Journal of Advanced Ceramics
2014, 3(1): 71–75
DOI: 10.1007/s40145-014-0095-z

ISSN 2226-4108
CN 10-1154/TQ

Research Article

Microstructure of reaction layer and its effect on the joining strength of SiC/SiC joints brazed using Ag–Cu–In–Ti alloy

Yan LIU*, Yunzhou ZHU, Yong YANG, Xuejian LIU, Zhengren HUANG

Key Laboratory of High Performance Ceramics and Superfine Microstructure of Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P.R. China

Received: September 10, 2013; Revised: December 31, 2013; Accepted: January 21, 2014

Abstract: The SiC/SiC joints were vacuum brazed at 700 ℃, 740 ℃, 780 ℃ and 800 ℃ for 10 min respectively, using Ag–Cu–In–Ti active filler alloy. The microstructure and joining strength of the joints were characterized by electron probe X-ray microanalyser (EPMA), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM) and four-point bending strength test. The interface of the joints was composed of three parts: SiC substrate, reaction layer and filler alloy. A representative microstructure of the reaction layer: In-containing layer/TiC layer/Ti_5Si_3 layer was found from the TEM image. The forming of the In-containing layer could be attributed to the crack or delamination of SiC/TiC interface. The In-containing layer intensified the coefficient of thermal expansion (CTE) mismatch of SiC and the reaction layer, and affected the joining strength. With the increase of the reaction layer's thickness, the joining strength firstly increased, then declined, and the maximum four-point bending strength reached 234 MPa.

Keywords: Ag–Cu–In–Ti; SiC/SiC joints; reaction layer; microstructure; joining strength

1 Introduction

SiC ceramics have become one of the most promising materials in many fields due to their excellent combination of low density, high-temperature resistance, high hardness and high thermal conductivity. However, it is difficult to fabricate SiC components with large size and complex shape because of the limitation of high cost and the equipments. Ceramic joining techniques provide a lower-cost and higher-reliable method to solve the problem. Different ceramic joining techniques, including adhesive, brazing, diffusion bonding, glass bonding and reaction bonding, have been developed to meet different demands [1–6]. Among these techniques, active brazing attracts great interest for its high joining strength and convenience in engineering applications.

Until now, a variety of active filler alloys, including Ag–Cu–Ti, Cu–Ti, Ti–Si, Ni–Cr, Ni–Si–B, Co-base, etc., are applied to join SiC ceramics [7–14]. Among all these active filler alloys, Ag–Cu–Ti is popular because of its good joining properties, and a lot of research focuses on the interfacial reaction between active element Ti and SiC substrate. Iseki *et al*. [15], López-Cuevas *et al*. [16] and Iwamoto and Tanaka [17] systematically investigated the reaction layer's

* Corresponding author.
E-mail: stony2000@mail.sic.ac.cn

microstructure and composition of SiC/Ag–Cu–Ti, and found that the classical interfacial reaction layer of SiC/Ag–Cu–Ti is composed of TiC layer and Ti_5Si_3 layer. The thickness, microstructure and composition of reaction layer have great influences on the joining strength [8,18].

In this work, a newly formed reaction layer structure was found when another lower-melting-point Ag–Cu–In–Ti active filler alloy was used to join SiC ceramics. In-containing layer was found to sit between SiC substrate and TiC layer. In order to clarify the formation mechanism of the newly formed reaction layer, electron probe X-ray microanalyser (EPMA), energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM) techniques were employed to investigate the interfacial microstructure. In addition, the effects of the newly formed reaction layer on the joining strength of SiC/SiC joints were discussed.

2 Experimental procedure

The sintered SiC bars used in this experiment were home-made, which contained a little carbon black and boron carbide as sintering aids. The average four-point bending strength and relative density of the sintered SiC bars are greater than 380 MPa and 99.8% of the theoretical density, respectively. The SiC bars with dimensions of 3 mm × 4 mm × 35 mm were ground at the surfaces of 3 mm × 4 mm (as joining surfaces) with 180 mesh diamond wheels. The thickness of Ag–Cu–In–Ti filler alloy foil (with composition of Ag – 27.25wt%Cu – 12.5wt%In – 1.25wt%Ti, Wesgo metal division, Morgan Advanced Ceramics Inc, U.S.A.) is 50 μm. Prior to joining, the SiC bars and the filler alloy foils were ultrasonically cleaned in acetone for 15 min and assembled into a jig with a sandwich structure of SiC/filler alloy/SiC. The joining was carried out at 700 ℃, 740 ℃, 780 ℃ and 800 ℃ for 10 min in a vacuum of 5×10^{-3} Pa, respectively. The samples were heated to brazing temperature at a rate of 8 ℃/min and cooled naturally after the process of holding-temperature. Six samples were prepared at each brazing condition. The joining strength of the samples was measured by four-point bending strength test on an Instron 5566 mechanical testing system with a displacement rate of 0.5 mm/min. The samples were ground and polished for EPMA test. Specimens with thickness of 0.5 mm for TEM test were treated by ion beam. The microstructure of the interface was observed by EPMA (JXA-8100, JEOL, accelerating voltage of 20 kV) and TEM (JEM-2010, JEOL, equipped with EDS, accelerating voltage of 200 kV). The thickness of reaction layers was measured from 10 different points on the EPMA and TEM images by Image-Pro Plus software and the average value was adopted.

