Thickness-dependent Phase Evolution and Bonding Strength of SiC ceramics Joints with active Ti Interlayer

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Keywords: *SiC; joining; diffusion; MAX phase*

chinaXiv:201607.00036v1

Abstract:

A robust solid state diffusion joining technique for SiC ceramics was designed with thickness-controlled Ti interlayer formed by Physical Vapor Deposition method and joined by Electric Field-Assisted Sintering Technology. The interface reaction and phase revolution process were investigated in details, and was analyzed in term of equilibrium phase diagram and also concentration-dependent potential diagram of Ti-Si-C ternary system. Interestingly, on the same joining conditions (fixed temperature and annealing duration), the thickness of Ti interlayer determined the concentration and distribution of reactants of Si and C elements in the resultant joint layer, and the respective diffusion distance of Si and C into Ti interlayer dramatically differentiated during the short joining process (only 5 min). In the case of 100nm thickness Ti interlayer, the C concentration saturated quickly in the joint layer and benefited the formation of TiC phase and following Ti_3SiC_2 phase. When the Ti thickness increase to 1μm, Si atoms easily diffuse through the diluted Ti-C alloy (dense TiC phase not formed), and amount of Ti_5Si_3 brittle phase was preferential formed. When the thickness of Ti interlayer is 100nm, SiC ceramics were successfully joined at low temperature of 1000°C for 20min with a flexural strength of 168.2MPa which satisfies the application in corrosion environment. All above findings revealed the importance of diffusion kinetics of reactants on the final composition in the solid state reaction, especially in the joining technique for the covalent SiC ceramics. The well-controlled composition in the joint layer of SiC couples will find its application merits in the harsh service environments, such as nuclear cladding for accident-tolerant fuel (ATF) in the environment of steam corrosion, high neutron irradiation, high temperature, etc.).

1. Introduction

Nuclear safety has attracted increasing attention especially after Japanese Fukushima Daiichi reactors disaster. The concept of Accident Tolerant Fuel (ATF) systems was proposed to replace existing Zr alloy cladding by full ceramic matrix composites. Four key performance features of ATF criteria for improved safety margins were suggested by S.J. Zinkle *et al.* [1]. One of the most important cladding materials candidate thus has been selected to be SiC fiber reinforced SiC composites (SiC_f/SiC) for their features of low neutron absorption cross section, excellent irradiation-damage-resistance, outstanding high temperature mechanical properties, appealing corrosion and oxidation resistance in air and steam up to temperatures of at least 1600°C [2-8]. Up to now, SiC_f/SiC composite has been world-widely identified as a potential cladding candidate in light water reactors and also as flow channel insert for fusion reactors. However, one of challenge to realize the application of SiC_f/SiC composites in these nuclear system is their poor machinability to get complicate component due to intrinsic hardness and also joining/sealing technique for the strict permeability requirement in the cladding tube application. It is well-known that low activated surface of SiC hinds the diffusion of constitutional atoms (Si and C) in the interface, thus the joining of SiC ceramics and/or SiC_f/SiC composites was always performed at much high temperature to overcome this diffusion barrier. In the SiC_f/SiC composites, intensive annealing at the high temperature will inevitably deteriorate the strength of continuous fibers and reduce the service lifetime of the whole composite component.

Various of methods have been employed to join SiC and/or SiC matrix composites, such as Si-C reaction joining [9], pre-ceramic polymer joining [10-12], transient eutectic-phase joining [13, 14], solid state diffusion bonding [15-17], metallic braze-based joining [18-21], pressure-less glass-ceramic joining [22] and MAX phase joining [10, 23, 24]. Most of them relied on traditional hot-pressure sintering technology in which high temperature, high pressure and long joining time were employed on the couples. Electric current field assisted sintering technology (FAST, sometimes referred to spark plasma sintering, SPS) is one of new approach to obtain fine ceramics at lower temperature [25, 26], and recently was successfully employed to join SiC, C_f/SiC and ZrB_2-SiC material systems [27-29]. The localized

heating and fast joining process achieved by FAST show great promising for joining refractory ceramics [24].

