Irradiation resistance of silicon carbide joint at light water reactor–relevant temperature*

T. Koyanagi,^{†1} Y. Katoh,¹ J.O. Kiggans,¹ T. Hinoki,² H.E. Khalifa,³ C.P. Deck,³ C.A. Back³

¹ Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

² Kyoto University, Uji, Kyoto 611–0011, Japan

³ General Atomics, San Diego, CA 92186, USA

Abstract

Monolithic silicon carbide (SiC) to SiC plate joints were fabricated and irradiated with neutrons at 270–310°C to 8.7 dpa for SiC. The joining methods included solid state diffusion bonding using titanium and molybdenum interlayers, SiC nanopowder sintering, reaction sintering with a Ti-Si-C system, and hybrid processing of polymer pyrolysis and chemical vapor infiltration (CVI). All the irradiated joints exhibited apparent shear strength of more than 84 MPa on average. Significant irradiation-induced cracking was found in the bonding layers of the Ti and Mo diffusion bonds and Ti-Si-C reaction sintered bond. The SiC-based bonding layers of the SiC nanopowder sintered and hybrid polymer pyrolysis and CVI joints all showed stable microstructure following the irradiation.

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[†] Corresponding author. E-mail address: koyanagit@ornl.gov

1. Introduction

Silicon carbide (SiC) fiber–reinforced SiC matrix composites have been widely studied for use in developing an accident-tolerant fuel cladding for light water reactors (LWRs) in recent years because of their superior oxidation and irradiation resistance and low neutron absorption cross section [1, 2].

Although SiC composites appear to be attractive for cladding applications, some technological hurdles, such as fuel compatibility, hydrothermal corrosion resistance, and manufacturability, must be addressed [3]. Regarding manufacturability, a reliable joining technology is essential for the end-plug joints of the cladding. These joints are required to retain fission products inside the cladding and withstand reactor environments such as irradiation and hydrothermal corrosion for normal operation and high-temperature oxidation for accident conditions. This paper focuses on the irradiation resistance of the candidate SiC joints because there is a significant lack of knowledge in that area.

Stempien et al. investigated the irradiation resistance of SiC bonds using glass-ceramics, titanium foil, and TiC/SiC tape under simulated pressurized water reactor conditions [4]. The study mainly focused on hydrothermal corrosion behavior, and a promising joint was not found. Katoh et al. have demonstrated irradiation-tolerant joining technologies under neutron irradiation at 500 and 800°C [5]. The joining methods included titanium diffusion bonding, transient eutectic phase sintering, calcia–alumina glass ceramics joining, and Ti-Si-C based reaction sintering. None of the joints exhibited obvious strength degradation from the irradiation; however, irradiation-induced cracking was observed in the bonding layers of the non-SiC phases. This cracking was likely caused by strain attributed to differential irradiation swelling between the bonding layer and SiC substrate. Since swelling of SiC has a negative correlation with temperature [6], the issue of differential swelling may be more critical at lower irradiation temperatures. This study explores the mechanical properties of six types of plate-to-plate SiC joints neutron-irradiated at an LWR coolant temperature of ~300°C to a dose of 8.7 displacements per atom (dpa). This dose level is higher than in previous studies and is the typical dose of a complete LWR fuel cycle [7]. The radiation resistance of the joints was evaluated using a shear strength test and microstructural observations.

2. Experimental methods

2.1 Neutron irradiation and post-irradiation experiments

Irradiation and post-irradiation testing methods for miniature SiC joint specimens were developed in our previous study [5]. The geometries of the specimens and irradiation vehicles used in this study were very

similar to those in the previous study. The neutron irradiation was conducted using rabbit vehicles in the target irradiation facility of the High Flux Isotope Reactor at Oak Ridge National Laboratory. The specimens were irradiated at 270–310°C to 8.7 dpa for SiC ($1.0 \times 10^{25} \text{ n/m}^2 = 1 \text{ dpa}$ [$E > 0.1 \text{ MeV}$] is assumed.). The irradiation temperature was investigated by post-irradiation annealing of passive SiC temperature monitors using dilatometry [8]. The temperature monitors were irradiated in contact with the substrates of the joint specimens.

