3.1 DEVELOPMENT OF SiC JOINING TECHNOLOGIES FOR FUSION: PRE-IRRADIATION EXPERIMENT —T. Koyanagi, J.O. Kiggans, and Y. Katoh (Oak Ridge National laboratory), T. Hinoki (Kyoto University, Japan), M. Ferraris (Politecnico di Torino, Italy), C.H. Henager (Pacific Northwest National Laboratory), C.A. Lewinsohn (Ceramatec Inc.), S. Grasso (Queen Mary University of London)

OBJECTIVE

The objective of this work is the development of an irradiation tolerant joining technology for fusion. This report presents mechanical property and microstructure data of various silicon carbide (SiC) joints in the unirradiated condition.

SUMMARY

Various SiC joints were prepared using diffusion bonding with active titanium and molybdenum inserts, pressurized and pressureless transient eutectic-phase (TEP) sintering, pressurized and pressureless reaction-formed Ti-Si-C MAX-phase bonding, $CaO–Al_2O_3$ (CA) glass ceramics, and Al-Si-C-O braze. Torsional shear strength, fracture behavior, and microstructural of the bonding layer were evaluated in the unirradiated condition. These results are being used as the basis to understand neutron irradiation effects on mechanical properties and microstructures of the SiC joints.

PROGRESS AND STATUS

Introduction

The development of SiC joints that retain adequate mechanical and functional properties in the anticipated service conditions is a critical step toward establishment of advanced SiC composite technology for fusion structural components [1]. Neutron irradiation is among the most critical factor for the fusion blanket components under the service operations. For the purpose of determining the effects on neutron irradiation at fusion-relevant temperatures on strength and microstructures of SiC joints, candidate SiC joints were irradiated in the High Flux Isotope Reactor at 500 and 800°C up to 5 dpa and evaluated by torsional shear tests and microstructural observations. The results show that the effect of irradiation on joint strength was insignificant for all the joints such as titanium diffusion bonding, Ti–Si–C MAX-phase joining, calcia–alumina glass–ceramic joining, and transient eutectic-phase SiC joining [1].
For further development of SiC joining technology, this work is being extended to different irradiation conditions (higher irradiation temperatures or higher neutron fluences) and different types of the joints. This report presents results of pre-irradiation experiments, baseline information on the SiC joints to be used for the irradiation experiments including data for torsional shear tests, microstructural observations, and phase identifications. The post-irradiation experiments on the SiC joints are in progress at ORNL.

Joining Procedure and the Microstructure

The various SiC joints were prepared at Oak Ridge National Laboratory or by outside collaborators, using diffusion bonding with the active titanium and molybdenum inserts, pressurized transient eutectic-phase (TEP) joining using slurry and green tape, pressureless TEP joining, reaction-formed Ti-Si-C MAX-phase bonding with pressure-less sintering, hot-pressing, or spark plasma sintering (SPS), CA glass ceramics joining, and Al-Si-C-O braze-based joining, as summarized in Table 1. High-purity chemical vapor deposited (CVD) SiC was used for substrate material for all the joints.

Table 1. SiC joints prepared in this work.

Method of joining	Joint alias	Main phases present in joint layer	Material provider
Ti diffusion	Ti dif	Ti_3SiC_2, TiC_x	ORNL
Mo diffusion	Mo dif	$Mo_{4.8}Si_3C_{0.6}$, Mo_2C	ORNL
Pressurized TEP using slurry	TEPs	SiC, Y-Al-Zr-O	Kyoto Univ.
Pressurized TEP using green tape	TEPt	SiC, Y-Al-Zr-O	Kyoto Univ.
Pressureless TEP	PL TEP	SiC, Y-Al-O	ORNL
Pressure-less Ti-Si-C MAX-phase	PL MAX	SiC, Ti_3SiC_2	ORNL
Ti-Si-C MAX-phase hot pressing (I)*	HP MAX(I)	SiC, Ti_3SiC_2	PNNL
Ti-Si-C MAX-phase hot pressing (II)*	HP MAX(II)	SiC, Ti_3SiC_2	PNNL
Ti-Si-C MAX-phase SPS	SPS MAX	Ti base phases	Queen Mary Univ.
Calcia-Alumina glass	CA glass	Ca-Al Oxides	Politecnico di Torino
Al-Si-C-O braze-based joining	Braze	Al-C-O, Al-Si-C-O and Al-O phases	Ceramatec

* The main difference between HP MAX (I) and (II) is joint thickness.

