Hydrothermal corrosion of silicon carbide joints without radiation^{*}

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Abstract

Hydrothermal corrosion of four types of the silicon carbide (SiC) to SiC plate joints were investigated under pressurized water reactor and boiling water reactor relevant chemical conditions without irradiation. The joints were formed by metal diffusion bonding using molybdenum or titanium interlayer, reaction sintering using Ti-Si-C system, and SiC nanopowder sintering. Most of the joints withstood the corrosion tests for five weeks. The recession of the SiC substrates was limited. Based on the recession of the bonding layers, it was concluded that all the joints except for the molybdenum diffusion bond are promising under the reducing environments without radiation. The SiC nanopowder sintered joint was the most corrosion tolerant under the oxidizing environment among the four joints.

1. Introduction

Silicon carbide (SiC) fiber reinforced SiC matrix composites are considered as a primary candidate of the accident tolerant fuel cladding of light water reactors (LWRs) because of the outstanding irradiation and oxidation resistance, and low neutron absorption cross section [1, 2]. For the successful development of the SiC based fuel cladding, joining the cladding to the end-plug is recognized as one of the technological hurdles [1, 2]. One of the processing difficulties regarding the end-cap joining for a long cladding with thin wall thickness is a limitation in the applied stress which can be employed during the joining. Moreover, the functional requirements of the joint are (1) gas-tightness to retain the fission products inside the cladding, (2) environmental resistance under normal operations (resistance to the hydrothermal corrosion and neutron irradiation) and (3) high-temperature oxidation resistance under a loss of coolant accident condition. This paper focuses on hydrothermal corrosion behavior of the SiC joints because of a significant lack of the knowledge. Stempien et al. reported in-pile corrosion behaviors of the SiC plate joints bonded utilizing TiC/SiC tape, calcium aluminate glass, or Ti foil [3]. All types of these joints were completely or partially debonded during the reactor coolant exposure for 44 days and 0.16 displacement per atom (dpa)-SiC. Therefore, development of the corrosion tolerant joint and the process method for SiC is a critical issue.

Various joining techniques utilizing different bonding phases are currently available for SiC materials. The candidate joining methods for the LWR cladding end-plug application can be converged based on the irradiation resistance. Katoh et al. demonstrated irradiation tolerant SiC joints fabricated by solid state diffusion bonding, Ti-Si-C reaction sintering based joining, SiC nanopowder sintering based joining, and

glass-ceramic joining following neutron irradiation at 500 and 800°C up to 5 dpa [4]. Those joining methods are potentially useful for the LWR pin end-plug applications in terms of the radiation resistance.

The solid state diffusion bonding typically utilizes an interlayer of a refractory metal such as titanium, molybdenum, and tungsten [5]. Metal silicides can be also used as the interlayer [6]. The joining method is well established and the advantage of this joining method is the relatively low joining temperature (~1500°C), which can avoid the potential damage to the cladding, especially for SiC fibers in the composite form. The strengths of Hi-Nicalon Type S and Tyranno SA SiC fibers are known to degrade by annealing at ~1800°C and ~1900°C, respectively [7]. The drawback is the need for applied stress during the joining, which is typically more than a few MPa [5]. Jung et al. recently overcame this limitation by solid state diffusion bonding using a Ti interlayer and addition of Si powder with applied stress of only ~0.1 MPa [8]. The diffusion bonds were typically robust [4, 9]. It may be possible to increase the environmental resistances of this type of the joint by choosing an appropriate interlayer.

The reaction sintering method utilizing the Ti-Si-C system yields a bonding layer of Ti_3SiC_2 (MAX phase) plus secondary phases including SiC, which was originally formed with applied stress of 30 MPa at 1200-1300°C [10]. The pressureless joining method with Ti-Si-C system has been commercially available. The apparent shear strength of the joint was reported to be ~100 MPa [4]. The main concern of this type of the bonding layer is poor oxidation resistance of Ti_3SiC_2 phase [11], which may be improved by modification of the composition [12].

