3.2 Process Development and Optimization for Silicon Carbide Joining and Irradiation Studies — T. Cheng, J. O. Kiggans, Jr., Y. Katoh, and L. L. Snead (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this task is to develop and optimize joining processes for silicon carbide (SiC) for future neutron irradiation effects study in the High Flux Isotope Reactor (HFIR).

SUMMARY

The candidate joint materials for the ongoing work to evaluate the neutron irradiation effects on chemically vapor-deposited (CVD) SiC includes bonds produced by the NITE (nano-infiltration and transient eutectic-phase) – like transient eutectic phase processes, diffusion bonding utilizing active titanium or molybdenum inserts, calcia-alumina (CA) glass/ceramics, and Ti-Si-C MAX phase through displacement reaction. During the present reporting period, joint specimens were successfully produced through the active metal insert methods and the NITE-like process, 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 titanium (Ti) foil (0.025 mm thick, 99.94%, 75 × 75 mm, Alfa Aesar), molybdenum (Mo) foil (0.025 mm thick, 99.95%, 150 × 150 mm, Alfa Aesar), Mo powder slurry (powder size of ~44 μm), or nano-infiltrated transient eutectic SiC slurry (NITE [1], 6wt% Y_2O_3-Al_2O_3-SiO_2 sintering additives). The CVD-SiC samples were ultrasonically cleaned in acetone, and then dried in an oven. For the specimens joined by NITE, a thin layer of NITE slurry was applied 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 furnace in a flowing Ar atmosphere with a uniaxial pressure of 15-20 MPa. High vacuum (10^{-5} torr) was applied and held for 12 h in the furnace before heating in order to remove gas impurities. Joining conditions for each of the joining materials were carefully designed; the processing conditions and the results of the testing are summarized in Table 1.

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

Insert materials	Specimen ID	Processing Conditions			Joint Strength		Observed Phases	Joint Microstructure	Failure location
		Temperature (°C)	Pressure (MPa)	Time (h)	Mean Shear Strength (MPa)	Standard Deviation (MPa)			
Mo foil	Mof-1500-1-15	1500	15	1	55.2	15.4	Mo_2C, Mo_5Si_3	No debonding	Through joint
Mo foil	Mof-1700-1-20	1700	20	1	85.2	58	Mo_2C, Mo_5Si_3	No debonding	SiC base
Mo foil	Mof-1300-5-20	1300	20	5	15.2	7.2	Mo_2C, Mo_5Si_3	No debonding	Interface and base
Mo foil	Mof-1500-5-20	1500	20	5	18.8	11.2	Mo_2C, Mo_5Si_3	Partially debonding	Primarily at base
Mo powder	Mop-1500-5-20	1500	20	5	9.3	3.6	Mo_2C, Mo_5Si_3	Porous/dense joint No debonding	Through porous joint
Mo powder	Mop-1300-5-20	1300	20	5	6.5	5.7	Mo_2C, Mo_5Si_3	Porous/dense joint, debonding at porous joint	Interface and base
Ti foil	Tif-1500-1-15	1500	15	1	97.6	8.8	85% TiC, Ti_3SiC_2	No debonding	Through joint
Ti foil	Tif-1300-1-20	1300	20	1	1.7		Ti_5Si_3, TiC	Ti_5Si_3/SiC debonding	Interface
Ti foil	Tif-1500-5-20	1500	20	5	28.4	13.7	Ti_3SiC_2	No debonding	Joint and interface
NITE slurry	NITEs-1860-1-20	1860	20	1	43.9	38.8	SiC	Porous/dense joint, debonding at porous joint	Interface

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

Mechanical testing and characterization

Planned irradiation testing will examine the strength of the SiC joints using torsional shear tests employing solid hourglass type specimens. The torsional shear test is nearly ideal for this purpose because of its simplicity and ability to apply true shear loading to the joint specimens. However, machining the torsional hourglass specimens is relatively expensive and time-consuming. Other test methods are more appropriate for the purpose of estimating the approximate strength in a timely manner to support joining process optimization studies.

In this work, 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 hot-pressed 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 1292).

