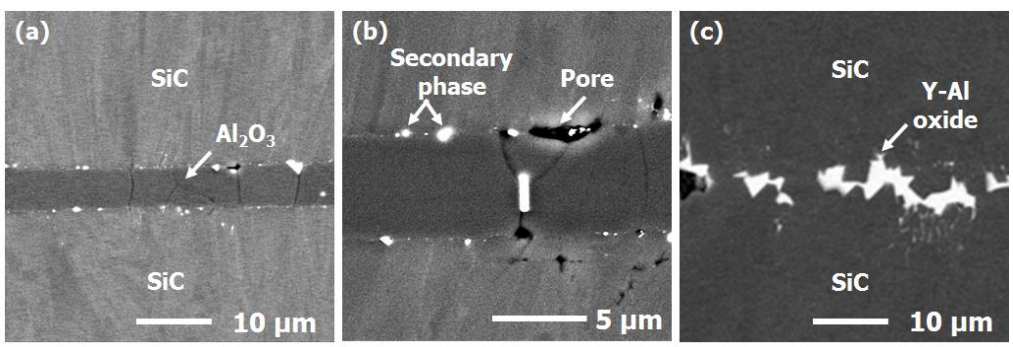

Fig. 8. Backscattered electron images of ultrasonic-spray coated YAG slurry joints hot pressed at 1875°C for 1 h. (a), (b) Specimen showing low strength (32 MPa), (c) Specimen showing high strength (122 MPa).

CONCLUSIONS

The candidate joint materials for the ongoing work to evaluate the neutron irradiation effects on CVD SiC includes bonds produced by diffusion bonding utilizing active titanium or molybdenum inserts, the NITE – like transient eutectic phase processes, YAG solder, and Ti-Si-C MAX phase through displacement reaction. In a previous report, the optimal processing conditions for Ti foil joining have been established. During the present reporting period, joint specimens with high shear strength were successfully produced through the active Mo metal insert methods, and then evaluated for as-fabricated properties.

A high level summary of the status of joining development at Oak Ridge National Laboratory is provided in Table 2. The Mo foil insert joint of CVD SiC hot pressed at 1500°C for 1 h in 5% H_2/Ar exhibited adequate strength.

Table 2. Status summary of SiC joint processing at ORNL.

Method	Insert Material	Status
Metallic diffusion bonding	Ti foil	Optimum joining condition established
	Mo foil	Optimum joining condition established
Transient eutectic-phase joining	NITE* slurry	Optimum joining condition being studied
	YAG solder	Optimum joining condition being studied

*NITE: Nano-Infiltration and Transient Eutectic-phase process for sintering SiC

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