The joint interlayer composition is another critical issue restricting the further potential application. For example, in the nuclear reactor environment, the joint interlayer will be the weakest location in the whole component when considering the corrosion resistance and irradiation resistance. Ti_3SiC_2 (TSC) is one of ternary MAX phases that exhibits properties of both metallic and ceramic, and owns features of excellent electrical and thermal conductivity, high temperature oxidation resistance, corrosion resistance, and irradiation damage tolerance [30-34]. Therefore, TSC is deemed as one of promising potential candidates as interlayer material for SiC_f/SiC joining. Yutai Katoh, *et al.* used TSC to join CVD SiC, and found that the joining couples exhibited minor or insignificant deterioration on shear strength and microstructures after neutron irradiation at 800°C to 5 dpa [35]. In our previous work, SiC ceramics were joined with 60 μm TSC tape layer by FAST at 1300°C, which is lower than hot pressure method almost 100°C [24]. Importantly, the macro cracks due to thermal mismatching between SiC and TSC (coefficient of thermal expansion (CTE) of SiC and TSC are $4.4\times10^{-6}K^{-1}$ and $9.1\times10^{-6}K^{-1}$, respectively) [36] must be concerned in the joint interface.

Ti is another good interlayer candidate for SiC joining. It can react with SiC to get high strength interface through formation of TiC and TSC phases at high temperature. M. Naka *et al.* [37] systematically investigated SiC couples bonded with 50μm Ti foil at temperatures from 1373K to 1773K in vacuum. They suggested that when the bonding was carried out at temperature of 1673K and for short bonding time (0.3Ks), the final composition sequence of joining interlayer is β-Ti/Ti+TiC/$Ti_5Si_3C_x$+TiC/SiC. Furthermore, at a bonding time of 3.6 ks, the complete diffusion path was observed as follows: β-Ti/Ti+TiC/$Ti_5Si_3C_x$+TiC/$Ti_5Si_3C_x$/Ti_3SiC_2/SiC. B. Gottselig *et al.* also extensively studied SiC joining with Ti interlayer (thickness of 1μm to 3μm) and interface phase evolution at different temperature ranges were investigated [38]. It was ascertained that between 1250 and 1500°C, mainly ternary phase of TSC is formed (＞90%). Recently, S. Grasso *et al.* [39] successfully joined β-SiC with 30μm Ti foil by SPS. The bend strength of 126±16MPa was reached in the samples joined at 1700 °C under a pressure of 60MPa. Stefano Rizzo *et al.* [40] reported the joining of CVD-SiC coated C/SiC composites with 30μm and 130 μm Ti foils. They pointed out

that SPS technique accelerated the diffusion rate at interface because of localized heating. It should be pointed out that the gradient phase distribution in the joint will largely alleviate the residual stress in the interface.

Until now, most of work on joining of SiC through active Ti method were based on the commercial Ti foil. However, the brittle silicide phases (such as Ti_5Si_3) were inevitably formed in the joint since these silicide phases are thermodynamically stable once formed, which is not favorable for the application of extreme nuclear environment due to their amorphousization tendency under neutron irradiation. Moreover, Ti_5Si_3 phase exhibits high thermal expansion anisotropy ($\alpha_c/\alpha_a \cong 2.7$), as a consequence of the large difference between the thermal expansion coefficients along the *a* (5.98×10^{-6} K^{-1}) and *c* (16.64×10^{-6} K^{-1}) axes [41], which accounts for the initiation of crack nucleation in the joints. In order to obtain a micro-crack free joint, these silicide phases must be avoided in the final composition.

In the present work, solid state diffusion joining technique for SiC ceramics was designed with active Ti interlayer and was achieved by Electric Field-Assisted Sintering Technology. The thickness of Ti interlayer was tentatively tuned from 100nm to micrometer by Physical Vapor Deposition method, to understand thickness-dependent interface reaction and phase evolution process. Finally, the acid corrosion behavior and bending strength of joined SiC couples were measured and discussed in terms of phase composition and distribution.

2. Experimental procedure

2.1. Starting materials

The commercial pressure-less sintered 6H-SiC (density of 3.15g/cm^3 and 98.5% purity, containing a few percent of C) was purchased from Zhejiang giant Rio tinto seal Co., Ltd. LTD in Ningbo with the size of Φ2020mm. The joined surface was polished up to 0.1μm by 0.1μm diamond polishing slurry. The titanium target (99.995 at. %) was provided by Routon in Hunan co., LTD.