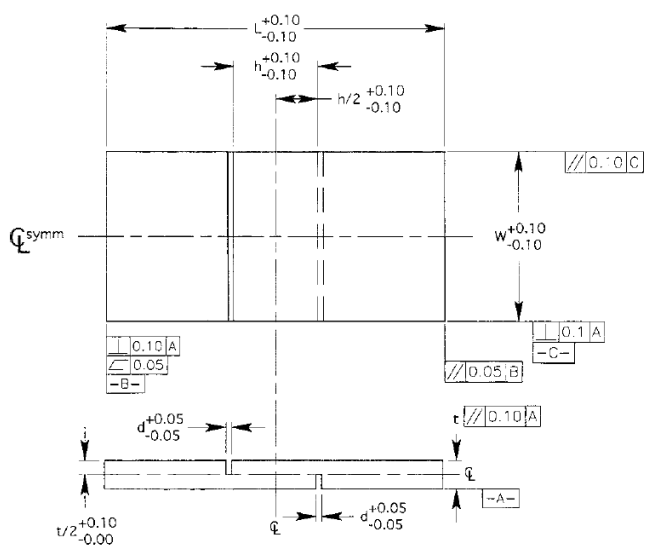


Fig. 1. Schematic of the double-notched compression test specimen. Note: All dimensions are in millimeters.

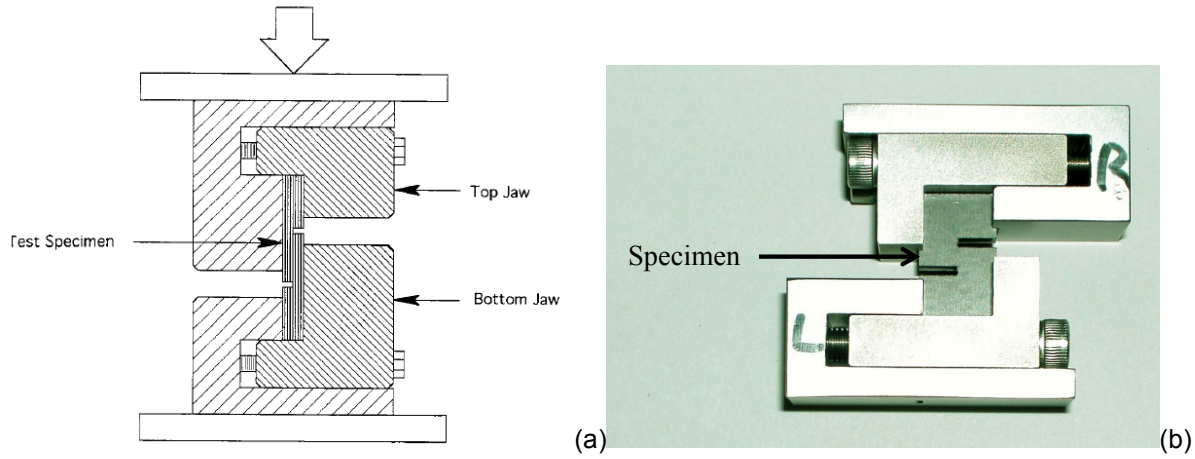


Fig. 2. Schematic (a) and an image (b) of test fixture for the double-notched compression test specimen.

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

The processing parameters including hot pressing temperature, pressure, time, and joining material thickness were selected based on thorough literature review, summarized in Table 2. 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, shear strengths, joint microstructures, and fracture behaviors of CVD-SiC joined by Ti foil, Mo foil, Mo powder slurry, or NITE slurry.

<u>Ti foil joint</u>

For Ti diffusion bonding, a scheme representing the Ti joint microstructure evolution at different hot-pressing temperatures was developed by Gottselig [5], shown in Fig. 3. Low temperature (<1250°C) may result into complex interlayer structures, which may not be favorable in robust process design and mechanical property control. Therefore, temperatures in a range of 1300-1500°C were selected for Ti joining in this work.

Pressure higher than 10 MPa has no effect on bonding quality [2, 5], therefore, slight variations in pressure, e.g., 15 MPa and 20 MPa should not result in obvious joint microstructure evolution. Temperature and time effects are examined in this work. Figure 4 shows the microstructure of the Ti joint formed after hot pressing at 1500°C for 1 h. The Ti foil was completely reacted with SiC by forming TiC (primary product) and Ti_3SiC_2 (Table 1), evidenced by the measured XRD spectrum (not shown here) in which no Ti metal phase was detected. In Fig. 4, the Ti joint seems homogenous and no phase contrast was observed, suggesting that the fine Ti_3SiC_2