The SiC nanopowder sintered joint is formed by sintering mixture of SiC nano-powder and oxide additives such as alumina-yttria [13, 14]. The additives form eutectic liquid during the heating, and then the liquid phase promotes sintering of SiC powder compact via the solution-precipitation process, which is commonly observed in liquid phase sintering [15]. If the eutectic liquid is a transient phase due to the evaporation, the joining method is specifically referred to as transient eutectic phase (TEP) sintering bonding [4, 16]. Although the SiC nanopowder sintering typically requires relatively high processing temperature (~1850°C) and applied pressure of ~10 MPa, this class of SiC joint exhibited the highest apparent shear strength among the different types of SiC joints [4]. The key development of this joint is a reduction of the joining pressure and control of the microstructure, especially for the secondary phases for improved environmental resistance [17, 18]. The applied stress during sintering is potentially reduced by pressureless sintering [16].

The glass ceramics bond was demonstrated without applying an external stress at relatively low temperature (~1500°C) for Ca-Al-O system [4, 19]. The joint strength was typically ~100 MPa in torsion.

Because of the discouraging results of the in-pile corrosion experiment on the glass ceramics joint [3], this joint was not investigated in this study.

The promising methods for the cladding end-plug application, which are not investigated in this study, are a selected area chemical vapor deposition (CVD) or infiltration (CVI) and a SiC forming polymer-derived joining [20], which can provide pure SiC bonding layer. Hybrid joining technique utilizing these two methods has been employed to the end-plug joining [21]. Hydrothermal corrosion behavior of high-purity SiC in simulated LWR coolant environments can be found elsewhere [22, 23].

In this study, the corrosion behaviors of four types of SiC to SiC plate joints fabricated via the solid state diffusion with Ti and Mo interlayers, Ti-Si-C reaction sintering, and SiC nanopowder sintering were investigated under three types of LWR relevant chemical conditions, for up to five weeks for screening purpose. The corrosion experiment was conducted in autoclaves without radiation. Based on the corrosion rate and the microstructures of the corroded joints, possible methods to improve the corrosion resistance and future direction of the development of the SiC joints for the LWR cladding application were discussed.

2. Experimental

CVD β -SiC from Dow Chemical Co. (Marlborough, MA) with 99.9995% purity was used for the substrate material for all the joint specimens. The Mo diffusion bond was formed using a molybdenum foil (25 μm thick, 99.95% pure, Alfa-Aesar, Ward Hill, MA) as the bonding agent. 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. During the hot-pressing, presence of both hydrogen and titanium powder facilitated effective oxygen gettering. To form the Ti diffusion bond, a titanium foil (25 μm thick, 99.94% pure, Alfa-Aesar, Ward Hill, MA) was used as the interlayer. 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. For the Ti-Si-C reaction forming 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). The Ti-Si-C phase-based joints of CVD SiC were produced based on a pressure-less slurry process per the Hyper-Therm formula. Details of the raw materials and the process conditions are Hyper-Therm proprietary information. The SiC nanopowder sintered joint was fabricated using slurry of SiC powder mixture. To prepare the slurry, SiC nano-phase powder (average diameters ~ 30 nm, Nanomakers, France), and Al_2O_3 powder (average diameters $\sim 0.3\mu\text{m}$,

Kojundo Chemical Lab. Co., Ltd., Japan), Y_2O_3 powder (average diameters $\sim 0.4\mu m$, Kojundo Chemical Lab. Co., Ltd., Japan) were dispersed in ethanol. The total amount of oxide additives was 6 wt.% (weight ratio: $Al_2O_3:Y_2O_3 = 3:2$). The powders were mixed using milling with zirconia balls. The slurry was sandwiched by CVD SiC plates, and then dried at $\sim 80^\circ C$. After that, the SiC nanopowder sintered joint was formed by hot-pressing at $1850^\circ C$, for 1 h, in an Ar atmosphere, under a pressure of 10 MPa. Note that the bonding layer contained the trace of zirconia from the milling media as shown in later. The processing conditions of the joints are summarized in Table 1. The bonded plates were machined into rectangular $12.0 \times 6.0 \times 1.5\text{ mm}^3$ bars for the Mo and Ti diffusion and Ti-Si-C reaction sintered bonds and into square $6.0 \times 6.0 \times 3.0\text{ mm}^3$ for the SiC nanopowder sintered joint. All the samples contained a hole with 2.0 mm diameter to hang on the specimens in autoclaves. The location of the bonding layers within the test specimens is shown in Fig. 1.