2.2. Physical vapor deposition of Ti interlayer on SiC substrates

Ti interlayers were deposited on the surface of SiC substrates that will be joined. Before being inserted into the load-lock, all substrates were supersonically cleaned with acetone and alcohol sequentially (5 min for each), and then blown dry with

nitrogen flow. Prior to the deposition, all substrates were dry etched at -200V at 100 kHz and 80% duty factor for 10 min. The base pressure was better than 9×10^{-5} Pa at room temperature. The Ti coatings were magnetron co-sputtered in Ar discharges in a custom-built system that has shown previously [42, 43]. Two cathodes, tilted towards the substrate holder, were installed in the process chamber and driven by a mid-frequency (MF) pulsed-DC power supply (AE Pinnacle Plus+ 5/5) at 350 W, 100 kHz, and 80% duty factor. The working pressure and the deposition temperature were set at 0.7Pa and room temperature, respectively. A DC negative bias of -20 V was applied to the substrate holder, which rotated at a rotation frequency of 12 rev/min. The coating grown at deposition rates is 20nm/min. Different thickness of Ti interlayers (100 nm, 500 nm, 1μm and 6μm) were deposited by PVD technique.

2.3. Process of joining

Before joining, the as received samples were ultrasonically cleaned in ethanol for 1h to remove dust particles, grease and any other contaminants. The joining couples consisting of one coated and one uncoated SiC substrate were loaded into a graphite die [24], and then placed into a FAST furnace (FCT, HPD25, FCT System GmbH, Germany). All samples were joined with the pulsed electric current field assistance. The joining temperature was controlled by the pyrometer placed on the top, which tested the inner bottom surface of the top graphite punch; the graphite punch was designed as a tubular type. It should be point out that the temperature of joining layer may higher than the measuring temperature, because of the contact resistance of interface is higher than SiC matrix. For all of samples, the heating and cooling rate (100°C/min), axial pressure (30 MPa) and dwelling time (5min) were unchanged. The different joining temperatures (500-1600°C) were designed to investigate the interface reaction evolution. Four kinds of thickness of Ti interlayers (100nm, 500nm, 1μm and 6μm) were joined at 900°C, 1000°C and 1100°C, respectively. The details of samples were shown in the table 1.

2.4. Characterizations

After joining, all samples were cut into 9-10 rectangle bars (3440 mm^3), and then polished to 0.05μm by diamond polishing slurry. The polished surface was then used to analyze the microstructure and the phase transition between the matrix and joining layer by scanning electron microscopy (SEM, Hitachi S-4800, Japan) equipped with

an energy dispersive spectroscopy (EDS) system and field emission transmission electron microscopy (TEM, Tecnai F20, FEI, USA). All foils for TEM observation were prepared by Focused Ion Beam (FIB, Auriga, Carl Zeiss AG). The phase analyses of the fracture surfaces of the joints were conducted by XRD (D8 Advance, Bruker AXS, Germany) with Cu Kα radiation. The corrosion resistance of the joining layer was detected by the following solutions with the ratio of HF: HNO_3:H_2O=1:1:5. The joining layers morphology after corrosion 5min were determined by SEM.

2.5. Mechanical property measurement

The four-point bending strength of all joining couples were determined by a universal electro mechanical testing system (CMT5105, MTS, USA) equipped with a precision load cell calibrated to 1/3000 KN force. The load speed for all the measurements was 0.5 mm/min. The bend strength can be calculated by the following equation:

where P is applied load in N, and L2 (30 mm) and L_1 (15 mm) are the outer and inner span, and a and b is width and thickness of the specimen in mm, respectively. At least five samples were tested for each type of joining conditions, and the average and maximum deviations were calculated.

3. Results and discussion

3.1. Microstructure and phase evolution in joint with 1μm Ti interlayer

For convenient, three distinct parts in as-synthesized SiC/Ti/SiC couples were named: the matrix of (M) SiC ceramic; the joint interlayer (J) of Ti; the interface (I) between M and interlayer. Fig. 1 (a-n) presents typical backscattered electron (BSE) images of cross-section of SiC joining couples joined with 1μm Ti interlayer at temperature ranging from 500°C to 1600°C, respectively. Obviously, SiC ceramics can be well joined together even at low temperature of 500°C within total time of 18 min by FAST technique (Fig. 1a). There are no any obvious cracks parallel or perpendicular to interface, meaning the thermal expansion mismatch between SiC substrates and interlayer is not remarkably since the joining temperature is low. At the same time, it can be seen that, the original surface defects (pores or micro cracks) of SiC matrix were gradually filled by pseudo-plastic phase at higher temperature (Fig. 1d-n) [44] as compared with ones at lower temperature (black rectangular in Fig.1a-c). Also, the

phase distribution perpendicular to the interface can be distinguished in Fig. 1h due to the Z contrast of elements. It is also interesting to note that part of interlayer disappear when the joining temperature is 1600°C (Fig. 1n). SiC grains from both sides seems sintered together.