(1) Titanium diffusion-bonded SiC

Pure titanium foil (25 μm thick, 99.94% pure, Alfa-Aesar, Ward Hill, MA) was used for diffusion bonding. The Ti foil joints were fabricated at ORNL. The joining of SiC/metal/SiC sandwiches was accomplished by hot-pressing at 1500°C, for 1 h, in vacuum, under a uniaxial pressure of 17 MPa. Estimated partial pressure of oxygen impurity in the furnace was ~0.6 Pa. To reduce oxygen partial pressure in the furnace, titanium powder was used as the oxygen getter. Reduction of oxidation during joining is a key for Ti foil joint to increase the joint strength and to reduce the processing defect at the joint layer [2].

The joint microstructure was reported in our previous work [2]. The joint thickness was ~40 μm. The joint layer exhibited Ti_3SiC_2 phase near the joint interface and mixed structure of Ti_3SiC_2 and TiC_x at the center of the joint layer. The joint layer contained micro-cracks as a pre-existing defect.

(2) Molybdenum diffusion-bonded SiC

Pure molybdenum foil (25 μm thick, 99.95% pure, Alfa-Aesar, Ward Hill, MA) was used for Mo diffusion bonding. The Mo foil joints were fabricated at ORNL. The joining of SiC/metal/SiC sandwiches was accomplished by hot-pressing at 1500°C, for 1 h, in flowing Ar-4% H_2 atmosphere, under a uniaxial pressure of 20 MPa. Estimated partial pressure of oxygen impurity in the furnace was ~0.02 Pa. During the hot-pressing, the presence of both hydrogen and titanium powder facilitated effective oxygen gettering.

The joint microstructure was also reported in our previous work [2]. Mo foil-joined SiC had a layered structure of $Mo_{4.8}Si_3C_{0.6}$ near the joint interface and Mo_2C phases at the center of the joint layer. The joint contained cracks roughly perpendicular to the joint boundary in the as-processed condition. The joint thickness was ~35 μm.

(3) SiC joints formed by pressurized TEP method using SiC-based slurry and green tape

Two types of TEP joining were prepared in this work: the joining using mixed powder slurry (TEPs) and the joining with a commercial green tape (TEPt). Both joints were fabricated at Kyoto University in Japan.

To make the slurry for the TEPs joining, SiC nano-phase powder (average diameters ~30 nm), and Al_2O_3 powder, Y_2O_3 powder were dispersed in ethanol. The total amount of oxide additives was 6 wt%. The powder mixture was prepared by milling with ZrC balls. For the fabrication of TEPs joint, the slurry was sandwiched by CVD SiC plates, and then dried at ~80°C. After that, the TEPs joint was formed by hot-pressing at 1850°C, for 1 h, in an Ar atmosphere, under a pressure of 10 MPa.

The feedstock of the green tape for the TEPt joint was same as that of the TEPs slurry except for the additional use of organic binder. The green tape was provided by in Gunze ltd. in Japan. The joining of SiC/green tape/SiC sandwiches was accomplished by hot-pressing. The hot-pressing conditions were same as those for the TEPs joint.

Cross-sectional backscattered electron image of the TEPs and TEPt joint was shown in Figure 1. The joint thickness was ~80 μm for TEPs joint and ~150 μm for TEPt joint. The TEPs joint layer appeared to be highly dense. On the other hand, the TEPt joint was partially deboned due to the presence of large (~50 to ~100 μm) pores (The image is not presented here). In addition, lineal segregation of the secondary phases was observed in the bonding layer, which was not present in the TEPs joint.

The composition of the secondary phases in the bonding layers was examined using SEM-EDS analysis (Figure 2 for TEPs joint and Figure 3 for TEPt joint). Yttrium, aluminum, and oxygen, which were in sintering additives, were clearly detected as elements of secondary phases in both joints. This is commonly observed in TEP sintered SiC [3]. In addition, the secondary phases contained zirconium as impurity. This may be come from ZrC as ball milling media during processing. Note that TEP joints which showed excellent irradiation tolerance in previous work did not contain Zr impurity [1].