Table 1 Processing conditions of SiC plate joints

Joining method	Interlayer	Joining temperature [$^\circ C$]	Holing time at max. temperature [h]	Joining atmosphere	Applied stress [MPa]
Mo diffusion	Mo foil	1500	1	Ar-4% H_2	20
Ti diffusion	Ti foil	1500	1	Vacuum	17
Ti-Si-C reaction sintering	Ti-Si-C powder	Proprietary information			~ 0
SiC nanopowder sintering	SiC nanopowder, 6wt.%($Al_2O_3+Y_2O_3$), ZrO_2 impurity	1850	1	Ar	10

Fig. 1 Dimensions and appearance of SiC joint specimens: (a) rectangular type for Ti and Mo diffusion bond and Ti-Si-C reaction sintered joints, (b) square type for SiC nanopowder sintered joint.

The hydrothermal corrosion experiments were conducted in 316 stainless steel autoclaves at GE Global Research Center (Schenectady, NY). The specimens were hung on a PTFE-insulated 304 stainless steel wire and immersed for 5 weeks in three LWR coolant environments, (1) pressurized water reactor (PWR) chemistry, (2) boiling water reactor (BWR) –normal water chemistry (NWC), and (3) BWR–hydrogen water chemistry (HWC) conditions. The details of test water chemistry conditions are summarized in Table 2. The PWR and BWR–HWC conditions were simulated reducing environments, while the BWR–NWC condition was representative of in-core oxidizing water chemistry in BWR. The water chemistries were controlled by injection of appropriate mixtures of argon, oxygen, and hydrogen. The water flow rate during the tests was 200ml/min. One specimen of each type of the joint was exposed to each water chemistry condition. The specimen of the SiC nanopowder sintered joint for the PWR condition was absent. The samples were removed from the test autoclaves after two weeks for examining the stability of the joining areas, and then put them back to the test autoclaves again for an additional three weeks. Details of the experimental setup were reported elsewhere [22]. Additives used in the coolant of commercial LWRs such as Li, B, and noble metals [24] were absent in water of the autoclave. Such additives may affect the chemical/physical stability of the joining area [24].

Table 2 Summary of environments of autoclave corrosion tests.

Autoclave environment	Chemistry	Temperature [°C]	pH	Pressure [MPa]
PWR	3.57 ppm H ₂	330	7.2	15
BWR-HWC	0.3 ppm H ₂	290	5.6	7
BWR-NWC	1.0 ppm O ₂	290	5.6	7

The recession of the SiC substrate was evaluated from weight loss of the rectangular specimens, ignoring the bonding layer, because volume of the bonding layer within the corrosion specimen was less than 1.5%. The relative recession of the bonding layer comparing with the substrate was usually evaluated by cross sectional analysis using a KEYENCE VHX-1000 optical microscope and a Hitachi 4800S or FEI Versa 3D DualBeam scanning electron microscope (SEM). The recession of the specific specimen was evaluated using 3D imaging of the optical microscope because of the difficulty of the cross sectional specimen preparation. Elemental analysis was conducted using Energy-dispersive X-ray spectroscopy

(EDS) using an AMETEK EDAX detector on the Hitachi 4800S. Electron backscatter diffraction (EBSD) analysis was also conducted using an Oxford instruments Nordlys detector on the Vresa SEM.

3. Results and Discussion

3.1 Corrosion behavior of SiC joints

Appearances of the joint specimens following corrosion tests for five weeks are shown in Fig. 2. Most of the SiC joints withstood the corrosion tests except for the Ti diffusion joint tested in the BWR–NWC environment. The changes in the specimen thickness of the CVD SiC substrate and the bonding layers are summarized in Table 3. The recession of the CVD SiC was less than 1 μm , which is consistent with previous work on the autoclave corrosion tests utilizing same grade of the material and water chemistries [22]. Since there was almost no recession of the CVD SiC substrate for this short term immersion test, the observed relative recession of the bonding layer compared with the substrate is nearly equal to the recession of the bonding layer itself. An example of the appearance of the recession of the joint layer in the cross sectional observation is shown in Fig. 3. As shown in Table 3 and Fig. 3, the Mo diffusion bond exhibited significant recessions in all the water chemistries. There was no relative recession of the Ti diffusion bonding layer compared with the SiC substrate under the PWR and BWR–HWC conditions. However, the joint failed during two to five weeks under the BWR–NWC test. There was also no relative recession of the bonding layer of the Ti–Si–C reaction sintered joint compared with the SiC substrate under the PWR and BWR–HWC conditions. On the other hand, gain of the joint thickness of the reaction sintered bond was confirmed by three dimensional optical microscope imaging as shown in Fig. 4. The SiC nanopowder sintered joint was the only joint which exhibited very limited recession of the bonding layer under both BWR–HWC and –NWC environments, though the recession was clearly observed under BWR–NWC using SEM shown later.