grains may disperse in the TiC matrix. Cracks were found in the joint indicating its brittle character. The formed TiC phase has good wetting behavior on SiC, evidenced from good contact at the joint/substrate interface. The effect of pressing time was analyzed by extending the hot pressing time to 5 h, keeping the temperature and pressure constant, and the microstructure of the resulting Ti joint is illustrated in Fig. 5. A uniform Ti_3SiC_2 interlayer was formed under the above conditions, indicating that Si diffusion dominated in the 5 h test by reacting with TiC, forming Ti_3SiC_2. No interfacial debonding was observed. Hot pressing at a lower temperature of 1300°C was also performed to examine the temperature effect. The microstructure of Ti joint formed at 1300°C for 1 h is shown in Fig. 6. The TiC phases (dark) with small and large grains are dispersed in Ti_5Si_3 (bright) matrix, which is adjacent to SiC base. Interfacial debonding is clearly observed in Fig. 6, possibly due to the large coefficient of thermal expansion (CTE) mismatch between SiC and Ti_5Si_3. These results suggest that the Ti foil joining requires high temperature, e.g. 1500°C, in order to achieve good interfacial bonding with the SiC base.

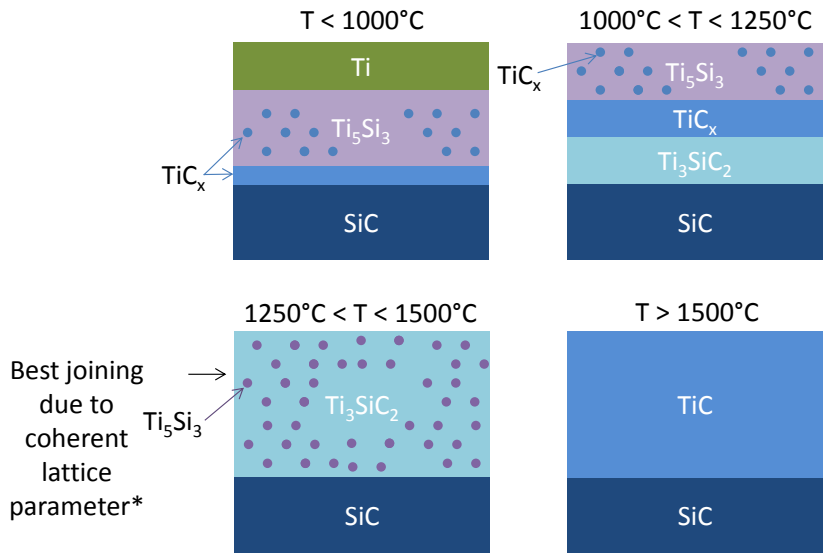


Fig. 3. A schematic illustration of Ti joint microstructure evolution at various temperatures.

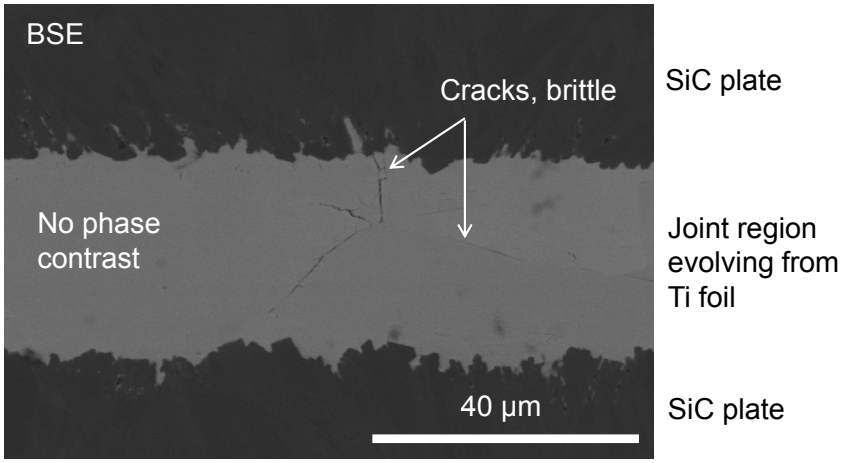


Fig. 4. Back Scattering Electron (BSE) cross section image of joint formed between two SiC plates and Ti foil hot pressed at 1500°C for 1 h.

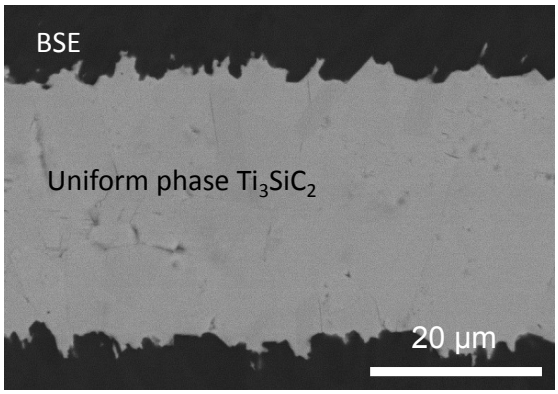


Fig. 5. As Fig.4, but hot pressed at 1500°C for 5 h.