Fig.2 presents typical XRD patterns of final interlayer phase of SiC couples with 1μm Ti interlayer at 600°C (a), 900°C (b), 1300°C (c) and 1600°C (d), respectively. The XRD results (Fig. 2a) indicate the interface reaction products is dominated by TiC and residual Ti phase at low temperature (600°C). As joining temperature increased to 900°C, TiC and Ti_5Si_3 were detected (Fig. 2b). TSC appeared in the interlayer when the joining temperature was 1300°C. The Ti_5Si_3 were nearly exhausted at temperature of 1600°C, only TiC and TSC phases left in the interlayer (Fig. 2d). Therefore, the following reaction accounts for the TSC formation [45]:

$$10TiC + Ti_5Si_3 + 2Si = 5Ti_3SiC_2 \qquad (3\text{-}1)$$

The above XRD results identified the phase composition in the final interlayer, but cannot indicated the phase distribution. As we known, TiC, TSC and SiC are refractory ceramics and have good resistance to acid corrosion [46, 47]. But Ti and Ti-Si intermetallic compounds can be easily etched by acid. Therefore, a simple acid corrosion experiments was additionally carried out to reveal the distribution of TiC, TSC, Ti and Ti-Si intermetallic compounds in joining layer joined at different temperatures. In the present work, the solutions with the ratio of HF: HNO_3:H_2O=1:1:5 was used. After 5 min etching in such solution, the interlayer of the samples joined at different temperatures were investigated again (Fig. 3). It shows that after joining performed at low temperature of 500°C and 600°C (Fig. 3a and 3d), nearly all of the interlayers were etched out completely although XRD result (Fig. 2a) identified the existence of TiC. It means that at low temperature, the as-formed TiC phase was dispersive in the Ti interlayers. At joining temperature of 900°C, the main composition was TiC phase filling the whole interlayer after etching of Ti_5Si_3 phase (Fig. 3e). At the joining temperature of 1000°C, a continuous TiC layer on SiC ceramic was observed and reserved after acid corrosion (Fig. 3f). At joining temperature up to 1500°C and 1600°C, no apparent corrosion phenomena was found in the joint (Fig. 3m and 3n). It indicates that the as-formed joints should compose of TiC and/or TSC that withstand the corrosion in harsh acid solution, which were also corroborated by the XRD results. The above corrosion experiment well illustrated the

spatial distribution and historic evolution of refractory phases (TiC and TSC) during joining, and also provided a feasible way to know the joining progress.

TEM observations were further conducted to investigate the interface phase of joint joined at 1600°C with 1 μm Ti interlayer (Fig. 4). Fig. 4b and 4c present the elemental distribution of sintered area and joining layer. It is interesting to find that, in the sintered area close to a bright particle, there is no any element of Ti, but only Si and C were detected (Fig. 4b). In the bright particle, TSC phase and TiC phase were identified from the element mapping (Fig. 4c) as well as high resolution transmission electron micrograph (HRTEM). In fact, the characteristic lattice spacing confirm the phase of marked locations "1" and "2" in Fig. 4a to be TiC and TSC phases, respectively. In the interface of matrix SiC and interlayer (location '3') it can be seen that there is an amorphous layer between them (Fig. 4f). Moreover, it should be pointed out that, the lattice distortion and dislocation are very common in the joining layer since the processing of FAST are so fast leaving enormous strain stress. The release of such residual strain stress is crucial for the application and will be discussed elsewhere.

The ternary TSC phase spontaneously decomposes into Si and TiC phases at high temperature of 1600°C (Eq. 3-2). At the same time, Si should be in liquid state and alloyed with nearby SiC grain to form Si-rich amorphous $Si_{1+x}C$ phase (Fig. 4f).

$$Ti_3SiC_2 \rightarrow Si+2TiC \qquad (3\text{-}2)$$

Meanwhile, the liquid phase of Si can further accelerate the decomposition of TSC and capture the carbon atom to more energy-stable SiC phase (Eq. 3-3) [28, 50], which may be the reasonable mechanism for the sintering-like joining phenomena (Fig. 1n).