Joint Materials	As-received	Autoclave environments		
		PWR	BWR-HWC	BWR-NWC
Mo diffusion bond
Ti diffusion bond				The joint failed.
Ti-Si-C reaction sintered joint
SiC nanopowder sintered joint		Not available

Fig. 2 Optical micrographs of SiC joints before and after corrosion tests for five weeks. The specimen dimensions are shown in Fig. 1.

Table 3 Changes in thickness of CVD SiC substrates and bonding layers following autoclave corrosion tests for five weeks. Unit for numbers is μm . Values for joint materials indicate relative values compared with SiC substrate. Negative values indicate thickness loss.

Material	PWR	BWR-HWC	BWR-NWC
SiC substrate	-0.20	-0.05	-0.25
Mo diffusion bond	-110	-95	-235
Ti diffusion bond	0	0	> -750
Ti-Si-C reaction sintered joint	0	0	+35
SiC nanopowder sintered joint	No data	0	-5

Fig. 3 Cross sectional optical micrograph of Mo diffusion bond after autoclave test with BWR-HWC for five weeks.

Fig. 4 Three dimensional optical micrograph of Ti-Si-C reaction sintered joint after BWR-NWC corrosion test for five weeks.

3.2 Microstructural investigations of corroded joint

(1) Mo diffusion bond

The phases in the Mo diffusion bond has been identified in previous study using x-ray diffraction [25]: layers of the ternary phase ($\text{Mo}_{<5}\text{Si}_3\text{C}_{<1}$) adjacent to the SiC substrates and a middle layer of molybdenum carbide (Mo_2C) as shown in Fig. 5. The thickness of the bonding layer was $\sim 30\mu\text{m}$. Pre-existing defects in the bonding layer were cracks propagating nearly vertical to the joint interface, which was likely caused by differential coefficients of thermal expansions (CTE) between SiC substrate and the joint phases. Although the molybdenum carbide exhibited slightly smaller recession than the ternary phase, the recessions of the both joint phases were significant under the three water chemistries as shown in Table 3.

The hydrothermal corrosion of the molybdenum ternary phase and carbide has not been reported in the literature. This study discusses about possibilities to improve the poor performance of the Mo joint under the corrosion environments rather than the corrosion kinetics based on the objective of screening of the joints for the LWR cladding application. The phases formed during diffusion of Si and C into Mo are (1) Mo_5Si_3 and Mo_2C at 1200–1400°C, (2) $\text{Mo}_{<5}\text{Si}_3\text{C}_{<1}$ and Mo_2C at 1400–1600°C, and (3) $\text{Mo}_{<5}\text{Si}_3\text{C}_{<1}$ and MoC at 1700°C, depending on the thermodynamic stability of the phases [26]. It appears that the bonding layers consists of at least one of $\text{Mo}_{<5}\text{Si}_3\text{C}_{<1}$ or Mo_2C phases which was not corrosion resistant, thus conventional diffusion bonding with Mo interlayer is not promising for the LWR end-plug application without an environmental barrier coating. One possible way to improve the corrosion resistance of the bulk Mo based material is by elemental doping [27]. However, at this time the processing of the elemental doping for the Mo joint layer has not been established.

Fig. 5 Backscatter electron image of Mo diffusion bond.

(2) Ti diffusion bond

The bonding layer of the Ti diffusion joint was evaluated using EBSD analysis as shown in Fig. 6. The phase map revealed that the joint phase is a sole Ti_3SiC_2 phase. The joint thickness was $\sim 30\mu\text{m}$. The crystal orientation map shows that there is no strong grain texture in both the SiC substrate and the Ti_3SiC_2 phase. The grain size of the Ti_3SiC_2 was more than a few microns in most cases. Note that low density cracks were observed in the bonding layer before the corrosion tests. Considering the

stoichiometry, silicon was produced during reaction between SiC and Ti to form Ti_3SiC_2 . The silicon may react to Ti to form finely dispersed TiSi_2 or evaporate during the joining [28].

Fig. 6 Microstructures of Ti diffusion bond obtained by EBSD analysis: (a) phase map and (b) surface normal-projected inverse pole figure orientation map.