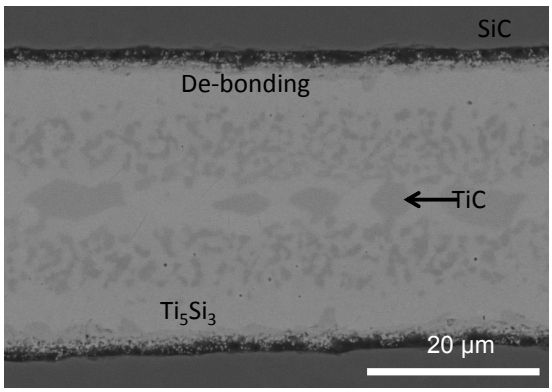


Fig. 6. As Fig. 4, but hot pressed at 1300°C for 1 h.

The Ti joint strengths of the specimens hot pressed under different conditions are listed in Table 1. The joints formed after hot pressing at 1500°C for 1 h show the highest shear strength of 98 MPa and acceptable standard deviation of 9 MPa. In contrast, the joints formed at 1300°C for 1 h show the lowest strength, some of which were actually broken during machining. These

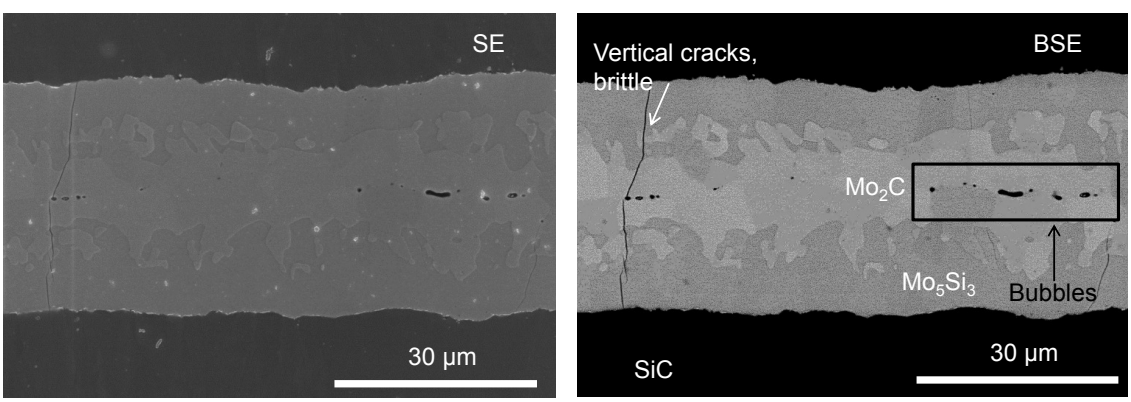
strength results are consistent with the microstructures presented in Figs. 4 and 6, showing good interfacial contact at 1500°C and interfacial de-bonding at 1300°C, respectively. The low strength provided by the Ti joints hot pressed at 1500°C for 5 h was surprising, because the uniform Ti_3SiC_2 phase formed was expected to show good strength due to the good CTE match with SiC. A small amount of oxygen (~8-9at%) was detected in the 5 h joint using SEM-EDS, but was absent in the Ti joint formed in 1 h hot pressing. Oxygen uptake during long duration processing may have led to the unexpected low joint strength. Ti sponge (as an oxygen getter) and hydrogen gas will be used during future hot pressing in order to eliminate oxygen in the furnace and eliminate oxide forming in the joint. The Ti joint hot pressed at 1500°C for 1 h exhibits the desired strength, therefore, its processing conditions have been chosen for fabricating the Ti joined CVD-SiC specimens to be produced for future irradiation tests.

Table 2. A review of processing conditions and joint microstructures reported in literature for CVD-SiC joined by Mo and Ti