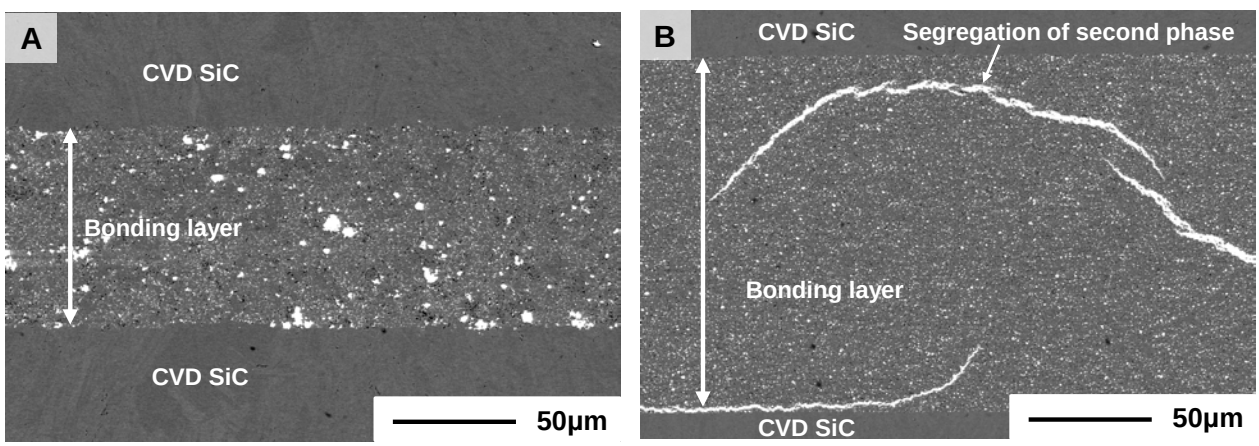

Figure 1. Cross-sectional backscattered electron images of (A) TEPs and (B) TEPt joints.

(4) Pressure-less TEP SiC joint

Pressureless (PL) TEP joint was prepared at ORNL. The joint was formed using the powder mixtures consisting of SiC nano-powder (average diameters ~30 nm), and sintering additives (Al_2O_3 powder and Y_2O_3 powder), with organic agents. The total amount of the oxide additives was 6 wt.%. The total amount of the organic agents was ~3.5 wt.%. The PL TEP joints were formed by sandwiching mixed powder between CVD SiC plates followed by cold-pressing at ~10 MPa in graphite die to partially densify the powder. The sandwiched materials were then heat-treated at 1875°C for 1 h in a flowing argon atmosphere in the graphite. Very small amount of pressure (~0.1 MPa) was applied during heating to hold the specimen in furnace. The detail of the processing condition can be found elsewhere [4].

The microstructure of the bonding layer was reported in previous work [5]. The bonding layer contains some amount of porosity and secondary phases. The secondary phases were analyzed by SEM-EDS as

shown in Figure 4. The mapping shows that large part of secondary phases is a Y-Al oxide material. The impurity element such as Zr was not observed in this joint.

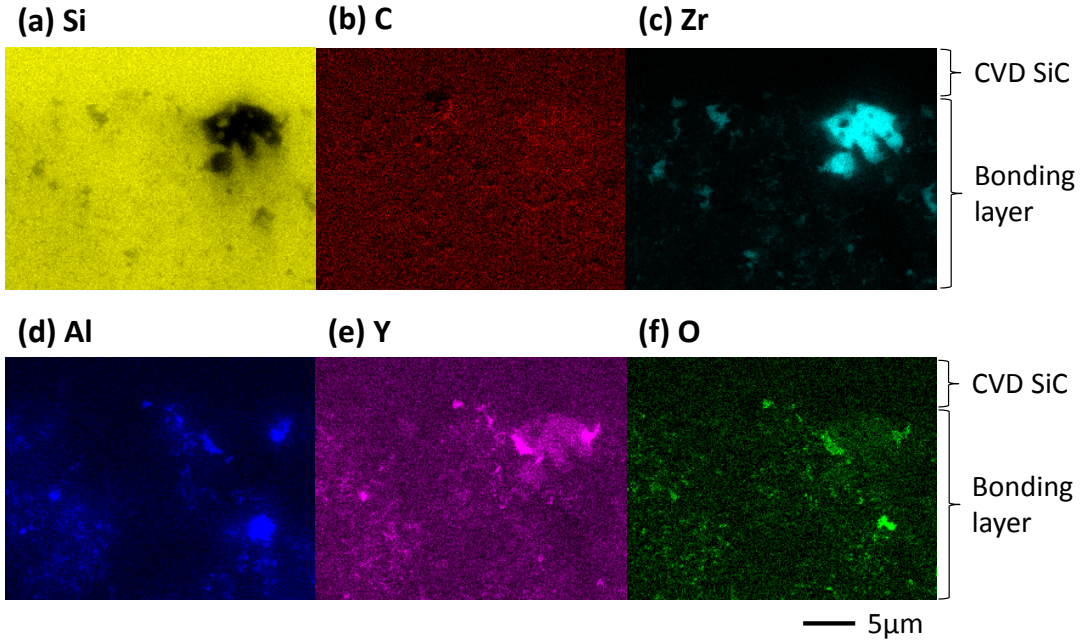

Figure 2. SEM-EDS maps for (a) Si, (b) C, (c) Zr, (d) Al, (e) Y, and (f) O for TEPs joint.