Cross sectional microstructural characterization was conducted for the joints tested under the PWR and BWR–HWC conditions. No difference of the recession between the Ti_3SiC_2 phase and SiC substrate was observed in SEM as shown in Fig. 7. The chemical composition of the corroded bonding layers was investigated by SEM-EDS. The EDS spectra shown in Fig. 8 were collected by area analysis. Very similar results were obtained from the joints tested in the PWR and BWR–HWC environments; oxidation of the bonding layer was detected at the very surface of the corrosion face, however relatively limited amount of oxygen was confirmed in the area $\sim 10\mu\text{m}$ away from the corrosion face. The limited recession and oxidation of the Ti diffusion bond indicate that this joint is promising under those two hydrogen injected water chemistries without irradiation. Note that the joint failed apart during testing with BWR–NWC, so the Ti diffusion bond was obviously not stable under the oxidizing activity environment.

Fig. 7 Cross sectional backscatter images of Ti foil diffusion bond after autoclave immersion: (a) PWR and (b) BWR–HWC conditions.

Fig. 8 EDS spectra collected from cross sectional prepared bonding layer of Ti diffusion bond after autoclave corrosion tests. The water chemistry and the analyzed area are shown in the table.

Zhang et al. investigated hydrothermal oxidation of the bulk Ti_3SiC_2 up to 100 h using an autoclave at 500, 600, and 700°C under a hydrostatic pressure of 35 MPa [29]. The proposed hydrothermal oxidation reaction below 550°C was as follows.

During this reaction, the formed SiO_2 dissolved in the water [29]. They found the oxide (TiO_2) layer on the corroded surface, which is consistent with the detection of oxide only near the surface of the Ti diffusion bond under the PWR and BWR–HWC conditions. On the other hand, they did not report a catastrophic oxidation or severe damage of Ti_3SiC_2 , which is inconsistent with the failure of the Ti

diffusion bond under the BWR–NWC. This may be caused by the different water chemistry (high temperature liquid water vs. super critical water). One way to modify the corrosion resistance of Ti_3SiC_2 may be elemental doping. Although the doing method has not been applied to the joint yet, the improved corrosion resistance by doping of Al was demonstrated in the super critical water [30]. Although it is not sure that Al doping works under the LWR coolant environment, the doping is an idea to change the corrosion resistance.

(3) Ti-Si-C reaction sintered bond

The EBSD analysis identified the phases in the Ti-Si-C reaction sintered joint without the corrosion test (Fig. 9). The phase map shows that the dominant joint phases were Ti_3SiC_2 and SiC (mainly 6H or 4H hexagonal structure) and the minor phase was TiC. Presence of both Ti_3SiC_2 and SiC were also reported in the other Ti-Si-C reaction sintered joints [10]. The volume fractions of the phases were roughly Ti_3SiC_2 : SiC : TiC = 4 : 4 : 2. No strong texture of the grains was observed in the crystal orientation map. The joint thickness was typically $\sim 150\mu\text{m}$. Grain sizes were a few microns for Ti_3SiC_2 and TiC and $\sim 15\mu\text{m}$ for 6H and 4H SiC. Pre-existing defects were cracks propagating vertical to the joint interface.

Fig. 9 Microstructure of Ti-Si-C reaction sintered joint obtained by EBSD: (a) phase map and (b) surface normal-projected inverse pole figure orientation map.

Cross sections of the bonding layers were observed following the autoclave tests. No obvious recession of the bonding layer was observed after the PWR and BWR–HWC tests (Fig. 10), which is reasonable based on the corrosion-resistant Ti diffusion bond containing Ti_3SiC_2 under those conditions. The EDS elemental maps in Fig. 10 show the limited and uniform presence of oxygen in the Ti_3SiC_2 and TiC phases. Oxygen can be dissolved in Ti during the fabrication at relatively low temperatures ($<1000^\circ\text{C}$) [31]. Following the PWR and BWR–HWC corrosion tests, local oxidations inside the bonding layer, $\sim 50\text{ }\mu\text{m}$ away from the corrosion face, were detected (Fig. 10). Although the effect of the local oxidation on joint reliability, i.e. strength and gas leak-tightness, is unknown from this study, the $\text{Ti}_3\text{SiC}_2/\text{SiC}$ bonding layer appeared to be corrosion resistant under the PWR and BWR–HWC reducing environments based on the recession rate. In case of the oxidizing activity BWR–NWC environment, the bonding layer was failed during specimen sectioning with a low-speed diamond saw for preparation of the polished cross section. This result indicates the bonding layer was highly damaged under the BWR–NWC. The failure location was the joint/substrate interface as shown in Fig. 10, which indicates that the hydrothermal oxidation weakened bonding at the interface. The EDS mapping revealed that the bonding layer, especially for the Ti_3SiC_2 phase (plus TiC phase), was highly oxidized. Therefore, the positive result of the recession rate appeared to be attributed to mass gain due to oxidation. The oxidation can cause volume expansion of the bonding layer, which results in weakened joint interface due to the residual stress there. The joint expansion may be isotropic since there is no strong grain texture based on EBSD analysis.