The shear strength of the joint test specimens was evaluated using hourglass-type specimens designed specifically for the rabbit irradiation experiment [5]. The specimen geometries and appearance are shown in Fig. 1. The bonding layer was located at the mid-plane of the specimen in the 2.9–3.0 mm thickness direction. The neck diameter of the hourglass specimen was 4 mm for the SiC nanopowder sintered joints and 5 mm for the other joints. The deviation in the neck diameter was typically within 0.1 mm, other than for the hybrid polymer pyrolysis/chemical vapor infiltration (CVI) joint, which had a deviation of 0.2 mm. The torsional test was conducted using a TestResources 160GT-125Nm system with pairs of flexible couplers and sample grips (Fig. 2). The flexible coupling was designed to maintain the alignment during loading. Aluminum-alloy tabs were installed at the square grip sections to obtain uniform stress distributions there. The rotation speed was 0.15 degree/min. Nominal shear strength values (τ) are given by the following equation:

$$\tau = 16T/\pi d^3, \quad (1)$$

where T is the applied torque and d is the specimen diameter of the neck [9]. The maximum force was applied on the surface of the hourglass neck based on Eq. (1). Note that Eq. (1) ignores the stress concentration factor for simplicity, although a slight stress concentration at the hourglass was reported [10]. The number of torsion tests was from four to nine for the unirradiated specimens and three or four for the irradiated specimens. All the tests were conducted at room temperature. The fracture appearance was visually observed or investigated using a conventional optical microscope.

Fig. 1 Appearance of typical unirradiated miniature hourglass specimen.

Fig. 2 Test apparatus for the torsional shear test.

The cross sections of the unirradiated and irradiated joint specimens that did not undergo torsional tests were investigated using scanning electron microscopes (SEMs; field-emission [FE] gun type Hitachi 4800S and FE gun type FEI Versa 3D DualBeam SEM/focused ion beam). The specimens were cut using

a low speed diamond saw followed by mechanical polishing with diamond films and a colloidal silica suspension. Elemental analysis was conducted by energy-dispersive x-ray spectroscopy (EDS) using an AMETEK EDAX detector on the Hitachi 4800S SEM. Electron backscatter diffraction analysis (EBSD) was conducted using an Oxford Instruments Nordlys detector on the FEI Versa SEM.

2.2 Fabrication of SiC joints

The SiC joints were prepared using diffusion bonding with titanium and molybdenum foil inserts, SiC nanopowder sintering-based joining using slurry and green tape, Ti-Si-C based reaction sintering, and hybrid preceramic polymer/CVI joining, as summarized in Table 1. The substrates of all the joints were high-purity chemical vapor-deposited (CVD) SiC (Dow Chemical Co., Marlborough, Massachusetts). The SiC-bonded plates of all the joints, other than hybrid polymer/CVI joint, were fabricated followed by machining of the miniature hourglass specimens. The SiC substrates of the hybrid polymer/CVI joint were machined into half pieces of the hourglass specimen, and then the halves were joined.

Table 1 Summary of SiC joining methods and the bonding phases

Joining method	Processing conditions Temperature/applied stress	Phases present in joint layer
Titanium foil diffusion	1500°C/17MPa	Ti ₃ SiC ₂ , TiSi ₂
Molybdenum foil diffusion	1500°C/20MPa	Mo ₆ Si ₃ C ₄ , Mo ₂ C
SiC nanopowder slurry sintering	1850°C/10MPa	SiC, Y-Al-Zr oxides
SiC nanopowder green sheet sintering	1850°C/10MPa	SiC, Y-Al-Zr oxides
Ti-Si-C reaction sintering	Proprietary	Ti ₃ SiC ₂ , SiC, minor TiC
Hybrid polymer/CVI	~1500°C/<1MPa	SiC

The interlayer of the titanium diffusion bond was a titanium foil (25 µm thick, 99.94% pure, Alfa-Aesar, Ward Hill, MA). The joining of the SiC/Ti foil/SiC sandwiches was accomplished by hot-pressing at 1500°C, for 1 h, in vacuum, under a uniaxial pressure of 17 MPa. To reduce oxygen partial pressure in the furnace, titanium powder was used as the oxygen getter. The Mo diffusion bonding utilized a molybdenum foil as an interlayer (25 µm thick, 99.95% pure, Alfa-Aesar, Ward Hill, MA). The joining of SiC/Mo foil/SiC sandwiches was accomplished by hot-pressing at 1500°C, for 1 h, in a flowing Ar-4%