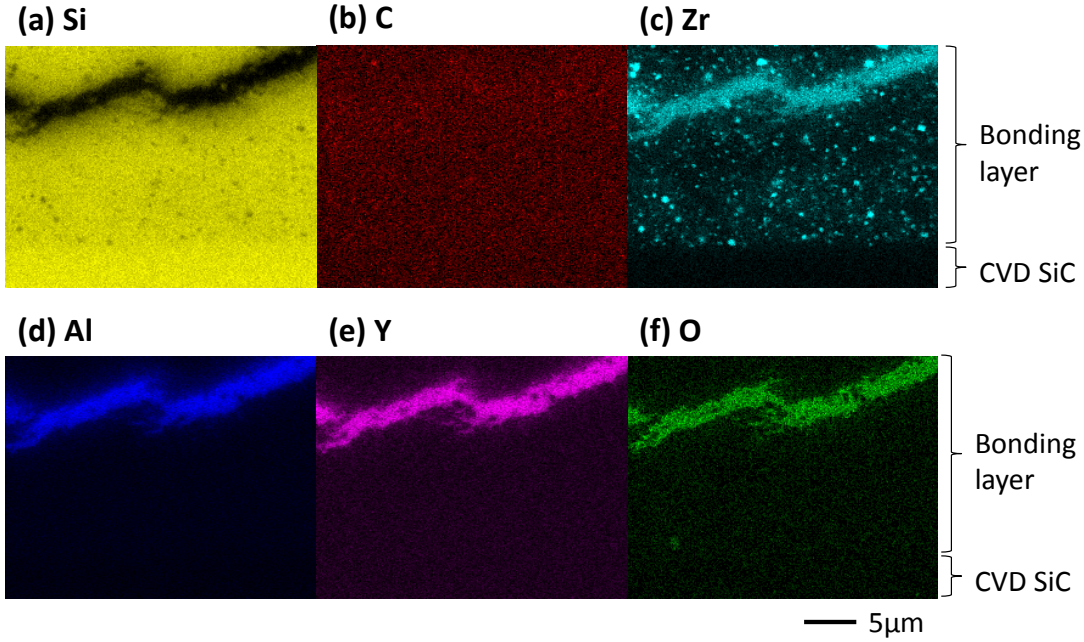

Figure 3. SEM-EDS maps for (a) Si, (b) C, (c) Zr, (d) Al, (e) Y, and (f) O for TEPt joint.