Fig. 10 Backscatter electron micrographs and EDS elemental maps of Ti-Si-C reaction sintered joints in as fabricated condition and after corrosion tests under PWR, BWR-HWC, and BWR-NWC conditions.

Although both the Ti-Si-C reaction sintered joint and Ti diffusion bond contained Ti_3SiC_2 phase as a dominant joint phase, the different corrosion behavior was observed. Under the reducing environments, the oxidation was found only at the corrosion face for the Ti diffusion bond, but found inside the bonding layer for the Ti-Si-C reaction sintered joint. Under the oxidizing activity environment, the diffusion bond failed, but the reaction sintered joint withstood the corrosion test. Considering the microstructural difference between the two joints, possible causes of those differences are (1) grain boundary diffusion of oxygen, and (2) effects of the secondary phases on the oxidation. However, the detailed mechanism of the oxidation is still not clear at this moment. One conclusion is that the material microstructures strongly affected the hydrothermal corrosion behavior of the Ti_3SiC_2 based bonding layer.

(4) SiC nanopowder sintered joint

The SiC nanopowder sintered joint was the only joint, which exhibited limited recession of the bonding layer under both the reducing and oxidizing environments among the joints investigated, as shown in Table 3 and Fig. 11. The backscattered electron images show that the bonding layer consisted of SiC grains (gray contrast) with the sizes of 0.5-1 μm and oxide phases (white contrast) attributed to the sintering additives. The oxide phases were finely dispersed rather than forming a network. The joint thickness was $\sim 100\ \mu\text{m}$. Cross-sectional observation of the corrosion face showed no obvious recession of the bonding layer relative to the SiC substrate and $\sim 5\ \mu\text{m}$ relative thickness loss of the joint layer after the test with the BWR-HWC and BWR-NWC, respectively. Under the BWR-HWC, there was no detectable microstructural change in the SEM micrograph. On the other hand, the oxide phases and the grain boundaries were preferentially attacked near the corrosion surface in the BWR-NWC condition (Fig. 11 (d)).

The EDS elemental mapping (Fig. 12) revealed that the oxide phases consisted of aluminum, yttrium, and zirconium in as-fabricated condition. The detection of the substantial amount of zirconium in the oxide phases was unexpected since the sintering additives used were only alumina and yttria. The zirconium contamination likely arrived from the milling media during the processing. The rough estimation of the oxide content in the bonding layer based on the EDS analysis was $\text{Al:Y:Zr:O}=1.7:2.0:5.1:1.0(\text{wt.}\%)$. After the corrosion tests with the BWR-HWC and -NWC, aluminum was almost entirely depleted from the oxide phases near the corrosion faces. In contrast, yttrium and zirconium still remained in the oxide phases.

Based on the Al depletions under the BWR-HWC and -NWC and grain boundaries preferentially attached under the BWR-NWC, a key to control the corrosion resistance of the SiC nanopowder sintered joint is optimization of the oxide phases. The oxide phases in this type of SiC ceramics usually exist not only at the grain pockets but also between the grain boundaries as a thin film with a nanometer thickness [32]. Kim et al. reported the superior hydrothermal corrosion resistance of the high-purity CVD SiC compared to a solid-state sintered SiC with additives of boron and carbon as sintering additives [23]. This work also suggests the importance of controlling secondary phases to optimize the corrosion resistance. An idea to improve the corrosion resistance is the reduction of the oxide phases. Sintering SiC nano-powder required much smaller amount of alumina-yttria sintering additives than sintering micron sized SiC powder [17]. The minimum amount of the additives for alumina-yttria system may be $\sim 5\ \text{wt.}\%$ [33, 34]. Another way to control the oxide phases is fabrication with different additive system. Noviyanto et al. investigated various systems of the sintering additives for SiC [34]. It was concluded that Al_2O_3 , MgO , Y_2O_3 and their mixed systems were found to be the effective sintering additives. Terrani et al. pursued new additives systems for SiC nanopowder sintering and demonstrated better hydrothermal