$$Ti_3SiC_2+7Si \rightarrow 3TiSi_2+2SiC \qquad (3\text{-}3)$$

The whole phase evolution process of above joint with 1 μm Ti interlayer was consistent with previous report by B. Gottselig *et al.* [38]. In their study, a sub-stoichiometric TiC_{1-x} layer around SiC grain and various Ti-Si intermetallic on the TiC particle have been observed at the temperature range of 700-1200°C. At the temperature range of 1200-1500°C, TSC predominated in the products with small fraction of TiC and Ti-Si intermetallic. At the high temperature of 1500-1700°C, TiC, i.e. the thermodynamically most stable phase of the Ti-Si-C system, is the end product

of the reaction after evaporation of the silicon present in the intermediate reaction products. In the present work, we decreased the joining temperature to 500°C, and also confirmed the sub-stoichiometric TiC_{1-x} with characteristic down shift of diffraction peak to low angels as shown in Fig. 2a. TSC still can be detected in the interlayer even at high temperature of 1600°C which is due to the short holding time (5min) in the present work as compared with 2h in previous study [38]. So, with increasing joining temperature, the phase evolution process at Ti interlayer of 1 μm can be determined as follows: TiTi+TiCTiC+Ti_5Si_3TiC+Ti_5Si_3+Ti_3SiC_2TiC+Ti_3SiC_2.

*3.2. **Microstructure and phase evolution in joint with thickness-varying Ti interlayer***

Four different kinds thickness of Ti interlayers (100nm, 500nm, 1μm and 6μm) were designed to join SiC couples in order to investigate diffusion-controlled interface reaction during joining using FAST technique. Fig.5a-5d presents cross-section morphologies of SiC couples joined with various thickness of Ti interlayers at 1000°C as well as the morphology changes after both acid corrosion (Fig.5e-5h). All these SiC couples joined at temperature of 1000°C are integrated even experience intensive shear stress and friction force during sample preparation. In the as-joined couples, the interlayers looks very dense and continuous (Fig. 5a-5d). Neither parallel interface cracks nor transverse cracks were observed. In the joint using 6μm Ti interlayer, there is visible phase contrast in the middle of interlayer as red dot line indicated (Fig. 5d). Ti element must be more abundant in the center of interlayer since heavy element (High Z) appear to be bright in the BSE mode. XRD investigation on these interlayers also revealed the varied phase composition after joining at 1000°C. When the thickness of Ti interlayer is 100nm, only TiC phase can be detected besides SiC signals from substrates. On the other hand, TiC, TSC and Ti_5Si_3 phases were identified when the thickness of Ti coating layer is equal and higher than 500nm.

As discussed in the last section, acid corrosion experiments can be an easy approach to reveal the existence and distribution of refractory phases (such as TiC and TSC) and metal phases (such as Ti and Ti-Si intermetallics) in the interlayer when these phases have been identified by XRD technique. It is interesting to find that the joint show a excellent resistant to the harsh HF corrosion and no corrosion ditch appeared when the thickness of Ti interlayer is 100nm (Fig.5a and 5e). This anti-

corrosion behavior well explain the predominant phase of refractory TiC in the interlayer as identified by XRD result. As the thickness of Ti interlayer increased to 500nm or more, the Ti-Si intermetallic compounds formed and was eroded out in the acid solution although a continuous layer of refractory phase preserved near the SiC ceramics (Fig. 5f-5h). The inserts of Fig. 5f and 5g clearly present the distribution of a dense layer of refractory phases and also dispersive particles filling the eroded gap. When the Ti interlay was as thick as 6μm, the corrosion-nonresistance phase of Ti_5Si_3 (bright area as indicated in Fig. 5h) totally dissolved in acid solution. Above corrosion experiment shows that the thickness of Ti interlayer well controlled the formation of phase and their distribution in the final joints.

In order to reveal the exact phase distribution in the interlayer, the sample joined at 1100°C with a 100nm Ti interlayer was observed by TEM (Fig. 6a). The interlayer and interface can be distinguished easily due to the phase contrast. There are some bulb-like defects in the interlayer which is due to the unavoidable damage by the FIB technique. These damages however have no influence on the phase identification. Fig. 6b and 6c are the HRTEM images of the crystal lattice located at 1 and 2 in Fig. 6a, respectively. Fig. 6d presents STEM image of a section of interlayer, and the element distribution of Ti, Si and C in the same area were collected (Fig. 6e-6g). In term of crystal structure feature (SAED patterns and sets of lattice spacing) and the elemental distribution (Fig. 6e, 6f and 6g), the phase composition of '1' marked in Fig. 6a composes of TiC and SiC with an amorphous grain boundary. The phase composition of '2' in Fig. 6a is determined to be TSC. In the middle of the TSC layer there are some tiny TiC particles. No micro-crack was observed in the interlayer, which is always found in the joints with silicide phase.