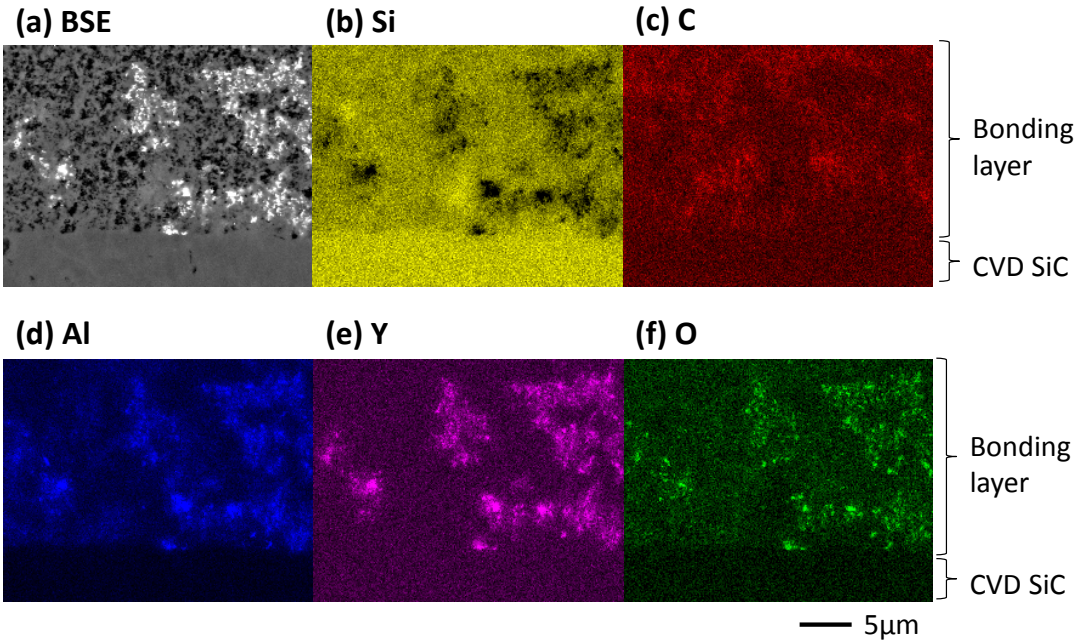

Figure 4 SEM-EDS maps for (a) backscattering electron, (b) Si, (c) C, (d) Al, (e) Y and (f) O, and for PL TEP joint.

(5) Pressureless Ti-Si-C MAX-phase bonded SiC

For PL MAX phase bonding, a set of joining agent materials were purchased from Hyper-Therm High Temperature Composites, Inc. (currently Rolls-Royce High Temperature Composites, Inc., Huntington Beach, CA). Ti-Si-C phase-based joints of CVD SiC were produced at ORNL based on a pressure-less slurry process per the Hyper-Therm formula. Details of the raw materials and the process conditions are proprietary.

The microstructure of the joint was reported in previous work [5]. The joint layer appeared to be dense, and the joint thickness was about 150 µm. The bonded zone consisted of SiC grains and Ti-Si-C phase. The Ti-Si-C phases were expected to be mainly Ti_3SiC_2, and the small amount of Ti-C and Si rich Ti-Si-C phases. The dominant processing defect in the joint layer was crack roughly perpendicular to the joint boundary.

(6) Ti-Si-C MAX-phase jointed SiC by hot-pressing

Two types of Ti-Si-C MAX-phase jointed SiC were prepared at PNNL (HP MAX(I) and (II) hereafter). The HP MAX(I) joint was used for the previous irradiation experiments [1]. The bonding layer was prepared using a tape casting method that includes organic binders and plasticizers together with a mixture of TiC and silicon powder, followed by hot-pressing SiC/bonding layer/SiC sandwich at ~1400°C.

Cross-section backscattering electron images of HP MAX(I) and (II) are shown in

Figure 5. Appearance of the bonding layer is very similar between them, except for the joint thickness. The thickness was approximately 15 to 20 µm for HP MAX(I) and less than 10 µm for HP MAX(II). SEM-EDS analysis revealed that the bonding layer manly consisted of two phases: SiC and Ti-Si-C phases. In addition to those phases, small amount of Fe impurity was contained in both joints, which might be attributed to the impurity of the starting powder.

X-ray diffraction (XRD) patterns of the HP MAX(I) and (II) joints are shown in Figure 6. Both types of joints contain SiC and Ti_3SiC_2 phase in the bonding area. Based on SEM-EDS and XRD results, the main phase in the HP MAX joints are Ti_3SiC_2 and SiC.

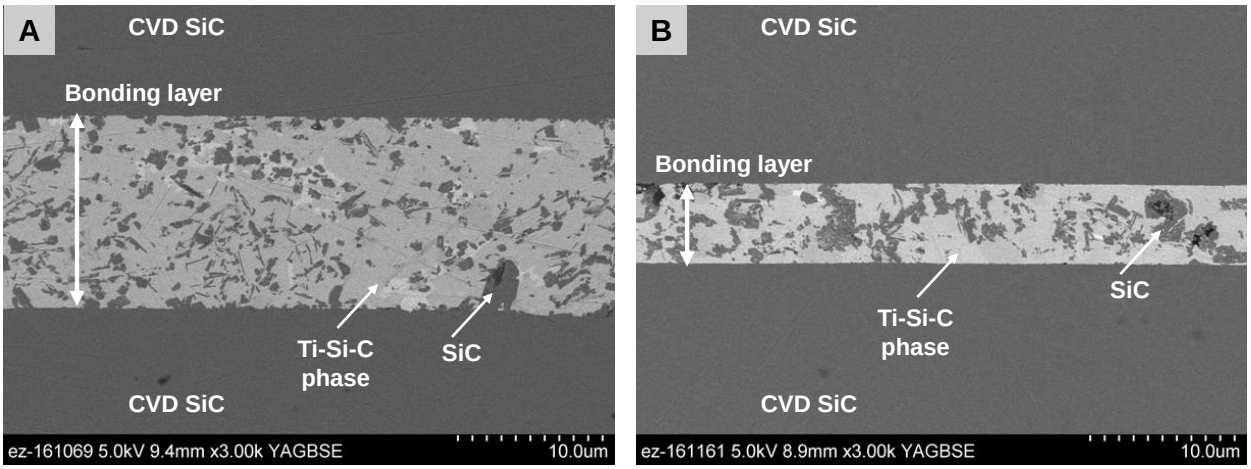

Figure 5 Cross-sectional backscattered electron images of (A) HP MAX(I) and (B) HP MAX(II) joints.