Joining material	Reference	Foil thickness	Temperature (°C)	Pressure (MPa)	Time (h)	Phases	Findings
Mo foil	Cockeram [2], 1999	12.7	1200	8.8	10	no bonding	no reaction
		12.7	1500	3.4-17.2	10	Mo_5Si_3, Mo_2C	pressure no effect on microstructure
		25.4	1500	17.2	10	Mo_5Si_3, Mo_2C	more defects
	Cockeram [3], 2005	25.4	1500	17.2	10	Mo_5Si_3, Mo_2C	strength comparable to the monolithic SiC
Mo plate (Diffusion couple)	Martinelli [4], 1995	2.5 mm	1200	5	2	___	no flaw, but no image showed
		2.5 mm	1250	5	2	Mo_5Si_3, Mo_2C	Phases agglomerate and separated into two layers at high temperature
		2.5 mm	1300	5	1	Mo_5Si_3, Mo_2C	
		2.5 mm	1400	5	1	Mo_5Si_3, Mo_2C	
		2.5 mm	1500	5	0.2, 1	Mo_5Si_3, Mo_2C, Mo_5Si_3C	debonding at 1h, well contact at 0.2 h
		2.5 mm	1650	5	0.5	Mo_5Si_3, Mo_2C, Mo_5Si_3C, MoC	Mo_5Si_3/Mo_2C+ Mo_5Si_3 /Mo_5Si_3C/SiC complex microstructure
		2.5 mm	1700	5	1	Mo_5Si_3, Mo_2C, Mo_5Si_3C, MoC	
Ti foil	Cockeram [2], 1999	25.4	1500	3.4	10	Ti_3SiC_2, Ti_5Si_3	bad quality, more defects
		5.1	1500	8.8	10	Ti_3SiC_2, Ti_5Si_4	good quality, less defects
		25.4	1400	13.8	10	___	bad quality
	Gottselig [5], 1990	3	700		2	$TiC_{0.45}$	pressure >10 MPa, high strength
		3	1100		2	Ti_3SiC_2, $TiC_{0.45}$, Ti_5Si_3, $TiSi_2$	
		3, 1	1450	5, 15, 30	0.5, 1, 2	Ti_3SiC_2, Ti_5Si_3	
		3	1600		2	$TiC_{0.8}$	

Mo foil and powder joints

The results of a literature review on Mo foil joining of SiC and SiC/Mo diffusion are summarized in Table 3. Similar to the Ti joining process, while pressure shows no effect on Mo joint quality, temperature and reaction time are the key factors controlling the Mo joint microstructure. Mo foil joining was performed at temperatures of 1300, 1500, and 1700°C and pressures of 15 and 20 MPa for 1 and 5 h (Table 1). Mo joints hot pressed at 1500°C and 1700°C for 1 h (Figs. 7 and 8) show similar microstructures: (1) vertical cracks though the joint indicate the brittle behavior of the formed joint; (2) Mo metal was completely reacted by forming the middle Mo_2C (bright) region and the Mo_5Si_3 (dark) phase adjacent to the SiC base; (3) No debonding was found at the joint/base interface, indicating the good quality of joints formed under both conditions; and (4) several pores (bubbles) were aligned at the middle of the joint, possibly related to gas formation during reaction. Lower temperature, e.g. 1300°C, testing is included in the test matrix but has not yet been performed. Hot pressing at 1500°C was extended to 5 h in order to determine the time effect on the microstructural evolution of the Mo joint, shown in Fig. 9. Complete Mo transformation to Mo_2C (bright) and Mo_5Si_3 (dark) phases were also observed. However, interfacial de-bonding occurs at the bottom left and top right locations, denoted by arrows (Fig. 9), along with the Mo_2C band deviating from the middle of the joint and approaching the SiC base in the debonding regions. De-bonding is likely owing to the large CTE mismatch between Mo_2C and SiC. While the formation mechanism of such tilted Mo_2C band morphology is still under study, these results suggest good joint/base bonding can be achieved in 1 h hence excessive pressing is unnecessary. Lower temperature hot pressing was conducted at 1300°C for 5 h to study the temperature dependence of the Mo_2C band location. As shown in Fig. 10, the joint is well adhered to the SiC base. While the Mo_2C phase is very close to the SiC base, a thin layer of Mo_5Si_3 phase is observed between the SiC and Mo_2C, which possibly prevents debonding. All those results indicate that short-time hot pressing is sufficient to obtain good quality joints.



Fig, 7. Secondary electron (SE) and BSE images of joint formed between SiC plate and Mo foil filler hot pressed at 1500°C for 1 h.