H₂ atmosphere under a uniaxial pressure of 20 MPa. During hot-pressing, the presence of both hydrogen and the titanium powder facilitated effective oxygen gettering. The size of the SiC substrate was 21.0 × 31.2 × 6.2 mm for both the titanium and molybdenum diffusion bonds. The metal diffusion bonding used an applied stress of ~20 MPa during processing, the application of which may be restricted for the end plug joining of an LWR cladding with a thin wall. However, this potential issue could be solved; Jung et al. recently achieved a significant reduction of the applied stress during the metal diffusion bonding of SiC by additional use of Si powders [11].

Two types of SiC nanopowder sintering-based joints were prepared in this study: joining using a mixed powder slurry and using a commercial green sheet. The green sheet consisted of the feedstocks for the SiC nanophase slurry plus an organic binder to give the sheet enough strength and flexibility for handling. The advantage of using the green sheet was the ease of controlling the joint thickness. However, the substantial amount of organic additives in the sheet may affect the quality of the final product. In contrast, the slurry method does not require organic additives, so a high-quality joint can be achieved. The drawback of the slurry method was the difficulty of controlling the joint thickness. The slurry was prepared by milling a mixed powder with zirconia balls in ethanol. The mixed powder consisted of a SiC nanosize powder (average diameters ~30 nm, Nanomakers, France), and an Al₂O₃ powder (average diameters ~0.3 μm, Kojundo Chemical Lab. Co. Ltd., Japan), a Y₂O₃ powder (average diameters ~0.4 μm, Kojundo Chemical Lab. Co. Ltd., Japan). The total amount of oxide additives was 6 wt % with a weight ratio of Al₂O₃:Y₂O₃ = 3:2. The slurry was sandwiched by CVD SiC plates and then dried at ~80°C before heating. After that, the joint was formed by hot-pressing at 1850°C, for 1 h, in an argon atmosphere, under a pressure of 10 MPa. The feedstock of the green tape was the same as that of the slurry sintered joint except for the additional use of organic binders. The green tape was provided by Gunze Ltd. in Japan. The joining of the SiC/green tape/SiC sandwiches was accomplished by hot-pressing. The hot-pressing conditions were the same as those for the SiC nanopowder slurry sintered joint. The dimensions of the SiC substrate were 40 × 40 × ~5 mm. Again, the applied stress during joining may need to be mitigated for end-plug joining. The stress could be mitigated by using a pressureless sintering process, which has been demonstrated for bulk nanopowder sintered SiC [12].

For fabrication of the Ti-Si-C reaction sintered joint, a joining agent material was purchased from Hyper-Therm High Temperature Composites Inc. (currently Rolls-Royce High Temperature Composites Inc., Huntington Beach, CA). The bonded SiC plate with a Ti-Si-C phase-based bonding layer was produced based on a pressureless slurry process according to the Hyper-Therm formula. Details of the raw materials and the process conditions are proprietary. The size of the bonding plate was same as the size for the metal diffusion bonds.

The bonds for hybrid preceramic polymer pyrolysis/CVI joining were formed by a two-step process. First, the half pieces of the hourglass specimens were joined using a SiC forming polymer with SiC whiskers. The polymer-driven bonding layer was typically porous. Next, the bonding layer near the specimen surface was densified via a CVI process. The outermost surface of the bonded specimen was a layer of dense CVI (or CVD) SiC coating, which connected the substrates. The maximum temperature and applied stress during processing were $\sim 1500^{\circ}\text{C}$ and $< 1\text{MPa}$, respectively. The details of the processing method can be found elsewhere [13].