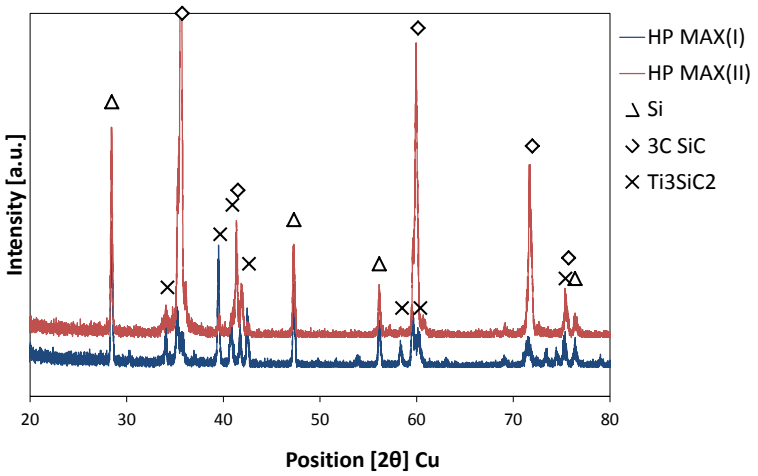

Figure 6 XRD patterns of HP MAX(I) and (II) joints. Silicon powder is used for an internal standard which was not contained in the joint.

(7) Calcia-Alumina glass ceramic bonded SiC

Calcia-Alumina glass-ceramic (CA glass) joint was prepared at Politecnico di Torino in Italy. The joint specimens are same as those used in previous irradiation experiments [1]. The joint phase was reportedly a mixture of $Ca_3Al_2O_6$ and $Ca_{12}Al_{14}O_{33}$ [6]. Details of processing condition and microstructure of the bonding layer can be found in references [1, 6].

(8)Ti reaction bonding by SPS

Additional Ti based SiC joint was formed by SPS with titanium foil as intermediate joining material at Queen Mary University of London. The joint is referred to as SPS MAX. During joining, constant force of 15 kN was applied on hourglass shape CVD SiC/Ti foil/CVD SiC sandwiches, which is used for torsion shear tests. Heating rate was 50°C/minute from 450 to 1700°C, and dwelling temperature was 1700°C for 5 minutes. Cooling condition was 50 °C /minute from 1700 to 450°C. The joining atmosphere was vacuum (5 Pa). Titanium foil with 30 um thickness (Ti000300 grade, Purity:99.6+%, Goodfellow) was used for this joining.

(9)Al-Si-C-O brazed SiC joint

The brazed CVD SiC joint was prepared using Al-Si-C-O system by Ceramatec, Inc. in Utah. The starting materials of the brazing filler metal and the processing conditions are proprietary. The joint thickness was very thin (~3 μm) as shown in Figure 7. The brazed area consisted of complex phases; Al-C-O (phase 1 in Figure 7 (A)), Al-Si-C-O (phase 2 in Figure 7 (A)), Al-O, and Si rich phases were detected by SEM-EDS analysis. In addition, a few micron-sized pores also existed in the bonding layer.