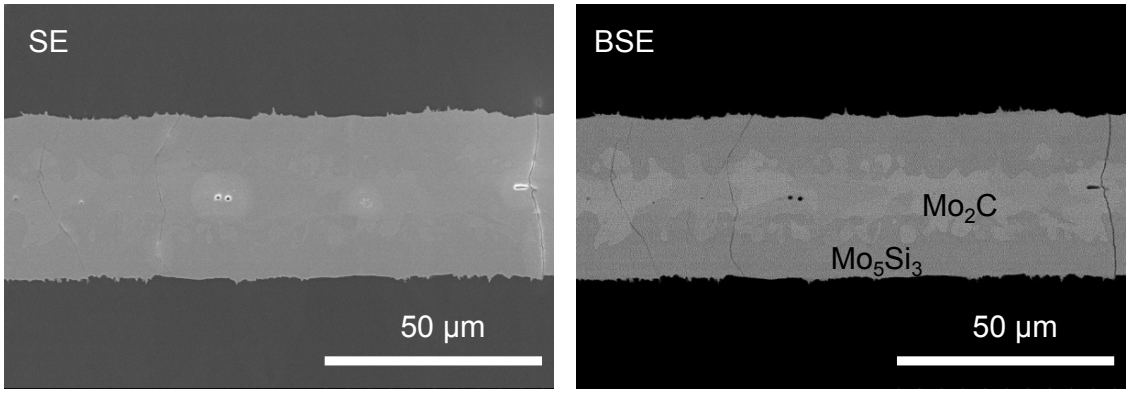


Fig. 8. SE and BSE images of Mo foil joint hot pressed at 1700°C for 1 h.

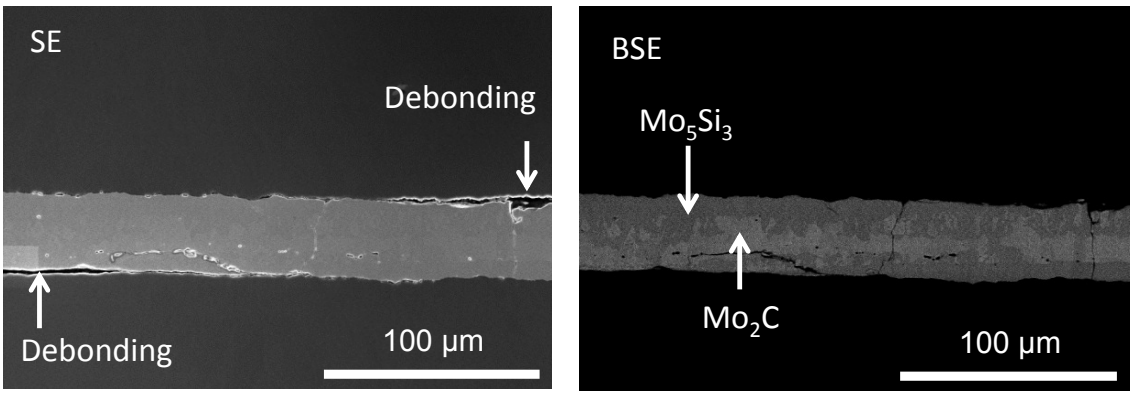


Fig. 9. SE and BSE images of Mo foil joint hot pressed at 1500°C for 5 h.

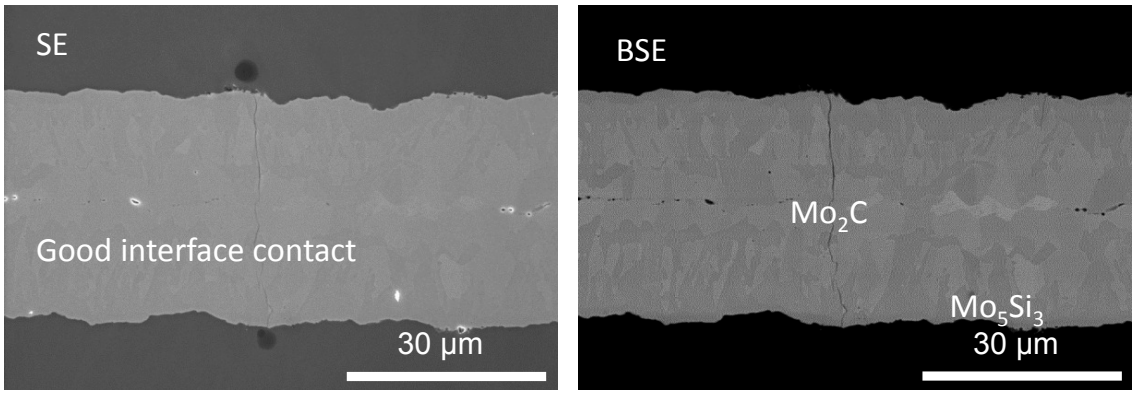


Fig. 10. SE and BSE images of Mo foil joint hot pressed at 1300°C for 5 h.