3. Results

3.1 Mechanical properties of the SiC joints

Figure 3 and Table 2 summarize the results of the torsional shear tests of the unirradiated and irradiated SiC joints. The torsional shear test can provide the shear strength based on Eq. (1) if the specimen fails in shear and a fracture initiates from the surface of the neck section. The fracture mode could be identified based on fractography. However, a clean shear failure did not occur for most of the joint types. In addition, the fracture initiation site could not be identified because multiple cracks were found after the testing. Therefore, the strength measured was the apparent shear strength. However, the data is still useful for comparing the strength of the joints before and after irradiation. All of the unirradiated joint types except the SiC nanopowder slurry sintered joint exhibited shear strengths of 93–147 MPa, on average. The SiC nanopowder slurry sintered joints showed relatively high average shear strengths of 320 MPa. The relatively high strength of this type of joint was also reported in a previous study [5]. Figure 3 also shows the effects of the irradiation on the joint strengths. The irradiation degraded the joint strength of the molybdenum joints by greater than 40%. The titanium diffusion bond and Ti-Si-C reaction sintered joint also showed reductions in their average strengths caused by irradiation. A large degree of data scatter was observed for the titanium diffusion bond and two types of the SiC nanopowder sintered joints. The SiC nanopowder green sheet joint and hybrid polymer pyrolysis/CVI bonds did not show strength degradation resulting from irradiation. Even though degradation in the average strength was found in some types of joints, the average apparent shear strengths were at least 84 MPa.

Fig. 3 Apparent torsional shear strengths of unirradiated and irradiated SiC joints. Error bars indicate one standard deviation.

Table 2 Summary of torsional shear tests of SiC joints before and after irradiation. Numbers in parentheses indicate one standard deviation. Examples of fracture appearance are shown in Fig. 4.

Joining method	Condition	Apparent shear strength [MPa]	Fracture surface	Number of test specimen
Titanium foil diffusion	Unirradiated	133 (22)	S ¹	6
	280–310°C/8.7dpa	86 (66)	S	3
Molybdenum foil diffusion	Unirradiated	146 (14)	S	7
	280–310°C/8.7dpa	84 (6)	J ²	3
SiC nanopowder slurry sintering	Unirradiated	320 (31)	S	6
	280°C/8.7dpa	226 (156)	S, P ³	3
SiC nanopowder green sheet sintering	Unirradiated	116 (24)	S, P	9
	280°C/8.7dpa	109 (54)	S, P	4
Ti-Si-C reaction sintering	Unirradiated	147 (12)	S	8
	290°C/8.7dpa	123 (13)	S	3
Hybrid polymer/CVI	Unirradiated	93 (12)	J	4
	270°C/8.7dpa	93 (17)	J	4

¹Substrate; ²Joint plane; ³Substrate and joint plane

Figure 4 shows the typical fracture appearances of the unirradiated joints. All the SiC joints showed fractured surfaces of the SiC substrate (Fig.4a) except for the SiC nanopowder green sheet and the hybrid polymer/CVI joints. The neck parts of those specimens were shattered into pieces during the tests, which made identification of the fracture initiation sites impossible. The hybrid polymer/CVI joint showed shear failure (Fig.4b). The joints formed with a SiC green sheet exhibited substrate failure or failure partially at the bonding plane (Fig.4c). A clear change in the fracture appearance after irradiation was observed in the molybdenum diffusion joints. Shear failure was observed following irradiation, whereas the unirradiated joints exhibited substrate failure. Another indication of the irradiation effect on the failure mode was observed in the SiC nanopowder slurry sintered joints. The irradiated specimen with the least strength (46 MPa) showed partial joint failure, similar to the image in Fig.4c. The other two specimens showed significantly higher strength values (~315 MPa) and substrate failure, which was similar to the failure mode in the unirradiated specimens. Therefore, the large strength deviation in the irradiated SiC nanopowder slurry joint was affected by one unusual joint. A change in the fracture mode resulting from radiation was not observed for the other types of joints.

Fig. 4 Examples of fracture surfaces of torsion tested joints: (a) failure at substrate, (b) failure at joint plane, and (c) failure at both substrate and joint plane.