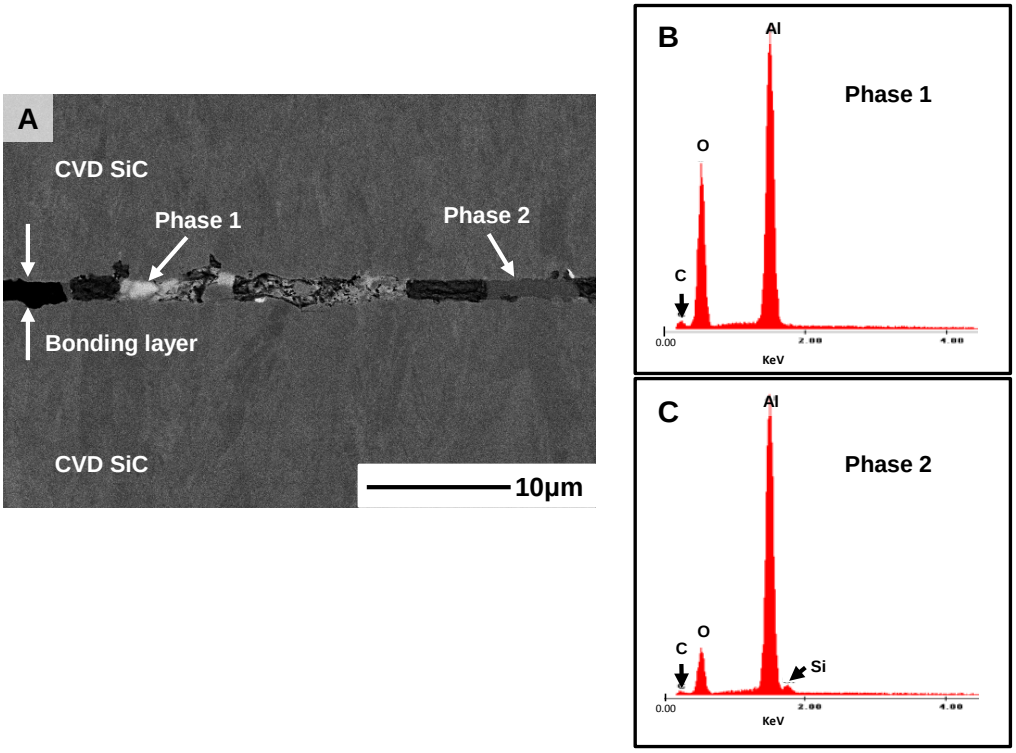

Figure 7. Cross-sectional backscattered electron image of the Al-Si-C-O braze-based joint (A). EDS spectrums of phase 1 and 2 indicated in image A are shown in image B and C, respectively.

Mechanical property of SiC joints

Shear strength of the joint test specimens was evaluated by the torsional shear testing of hourglass-type specimens that had specifically been designed and established for neutron irradiation studies [1]. Detail of the test method can be found elsewhere [4]. Two types of specimen geometries were used in this work; type 6SQ-4D specimen [1] was used for the TEPt, TEPs, and PL TEP joints, and type 6SQ-5D specimen [1] was for the other joints.

Results of pre-irradiation torsion tests on various SiC joints are summarized in Figure 8. The graph shows individual testing result. Three to ten specimens were tested for each joint. All the joints except for TEPs joint exhibited primary a shear strength of 50 to 150 MPa. Relatively high shear strengths of 250 to 350 MPa were obtained from TEPs joints. The typical fracture appearances of the joints are shown in Figure 9. The Ti diff, Mo diff, TEPs, PL TEP, PL MAX, SPS MAX, and Braze joints failed within SiC substrate as shown in Figure 9A, which is typical for the robust joints. It is difficult to identify the location of the crack initiation for these joints, because the neck part of the specimen was shattered into pieces during the test. The TEPt joints exhibited the substrate failure or failure at partially joint interface (Figure 9 (C)). The HP MAX(I) joints mostly failed at the joint plane (Figure 9B). The MAX(II) and CA glass joints completely or partially failed at the joint plane or partially at the joint plan. The differential strength value and the fracture appearance were observed among PL MAX, HP MAX(I) and (II), and SPS MAX joints, though those joints contained SiC and Ti-Si-C phases in the bonding area. The torsional shear strength evaluated in this work may be affected by not only the bonding strength but also

residual stress, surface condition, and differential elastic modulus between bonding layer and SiC substrate.