oxidation resistance of bulk sintered SiC with yttria-zirconia(-limited amount of alumina) with respect to the SiC with conventional alumina-yttria system [35]. According to their study, the zirconia contamination in this study may positively affect the corrosion resistance of the bonding layer. This modification of the sintering additives is applicable to the joining process, and addition of a corrosion resistant oxide such as zirconia in the bonding layer is an effective way to improve the corrosion resistance of the joint.

Fig. 11 Backscattered electron images of cross-section SiC nanopowder sintered joint after autoclave corrosion tests for five weeks: (a, b) BWR-HWC, and (c, d) BWR-NWC conditions.

Fig. 12 Backscatter electron images and EDS elemental maps of as-fabricated and autoclave tested bonding layers of SiC nanopowder sintered joint.

4. Future direction

This paper studies hydrothermal corrosion behavior of the SiC joints under the simulated LWR coolant environments using autoclave immersion tests. Since neutron irradiation was absent in this test, the effects of radiolysis of light water and effects of irradiation-induced property changes of material on the corrosion were not studied. An in-pile corrosion experiment of SiC conducted by Carpenter [36] indicated that radiolysis and/or irradiation induced defects significantly affects the corrosion behavior of SiC tubes, depending on the material quality. Recent autoclave hydrothermal oxidation experiment using ion irradiated CVD SiC indicates that irradiation-induced defect significantly affects the corrosion of SiC [37]. This radiation assisted corrosion can also occur in the phases of the bonding layers. Therefore, understanding the effects of irradiation under the LWR condition on the SiC joints and evaluation of in-pile corrosion resistance of the SiC joints would be important next steps for the development of the SiC joining technology for the accident tolerant LWR cladding.

5. Conclusion

Hydrothermal corrosion behavior of four types of SiC joints was investigated under three water chemistries: PWR, BWR–HWC, and BWR–NWC conditions, all three without irradiation, for five weeks. The findings are as follows.

- (1) The CVD SiC substrate exhibited limited recession under the simulated LWR coolant environments consistent with prior observations.
- (2) Both $\text{Mo}_{<5}\text{Si}_3\text{C}_{<1}$ and Mo_2C phases in the Mo diffusion bond showed significant recession in all three water chemistries. Based on the possible phases formed under Mo–SiC solid state diffusion, it was concluded that conventional Mo diffusion bonding does not provide corrosion resistant joint under the LWR coolant environments.
- (3) The bonding layer of Ti diffusion bond with the single bonding phase of Ti_3SiC_2 showed the recession comparable to the CVD SiC substrate under the reducing environments (PWR and BWR–HWC). In addition, oxidation of the bonding layer was observed only near the corrosion face. On the other hand, the joint failed during the corrosion test under the oxidizing conditions (BWR–NWC).
- (4) The Ti–Si–C reaction sintering provided the bonding layer consisting of dominant phases of Ti_3SiC_2 and SiC and minor phase of TiC. The recession of the bonding layer was limited under the reducing conditions, but local oxidation was observed away from the corrosion face. The joint was highly oxidized under the oxidizing conditions. The differential corrosion behavior between the Ti diffusion and the reaction sintered bonds indicates that the microstructure of Ti_3SiC_2 such as presence of secondary phase and grain boundaries affects the hydrothermal oxidation.
- (5) The SiC nanopowder sintering method formed the SiC based bonding layer with the Al–Y–Zr oxide phases. This joint was the only one showing limited recession under both the reducing and oxidizing environments in this study. Controlling the oxide phases and distribution is a key to improve the hydrothermal oxidation resistance.

Acknowledgements

This work was sponsored by the U.S. Department of Energy, Office of Nuclear Energy, for Advanced Fuel Campaign of the Fuel Cycle Research & Development program under contact DE-AC05-00OR22725 with Oak Ridge National Laboratories managed by UT-Battelle, LLC. C. Ang provided useful comments on the manuscript.

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