3.2 Microstructures of SiC joints

3.2.1 Titanium diffusion bond

The phases in the titanium diffusion joint were identified by EBSD analysis of the cross section of a joint specimen, as shown in Fig. 5a-c. The bonding layer consisted of the layered structure of the Ti_3SiC_2 adjacent to the SiC substrates and TiSi_2 at the middle of the bonding layer. The joint thickness was approximately 50 μm . No strong texture was observed for the Ti_3SiC_2 phase, and the TiSi_2 phase had a

continuous single grain. Both Ti_3SiC_2 and TiSi_2 were also detected following irradiation, but the quality of the mapping was degraded. A TiC phase was rarely detected in the irradiated material in this study, although TiC has been reported to be formed from Ti_3SiC_2 by radiation-enhanced dissociation [14]. The backscattered electron images of the joint before and after irradiation are shown in Fig. 5c, d. The as-fabricated bonding layer contained micro-cracks within the bonding layer. Irradiation clearly increased the number of cracks, which mainly propagated vertically to the joint interface. The cracks appeared to start from or end at the SiC substrate. The nature of the cracks (intergranular or intragranular) was not identified in this study owing to the poor quality of the EBSD signal of the Ti_3SiC_2 phase. The degradation of the EBSD phase map, especially for Ti_3SiC_2 , is expected to be due to lattice distortion by irradiation damage because the surface preparation for the EBSD analysis was similar between the unirradiated and irradiated specimens.

Fig. 5 EBSD analysis of titanium diffusion bond (a) phase map of unirradiated joint, (b) Euler color maps of unirradiated joint, and (c) phase map of irradiated joint. TiC was not found in the irradiated joint, although it can be formed by radiation-enhanced dissociation of Ti_3SiC_2 . Backscattered electron micrographs of titanium diffusion bond ((a) unirradiated and (b) irradiated) are also shown.

3.2.2 Molybdenum diffusion bond

The bonding layer of the unirradiated molybdenum diffusion joint consisted of a layered structure of $\text{Mo}_{0.5}\text{Si}_3\text{C}_{4.1}$ adjacent to the substrate and Mo_2C at the center of the joint layer (Fig. 6a, b). The phases were identified using SEM EDS and x-ray diffraction. The phases were similar to those reported in the previous work [15]. The preexisting defects in the unirradiated condition were cracks vertical to the joint interface. The irradiation significantly introduced “vertical” cracks in the bonding layer (Fig. 6c), which is similar to the phenomenon observed in the titanium diffusion bond. Moreover, the cracks in the irradiated joint formed networks, as shown in Fig. 6d.

Fig. 6 Backscattered electron images of Mo diffusion bond: (a, b) unirradiated and (c, d) irradiated.

3.2.3 SiC nanopowder sintered joint

Figures 7 show cross-section backscattered electron micrographs of two types of SiC nanopowder sintered joints before and after irradiation. Sintering the SiC nanopowder with oxide additives formed a SiC-based bonding layer with secondary phases. The joint thicknesses were ~ 80 and ~ 150 μm for the SiC

joints formed using a slurry and a green sheet, respectively. The joint layer appeared to be highly dense for the slurry system. In addition, the secondary phases attributed to the oxide additives were well dispersed. The microstructure of the green sheet joint was clearly different from that of the slurry joint. The green sheet joint was partially debonded as a result of the presence of large pores. In addition, significant segregation of the secondary phases was observed in the bonding layer. Those results show that the microstructure of the green sheet joint was not uniform. SEM-EDS mapping shown in Fig. 8 reveals that the secondary phases consisted of aluminum, yttrium, and zirconium oxides in the as-fabricated condition. The detection of a substantial amount of zirconium in the oxide phases was unexpected because the only sintering additives used were alumina and yttria. The zirconium contamination likely came from the milling media during the processing. The EDS analysis estimated the inclusion of zirconium in the bonding layer was ~5 wt %. The SEM observation following the irradiation (Fig. 7b, e) did not show any obvious microstructural changes.

Fig. 7 Cross-section backscattered electron micrographs of SiC nanopowder sintered joints: (a) slurry method, unirradiated, (b) slurry method, irradiated, (c, d) green sheet method, unirradiated, and (e) green sheet method, irradiated. Bonding layer is indicated by arrow.

Fig. 8 SEM-EDS elemental maps of unirradiated SiC nanopowder sintered joint formed using slurry.