Another Mo joining approach was attempted by replacing the thin Mo foil with Mo powder slurry to study whether fine Mo powder can lead to a better joint by increasing the reactive surface area. The microstructures of Mo joints formed at 1500 and 1700°C in 5 h are shown in Figs. 11 and 12, respectively. The Mo slurry experienced significant volume shrinkage by gasification of binders and sintering during hot pressing, resulting in a joint exhibiting regions characterized as partial porous and partial dense. The dense joint has good contact with SiC (Fig. 12 b), whereas the porous joint usually leads to debonding at one side of the interfaces (Fig. 11 and Fig. 12 a). Therefore, Mo foil is favored over Mo powder slurry as the joining material because it experiences much less volume shrinkage during hot pressing.

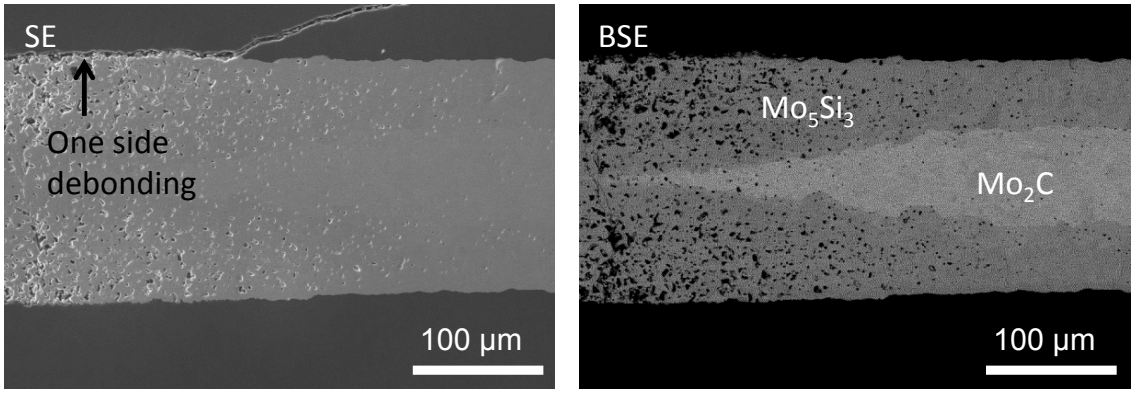


Fig. 11. SE and BSE images of joint formed between SiC plate using Mo slurry hot pressed at 1500°C for 5 h.

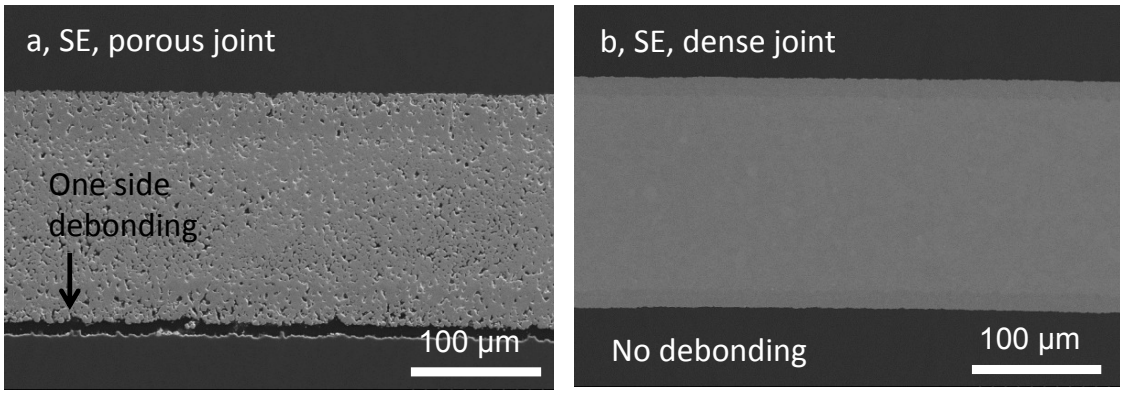


Fig. 12. SE images of partial porous (a) and partial dense (b) joint formed by hot pressing Mo powder slurry at 1700°C for 5 h.

The Mo joint strengths of specimens hot pressed under above conditions are listed in Table 1. The Mo joints formed by hot pressing Mo foil at 1500 and 1700°C for 1 h show good and comparable (within scattering range) shear strengths, which is consistent with the similar microstructure results shown in Figs. 7 and 8. The joint (foil) formed at 1500°C for 5 h shows lower shear strength around 20 MPa, which is predictable due to the interfacial debonding observed in Fig. 9. Surprisingly, the joint (foil) formed at 1300°C in 5 h also shows low shear strength around 15 MPa, even though debonding was not found in Fig. 10. Similar to the low strength results of the Ti foil joints hot pressed for 5 h, oxygen is suspected to have caused

such low strength because a detectable amount of oxygen was observed in the Energy Dispersive X-ray spectrum of the joint (not shown here). An oxygen getter will be used in future Mo foil joining processes. All specimens joined by Mo powder slurry show low shear strength values, possibly due to interface debonding at the porous joint (Figs. 11 and 12). All microstructure and strength data shown above suggest using metal foils and short hot pressing time to achieve good joints.