3.3 thermodynamic and kinetic analyses on the phase evolution of joint

The reaction of SiC with active Ti can form both TiC and silicides (such as Ti_5Si_3 , TiSi and $TiSi_2$) [48]as listed below:

$$3SiC+5Ti=Ti_5Si_3+3C \quad (3\text{-}4)$$
$$SiC+Ti=TiC+Si \quad (3\text{-}5)$$
$$5Ti+3Si=Ti_5Si_3 \quad (3\text{-}6)$$
$$Ti+Si=TiSi \quad (3\text{-}7)$$
$$Ti+2Si=TiSi_2 \quad (3\text{-}8)$$

From thermodynamically point, the difference in the Gibbs free formation energy

is the decisive factor to control the reaction route. The $\Delta_r G^\theta$ of reactions (Eq. 3-4) and (Eq. 3-5) were calculated in the temperature range of 500°C~1600°C. It is easy to find out the $\Delta_r G^\theta$ of reaction of Equation (3-5) is (527.300 and 550.290 KJ) lower than that of Equation (3-4) (389.521 and 416.242 KJ) at the respective temperature of 500 and1600°C. It indicates that when Ti contacts SiC, the formation of TiC could spontaneously happen following the chemical bond breaking of SiC. According to further calculation of possible reaction between Si and Ti (see Eq. (3-6), (3-7) and (3-8)), these Ti-Si intermetallic compounds can form in the final products. That is true for the circumstance that Si atoms have enough energy and viable route to in touch of Ti atoms. In fact, all previous work on the joining of SiC by a Ti foil (that means Ti was abundant) at high temperature for a long time have proven the existence of these Ti-Si intermetallic phases. It is same situation in the case of 6 μm Ti interlayer in the current study, Ti-Si intermetallic phases existed in the middle of the interlayer (Fig. 5d). However, when a dense and continuous layer of TiC forms near to the SiC reactant (Fig. 5a), Si atoms cannot diffuse across this barrier to react with residual Ti atoms. The limitation of Si diffusion will consequently change the next step of reaction toute. As shown in Fig. 6d, the Si-rich SiC will react with TiC to form the TSC phase in the case of 100nm Ti interlayer.

The equilibrium diagram provides the framework for understanding interfacial reaction in the SiC/Ti system from a thermodynamically point of view. In the present work, the joining process of SiC ceramics is actually the solid state reaction between low-activity SiC and highly chemically active Ti. The initial stage of reaction should be determined by the diffusion of Si and C into Ti metal, the kinetic process become more important than thermodynamic consideration to understand the real reaction route. In the equilibrium state determined by isothermal phase diagram of Ti-Si-C ternary system (Fig. 7a), the final composition of the reaction of Ti and SiC falls into the triangle of $TiSi_2$-SiC-Ti_3SiC_2, and close to the SiC point since the Ti reactant was confined in the interlayer. However, due to the isolation of Si from Ti if a dense TiC layer forms on the surface of SiC, the formation of Ti-Si intermetallic components was largely inhibited. A potential-dependent phase diagram of Ti-Si-C system at 1100°C well explains such complexity of the reaction route (Fig. 7b) [52]. Masaaki Naka *et al.*, also investigated the interface reaction between Ti and SiC at 1673 K, and found interesting interface phase sequence that depended on bonding time:

SiC/$Ti_5Si_3C_X$+TiC/TiC/Ti), (SiC/$Ti_5Si_3C_X$ /$Ti_5Si_3C_X$+TiC/TiC/Ti) and (SiC/Ti_3SiC_2 / $Ti_5Si_3C_X$ /$Ti_5Si_3C_X$+TiC/TiC/Ti) for bonding time of 0.3 ks, 0.9 ks and 3.6 ks, respectively [50]. This kind of phase formation sequence is hard to be illustrated by the isothermal phase diagram of ternary Ti-Si-C which only tell us the homogeneous distribution and weight percentage of each final phase. In term of potential diagram the above phase sequence can thus reasonably explained.

In the present work, since the joining time is too short, the generated phases and their distribution are also different from these in the equilibrium diagram. Therefore, the underlying diffusion-controlled reaction mechanism could be setup for the understanding of joining process in terms of potential diagram of the Ti-Si-C system analysis. At the same joining condition, the energy at the interface for atomic diffusion and nucleation is certain, the diffusion distance of each element is determined; the relative contents of Ti, Si, and C in the joining layer were decided by the thickness of joining layer. So the diffusion path should be different for different thickness joining layer. It already indicated that SiC should decompose into silicon and carbon at SiC/Ti interface firstly. And because C atom radius is less than Si atom, in Ti-Si-C system, C atom is the fastest diffusing element. For example, at 1200°C, the diffusion of carbon is about 10 times faster than that of Si in Ti [51]. So C easily diffuse into Ti interlayer, but Si still stay at the interface on the side of SiC. If the Ti interlayer is thin (such as 100 nm) the concentration of C in Ti soon becomes saturated and lead to the formation of TiC. The *in-situ* formed TiC further hamper the diffusion of Si atom into interlayer. The formation of Ti-Si brittle intermetallic phases were thus inhibited as the acid corrosion experiment confirmed as shown in Fig. 6e. If the joining temperature increased to 1100°C, the *in-situ* generated TiC can react with residual Ti and Si, to form TSC as follow [52]:

$$2TiC+Ti+Si=Ti_3SiC_2 \qquad (3\text{-}9)$$

In fact, when C/(C+Ti) mole ratio is between 0.4 and 0.5 and activity/concentration of Si is low enough, the TiC phase is the predominant one in the product without the formation of Ti_5Si_3 phase. Approaching appropriate concentration, Si atoms reacts with TiC phase to form the Ti_3SiC_2 phase (the inverse of decomposition of Ti_3SiC_2 phase, Eq. 3-2). This reaction route without formation intermediate phase of silicide (TiC_{1-x} to T+ TiC_{1-x}) well corroborates the phase evolution of joints in the case of 100nm Ti interlayer (marked in the Fig. 7b). In the

cases of micro and sub-micro size of Ti interlayer, the C atoms was diluted in the Ti, and the nucleation density of TiC was lower than that in the case of 100nm Ti interlayer. That is the reason the layer of TiC become less continuous and finally in the form of dispersoid in the joints (Fig. 5f and 5g). In the 6μm Ti interlayer, only big particles was formed due to rapid grain growth of low concentration TiC nuclei (Fig. 5h). The latter case ensured the Si diffusion into Ti interlayer and to form some brittle phase such as Ti_5Si_3. It can be of evidence in the potential phase diagram that lowering carbon concentration intrigues the formation of Ti_5Si_3 phase.

From above discussion, the interface reaction and phase evolution can be proposed tentatively as follow (scheme 1):

(i) joining with 100nm Ti interlayer

The reaction began with rapid decomposition of SiC into carbon and silicon when contacted active Ti. Carbon atoms diffused to Ti interlayer to achieve a sutured concentration which led to the formation of a dense TiC layer (scheme 1). Then, the as-formed dense TiC layer can act as a diffusion barrier to inhibit the Si diffusion from SiC substrate side into the Ti interlayer. As joining temperature increased, ternary phase of TSC appeared through the reaction of (Eq. 3-9). As the temperature reaching 1500°C or higher, TSC decomposed into TiC and Ti-Si silicides which aided the sintering of SiC grain in the interface.

(ii) joining with micro and sub-micro size Ti interlayer.

Following the same initial decomposition of SiC in touch of active Ti interlayer, carbon seemed largely dissolved into the Ti solution without forming a layer of dense barrier. Meanwhile, Si also diffused into Ti interlayer and thermodynamically satisfied the formation of intermetallic phases, such as Ti_5Si_3. The particle size and distribution of TiC and intermetallic phases were dependent on the thickness of Ti interlayers (Scheme 1).

3.4 Mechanical property of jointed SiC couples

Table 1 shows four-point bending strength and failure location for the SiC couples joined at different temperature. Even at temperature as low as 600°C, the bending strength of 169.7MPa was achieved in the samples of 1μm Ti interlayer. When the thickness of Ti coating film is 100nm, the bending strength of the joining couples increased with the joining temperature. That is due to the densification of interlayer

and the ternary phase of TSC formation at high temperature [53-55]. When fixed joining temperature of 1000°C, the bending strength highly depended on the existence of brittle phase. In the joint of 100nm Ti interlayer, part of fracture located in the matrix, meaning the strong interface strength after formation of TSC phase. On the contrary, in the samples of thick Ti interlayer (6μm), the strength as low as about 50MPa was maintained due to the deteriorative phases of Ti and Ti_5Si_3. The sample with 500 nm Ti interlayer achieved the highest average bending strength of 205.7MPa. However, the existence of Ti_5Si_3 will influence the joint reliability in the corrosion environment.