3.2.4 Ti-Si-C reaction sintered joint

Cross-section backscattered electron images of the unirradiated Ti-Si-C reaction sintered joint are shown in Fig. 9a, b. The joint layer appears to be dense, and the joint thickness is about 150 μm . The dominant processing defect in the joint layer is a crack perpendicular to the joint boundary. Figure 10 presents results of the EBSD analysis showing the bonding phases in the unirradiated material. The bonded zone consisted of SiC grains and Ti-Si-C phases. The phase mapping shows that the bonding layer consisted of 43 vol % Ti_3SiC_2 , 42 vol % SiC phases (mainly 6H and 4H SiC), and 15 vol % of TiC. No strong grain texture in the joint phases was observed in the Euler color map.

Irradiation resulted in significant micro-cracking, as shown in Fig. 9c. The cracks were formed within the Ti_3SiC_2 and TiC phases. The overall crack path could not be identified because of the poor quality of the EBSD signal, which was the same phenomenon observed in the titanium diffusion bond. Only specific cracks were characterized using EBSD; the irradiation-induced cracks within a relatively large Ti_3SiC_2 grain were analyzed, as shown in Fig. 11. The band contrast image shows three cracks in the Ti_3SiC_2 propagating in the same direction. The crystallographic orientation view shows that the crack length direction was nearly parallel to the c-axis of the Ti_3SiC_2 .

Fig. 9 Cross-sectional backscattered electron micrographs of Ti-Si-C based reaction sintered joint: (a, b) unirradiated, and (c) irradiated.

Fig. 10 EBSD analysis of bonding layer of unirradiated Ti-Si-C based reaction sintered SiC joint: (a) band contrast image, (b) phase map, and (c) Euler color map.

Fig. 11 EBSD analysis of irradiated Ti-Si-C based reaction sintered SiC joint: (a) band contrast image, (b, c, d) surface normal crystallographic orientation of 6H SiC grains, and (e) surface normal crystallographic orientation of Ti_3SiC_2 grain. Figs (b,c,d,e) show schematic unit cells of hexagonal structure.

3.2.5 Hybrid polymer pyrolysis/CVI joint

Both the polymer pyrolysis and CVI joining methods provided pure SiC bonding layers. The cross-section secondary electron micrograph of the unirradiated torsion specimen shows the porous polymer bonding layer between the SiC substrates. The CVI SiC was applied in such a way that it partially penetrated the porous, polymer-derived SiC layer on the outer $\sim 500\ \mu\text{m}$ of the joint diameter, as shown in Fig. 12a, and deposited a thin CVI SiC layer on the outside of the joint. The CVI layer connected the SiC substrates. Both the densified polymer bonding layer and the CVI layer contributed to the joint strength, since the maximum force was applied at the surface of the hourglass specimen during the torsion test. The joint microstructure did not appear to be changed by irradiation: no indication of damage such as micro-cracks was observed (Fig. 12b). This result was consistent with the retention of the torsional shear strength (Fig. 3). EBSD identified the bonding phases in the unirradiated joint, as shown in Fig. 13. The band contrast image, phase map, and Euler color map revealed that the phases of the polymer/CVI joint

consisted of mainly beta (3C) SiC grains with a few micron sizes and random orientations. The unidentified area in the phase map indicates the porous region. On the other hand, the phases in the CVI layer appeared to be a mixture of beta and alpha (6H and 4H) SiC. The grain size was sub-micron. In addition, a large fraction of the phases could not be identified, even though the CVI layer was dense. The grain size appeared to be smaller than the resolution limit (~ 100 nm) or amorphous-like SiC phases.

Fig. 12 Secondary electron micrographs of hybrid polymer/CVI joint: (a) unirradiated, and (b) irradiated. A cross-section of hourglass torsion near the edge was observed.

Fig. 13 EBSD analysis of unirradiated hybrid polymer/CVI SiC joint: (a) band contrast image, (b) phase map, and (c) Euler color map.

4. Discussion

4.1 Effects of irradiation on strengths of SiC joints

This study observed three types of fracture behavior of the SiC joints, as shown in Fig. 4. Failure at the joint plane is expected to initiate within the bonding plane or joint interface. Substrate failure and partial joint failure can occur as a result of fracture initiation from either the joint interface, bonding layer, or substrate. The torsional shear strength and the fracture appearance are expected to be affected by the strength of the bond at the joint interface, strength of the bonding layer, internal residual stress, surface condition, and elastic modulus of the bonding layer.