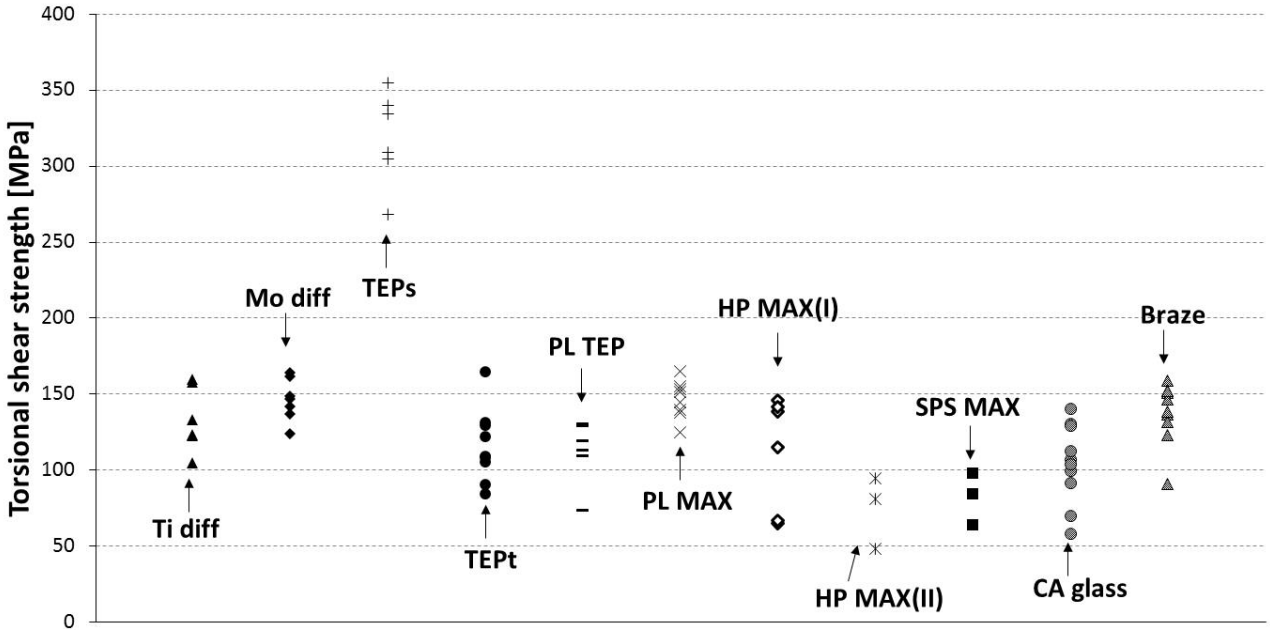

Figure 8. Shear strength of various SiC joints tested in unirradiated condition. The specimen ID is listed in Table 1.

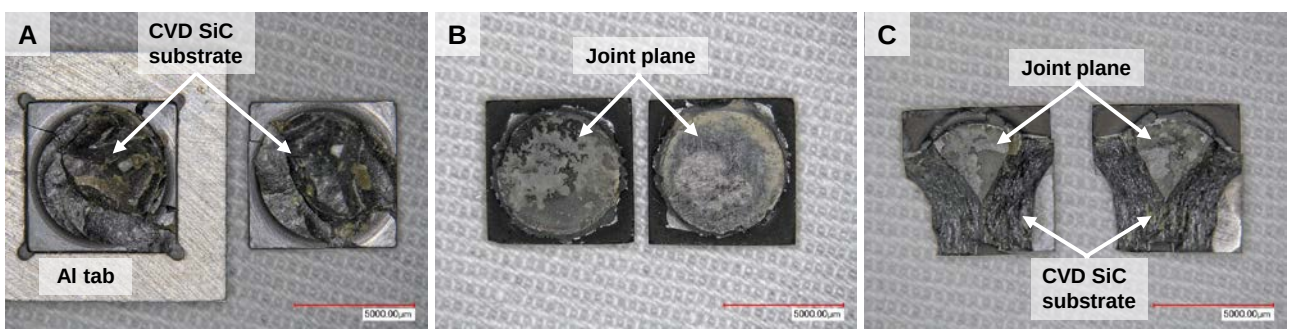

Figure 9. Typical fracture appearance of torsion tested specimens: (A) failure in CVD SiC substrate, (B) failure at joint plane, and (C) failure partially at joint plane.

Acknowledgements

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References

[1] Y. Katoh, L. L. Snead, T. Cheng, C. Shih, W. D. Lewis, T. Koyanagi, T. Hinoki, C. H. Henager Jr., and M. Ferraris, J. Nucl. Mater., 448 (2014) 497–511.

[2] T. Koyanagi, J. Kiggans, C. Shih, Y. Katoh, Ceram. Eng. Sci. Proc., 35 (2015) 151–160–.

[3] T. Koyanagi, S. Kondo, T. Hinoki, Ceram. Eng. Sci. Proc. 32 (2011) 53–62.

[4] T. Koyanagi, J. Kiggans, C. Shih, Y. Katoh, Fusion Reactor Materials Program Report, DOE/ER-0313/56, 94–102.
[5] T. Koyanagi, J. Kiggans, C. Shih, Y. Katoh, Fusion Reactor Materials Program Report, DOE/ER-0313/55, 11–22.
[6] M. Ferraris, M. Salvo, C. Isola, M. Appendino Montorsi, A. Kohyama, J. Nucl. Mater. 258–263 (1998) 1546–1550.