The typical failure modes are showing in the Fig. 8 and also indicated in the Table 1. The failure mostly occurred at the interface (I) for the samples joined at 600°C. When the joining temperature is 900°C, failure cracks propagated partially cross interlayer and partially along interface (I+J) and some samples fracture at the SiC matrix (M), meaning improved interface bonding at high temperature. When the joining temperature increased to 1300°C and 1600°C, all fracture occurred at the matrix of SiC ceramics. In these cases, the shear strength of interlayer and interface were stronger than the bending strength of SiC jointed. These distinct fracture behaviors in the SiC with 1μm Ti interlayer at different temperature directly related to the final interlayer phases as listed in Table 1. Obviously, the residual Ti metal and amounts of intermetallic phase weakened the interface strength. The refractory phases in the interlayers, such as TiC and Ti_3SiC_2, largely strengthened the robust joints.

The above bending strength evaluation on the joints illustrated the importance of phase composition and underlying fracture mechanism. Future studies will address suitability of the above robust joining technique for nuclear energy application which requires joints to be corrosion-resistant, irradiation tolerant and structure-integrity at high temperature.

4. Conclusions

Monolithic 6H-SiC were successfully joined with active Ti as interlayer by FAST. The interface reaction mechanism and phase evolution in the final interlayer after joining were carefully characterized, and also analyzed based on diffusion-controlled potential diagram of ternary Ti-Si-C system. When 100nm Ti interlayer was used to join SiC, Ti_5Si_3 brittle phase that is very harmful to the joint property for its intrinsic thermal expansion anisotropy, was found largely depressed due to a continuous and

dense TiC formed on the joining interface. The isolation of Si from Ti interlayer by such TiC layer consequently participated the formation of Ti_3SiC_2 phase without the intermediate phase formation of Ti_5Si_3 brittle phase at low temperature. On the contrary, when the Ti interlayer was thick enough, the Ti_5Si_3 phase always co-existed in the interlayer with TiC and Ti_3SiC_2 phases. The bending strength of SiC couples also indicated the importance of the phase composition and their distribution in the joint interlayer. Due to their excellent features of anti-corrosion and irradiation damage of the TiC and Ti_3SiC_2 phases, the interlayer phase controlled joining technique will have an important application in the nuclear energy materials, such as SiC_f/SiC composite cladding materials in accident-tolerant fuel system.

Acknowledgements

This work was supported financially by the National Natural Science Foundation of China (Grant No. 91426304 and 51502310), CAS Interdisciplinary Innovation Team, the Strategic Priority Research Program of Chinese Academy of Science (Grant No. XDA03010305) and the Natural Science Foundation of Zhejiang Province (Grant No. LY15E020007).

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Figure captions

Fig.1 SEM images of as-formed SiC joints using 1μmTi interlayer and joined at temperature of (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C, (f) 1000°C, (g) 1100°C, (h) 1200°C, (r) 1300°C, (s) 1400°C, (m) 1500°C and (n) 1600°C.

Fig.2 XRD patterns of final interlayer phase of SiC couples using 1μm Ti interlayer and joined at temperature of (a) 600°C, (b) 900°C, (c) 1300°C and (d) 1600°C, respectively.

Fig.3 SEM images of acid-corroded SiC joints using 1μm Ti interlayer and joined at temperature of (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C, (f) 1000°C, (g) 1100°C, (h) 1200°C, (r) 1300°C, (s) 1400°C, (m) 1500°C and (n)1600°C.

Fig. 4 (a) TEM image of sample joined at 1600°C with 1 μm Ti interlayer of sintered region; (b) and (c) is the STEM mapping and element distributions (Ti, Si and C) in the locations of yellow (b) and orange (c) rectangle areas pointed out in (a); (d), (e) and (f) is the high resolution transmission electron micrograph (HRTEM) of the point 1, 2 and 3 in (a), respectively.

Fig. 5 Backscattered electron images of as-joined and acid-corroded cross sections of SiC joints with initial Ti thickness of 100 nm (a and e), 500 nm (b, and f), 1 μm (c and g) and 6 μm (d and h) and joined at 1000°C.

Fig. 6 (a) TEM image of sample joined at 1100°C with 100 nm Ti coating as joining layer; (b) and (c) is HRTEM of the region as marked 1 and 2 in (a), respectively; (d) STEM image of the sample and element mapping of same area; the elemental distribution of (e) Ti, (f) Si and (g) C.

Fig.7 (a) Isothermal phase diagram for Ti-Si-C system at 1100°C; (b) Potential diagram of the Ti-Si-C system at 1100°C [49]. T means Ti_3SiC_2 phase.

Fig.8 Typical failure modes of the SiC couples joined at temperature of (a) 600°C, (b) 900°C, (c) 1300°C and (d)1600°C, respectively.

Scheme 1 Phase evolution process in SiC/Ti system with varied thickness of interlayers.