The strength degradation of the irradiated titanium and molybdenum diffusion bonds and the Ti-Si-C reaction sintered joint can be explained by the irradiation-induced cracking observed using SEM. The cracking resulted not only in degradation of the strength of the bonding layer but also in a decrease in the modulus of the bonding layer. The reduction in the joint modulus caused an increase in the effective loading on the bonding layer during the torsion test and consequently reduced the degradation of the torsion strength based on a fine element analysis [16]. Therefore, the significance of the radiation-induced cracking is that it helps explain the strength degradation mechanism, although other factors affecting the torsional strength, such as residual stress, cannot be clearly discussed because they are difficult to characterize. The degradation of the joint strength was most significant in the molybdenum diffusion bond, which was consistent with the substantial network cracking in the bonding layer. Despite the strength degradation, those joints showed an average apparent shear strength of more than 84 MPa. However, the substantial irradiation-induced cracking would cause an issue in LWR cladding applications because of the expected loss of leak-tightness at the joint section.

The strength of the SiC nano-powder slurry joint was relatively high compared with the other joints (Fig. 3). This might be attributed to the higher modulus and/or strength of the bonding layer and lower residual stress at the joint interface. The torsional shear test demonstrated the SiC nano-powder slurry joint was much stronger than the green sheet joint. This result is reasonable because the green sheet joint contained substantial defects, such as pores and significant oxide phase formation. The presence of these defects can also explain the differential fracture behavior of the torsion specimens: substrate failure for the slurry joint and partial joint failure for the green sheet joint. A discussion point is the cause of the substantial strength deviations for both of these types of SiC joints following irradiation. A possibility is nonuniformity of the microstructures of the joints among the test specimens. The torsional tests found that the relatively weak joint specimens were taken from a particular part of the original bonded plates, such as the near edges of the plates. Since the strength deviations in the unirradiated joint were moderate, the

strength of the irradiated joints is suspected of being more sensitive to behaviors in the microstructure, possibly because of poor irradiation resistance in the secondary phases [17]. Since some specimens did not show strength degradation resulting from irradiation, and no obvious microstructural change in the bonding layer was observed using SEM, SiC nanopowder sintered joints are potentially useful for LWR clad applications when microstructures such as secondary phase formation are well controlled.

The hybrid polymer pyrolysis/CVI joint did not show strength degradation, a finding consistent with its stable microstructure following irradiation. Although the strength of the hybrid polymer/CVI joint was comparatively lower than that of the other joints in the unirradiated condition, previous work has shown that cylindrical joints made using this material provide ample strength and permeability for LWR applications [18].

3.2 Effects of irradiation on the microstructure of the SiC joints

The cracks within the bonding layers are defects observed in both unirradiated and irradiated joints formed by titanium and molybdenum diffusions and Ti-Si-C reaction sintering. These bonding layers consisted of the metal-SiC reactants, including metal silicide, metal carbide, and metal silicon carbide. The “vertical” cracks observed in these unirradiated bonding layers are known to be formed by a mismatch of the coefficient of thermal expansion (CTE) between the bonding layer and the SiC. The CTE of SiC is typically smaller than those of the metal-SiC reactants [15], and the difference results in the cracking attributed to tensile residual stress within the bonding phases during the cooling of the joint.

Similar to the cracks caused by CTE mismatch, the differential dimensional stability between the substrate and the joint phases under irradiation explains the irradiation-induced cracks. The cracking was likely due to the differential swelling between SiC and the bonding layer, which was also discussed in the previous work on the effects of irradiation on SiC joints [5]. The larger swelling of the SiC substrate compared with the bonding phases can explain the vertical cracks in the bonding layers of the titanium and molybdenum diffusion bonds. For example, the volumetric swelling of SiC at 300°C to more than ~0.1 dpa was reported to be ~1.5% [6]. On the other hand, the volumetric swelling of Ti_3SiC_2 obtained from x-ray diffraction was reported to be ~0.7 % at 300°C to ~0.4 dpa for SiC [14]. The larger swelling of the substrate compared with the joint phases results in tensile residual stresses within the bonding layer, causing cracking in the bonding phase. The swelling behaviors of TiSi_2 , $\text{Mo}_{0.5}\text{Si}_{3\text{C}_{<1}}$, and Mo_2C are unknown under irradiation at ~300°C. The irradiation-induced vertical cracks implied larger swelling of SiC than of those phases.