NITE slurry joint

The microstructure of a NITE slurry joint hot pressed at 1860°C for 1 h at 20 MPa is shown in Fig. 13. Similar to the Mo slurry joint, partially dense and partially porous joints were also observed in NITE joints. The dense joint has good contact with the SiC base, but the porous joint has apparent debonding at both interfaces. This fair/bad unit is repeated along the joint, which is schematically illustrated in Fig. 14. Considerable volume shrinkage due to release of organic binders and sintering aids during hot pressing may lead to this observed microstructure. The shear strength of the NITE joint, shown in Table 1, is weak compared to the Ti and Mo joints. The fracture occurred at the joint/base interface and is possibly due to debonding at the porous joint (Fig. 13). Achieving a uniform and dense NITE joint with good contact with the SiC base is the key to guide future joining design.

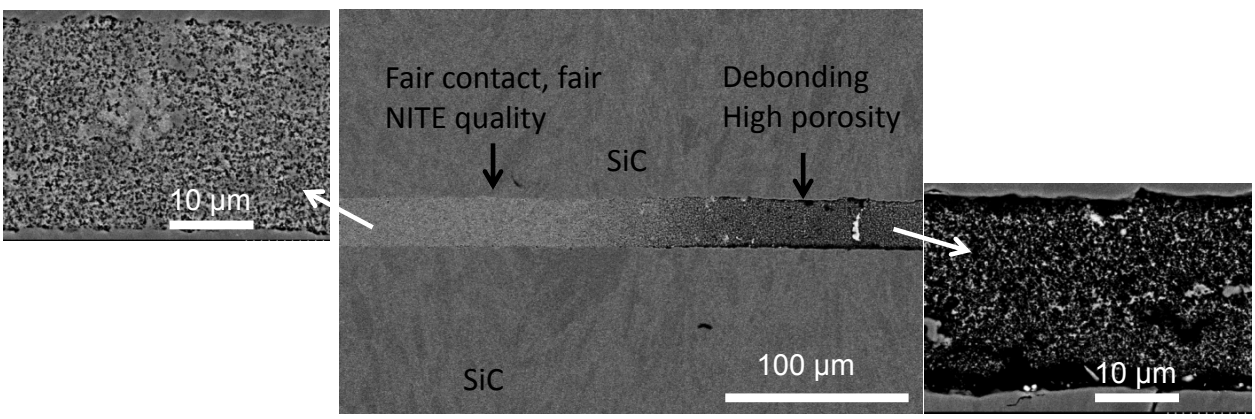


Fig. 13. BSE images of NITE slurry joint hot pressed at 1860°C for 1 h.

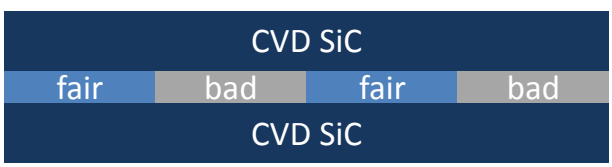


Fig. 14. Schematic of NITE slurry joint hot pressed at 1860°C for 1 h.

CONCLUSIONS

The candidate joint materials for the ongoing work to evaluate the neutron irradiation effect include chemically vapor-deposited (CVD) SiC bonded together with the NITE (nano-infiltration and transient eutectic-phase) – like transient eutectic phase processes, diffusion bonding utilizing active titanium or molybdenum inserts, calcia-alumina (CA) glass/ceramics, and Ti-Si-C

MAX phase through displacement reaction. Joint specimens were produced through the active metal insert methods and the NITE-like process then evaluated for as-fabricated properties during the present reporting period.

A high level summary of the status of joining development at Oak Ridge National Laboratory is provided in Table 3. The Ti foil insert joint of CVD SiC hot pressed at 1500°C for 1 h exhibited adequate strength. Hot-pressing at the lower temperature of 1300°C appeared sufficient to obtain a Mo joint of reasonable quality. Metal thin foils are favored over the powder slurries as the form of insert materials because of lower volume reduction during the pressurized process, used to form dense and uniform joints.

Table 3. 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 being studied
	Mo powder slurry	Optimum joining condition being studied
MAX-phase bonding	TiC/Si powder slurry	Commercial joining kit purchased
Transient eutectic-phase joining	NITE* slurry	Optimum joining condition being studied

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

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