The irradiation-induced cracks in the Ti-Si-C reaction sintered joint propagated in relatively random directions. The differential swelling among the joint phases would explain the cracking observed within Ti_3SiC_2 grains surrounded by SiC grains (Fig. 11). Since the c-axis and the a-axis of Ti_3SiC_2 expand and slightly shrink, respectively [14], and the surrounding SiC grains swell under irradiation, the differential swelling could generate tensile residual stresses within the basal plane and consequently introduce cracks along the c-axis of the Ti_3SiC_2 phase. The differential swelling would reasonably explain the irradiation-induced cracking mainly observed in the Ti_3SiC_2 phases. Note that grain boundary cracking was also possible as a result of the anisotropic swelling of Ti_3SiC_2 [14], which was not clearly detected in this study because of the difficulty of the analysis. The cracking due to anisotropic swelling along the a- and c-axes was reported in $\text{Ti}_3\text{AlC}_2\text{--Ti}_5\text{Al}_2\text{C}_3$ material [19].

Irradiation-induced cracking was not observed in the SiC-based bonding layers of the SiC nanopowder sintered joint and the hybrid polymer pyrolysis/CVI joint. These results indicate similar swelling behaviors between the bonding layers and the substrates in these joints. The swelling of nanopowder sintered SiC with Y-Al oxides was only slightly higher than that of CVD SiC at $\sim 300^\circ\text{C}$ [20]. This study revealed that the secondary phases did not appear to affect the microstructural stability of the irradiated nanopowder sintered SiC joint. The swelling of the SiC phases in the hybrid polymer/CVI joint was expected to show similar swelling to the substrate because of the pure SiC phases. Since the SiC phases in the CVI layer contained hexagonal SiC, a concern was grain boundary cracking due to the anisotropic lattice swelling of the hexagonal phases. However, this phenomenon was not observed in this study. Snead et al. revealed isotropic lattice expansion of single-crystal alpha SiC irradiated at $\sim 60^\circ\text{C}$ [21], which is consistent with our observation, although the irradiation temperature was different. Therefore, the presence of the hexagonal phases was not an issue for the irradiation resistance of the CVI SiC layer. The proven irradiation tolerance of SiC [6] in the hybrid polymer/CVI bonding layer is the most likely reason the joint strength and the microstructure were maintained.

5. Conclusions

The irradiation resistance of candidate SiC joints for LWR cladding applications was investigated by neutron irradiation at $270\text{--}310^\circ\text{C}$ to 8.7 dpa for SiC, followed by a torsional shear test and microstructural observation. The main conclusion is that bonding layers dissimilar to the substrate are not preferred for use under the irradiation condition, in terms of strength retention and microstructural stability. Findings for the individual joint are shown below.

- The titanium diffusion bond with Ti_3SiC_2 and TiSi_2 joint phases was degraded by irradiation. The joint strength appeared to be lowered by 35%, and irradiation-induced cracking was found.
- The molybdenum diffusion bond with the bonding phases of $\text{Mo}_{<5}\text{Si}_3\text{C}_{<1}$ and Mo_2C was also degraded by irradiation. The joint strengths clearly decreased by greater than 40%, and irradiation-induced network cracking was observed.
- The SiC nanopowder sintered joints using a slurry or a green sheet consisted of bonding layers of SiC grains and secondary phases of Y-Al-Zr oxides. Although the deviation in the irradiated strength was large, these joints exhibited excellent microstructural stabilities.
- The Ti-Si-C based reaction sintering method provided a bonding layer of Ti_3SiC_2 , SiC, and TiC. The joint strength showed a slight decrease, which was attributed to irradiation-induced micro-cracking.
- The hybrid polymer pyrolysis/CVI method formed SiC bonding layers. The joint retained its strength and showed excellent microstructural stability following irradiation.
- In cases in which the majority of the bonding layer was a non-SiC phase, the differential swelling between the joint phases and the SiC substrate likely caused the observed cracking. On the other hand, the differential swelling did not occur in the SiC-based bonding layers, even though the secondary phases were present or both the cubic and hexagonal SiC phases existed.

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