3 Results and discussion

3.1 Reaction layer microstructure of SiC/SiC joints

Figure 1 shows the interfacial microstructure and element map-scanning analysis of SiC/SiC joints brazed by Ag–Cu–In–Ti filler alloy at 780 ℃ for 10 min. It reveals that the interface is composed of three parts: SiC substrate, reaction layer and filler alloy. The reaction layer connects SiC substrate and filler alloy tightly, and the thickness is about 0.4–0.5 μm. From the element map-scanning analysis, it can be found that grey phases are Cu and white phases mainly comprise Ag and In. Ti distribution peak appears in the reaction layer. In order to clarify the microstructure and composition of the reaction layer, TEM study was carried out. It can be found from the TEM image, as shown in Fig. 2, that the interface is composed of five layers (marked as layer 1 to layer 5). The boundaries between different neighboring layers are very clear. Layer 1 and layer 5 are on the edges of the interface, which are inferred as the SiC substrate and filler alloy (later confirmed by EDS), respectively. Therefore, the reaction layer is composed of three parts: layer 2, layer

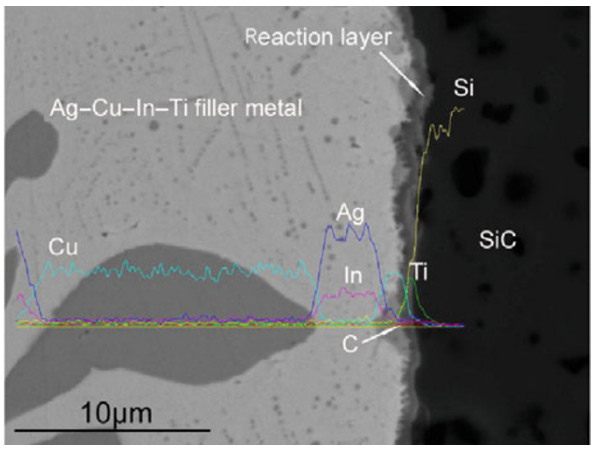

Fig. 1 Interfacial microstructure and element map-scanning analysis of SiC/SiC joints.

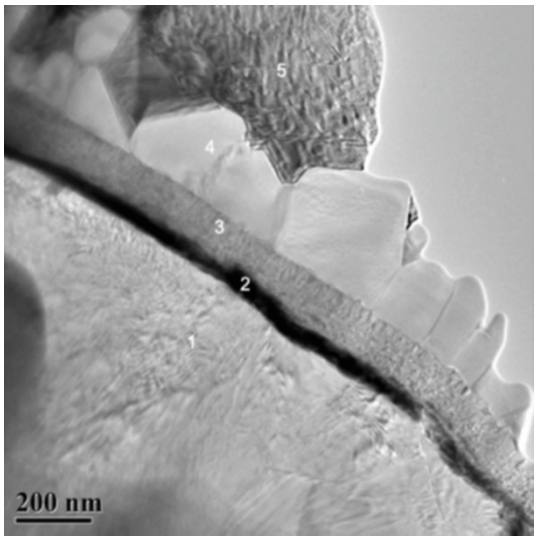

Fig. 2 TEM image of the reaction layer.

3 and layer 4. The thickness of layer 2 is about 50 nm, and the thickness of layer 3 is about 110–120 nm. Layer 4 is composed of many connecting grains, which means that the thickness of layer 4 is determined by the grain size. The grain size of layer 4 ranges from 200 nm to 380 nm. Compared with the reaction layer brazed by Ag–Cu–Ti filler alloy, layer 2 is a newly formed structure [18].

In order to identify the composition of the formed layers, EDS analysis was carried out. The results are shown in Table 1. The composition of layer 1 is consistent with SiC, indicating that layer 1 is the substrate itself. Layer 2 is composed of elements In, Si and Ag, and a little Ti, C and Cu. It is only in layer 2 that the element In was detected. Then, layer 2 is called In-containing layer. According to the results of EDS, the content of indium in layer 2 is about 8.1 at%, and the thickness of layer 2 is about 50 nm. However, the thickness of the as-received active filler alloy (including 12.5 wt%, i.e., 9.8 at% In) is 50 μm. Therefore, only about 0.1% of indium enters into the reaction layer, and most of indium stays in the filler alloy. The element map-scanning analysis of the joints confirms that most indium keeps in the white phases of the filler alloy. The formation mechanism of layer 2 and its effect on the joining strength will be discussed in the later section. Layer 3 is composed of C and Ti, and a little Ag, Cu and Si, and layer 4 is composed of only Ti and Si. To confirm the accurate phase structure, electron diffraction was used to detect layer 3 and layer 4. Figure 3 shows the electron diffraction patterns of layer 3 (Fig. 3(a)) and layer 4 (Fig. 3(b)). It can be found that layer 3 is TiC phase and the diffraction

Table 1 Chemical composition of different positions in the reaction layer

Position	Composition (at%)					
	C	Si	Ag	Cu	In	Ti
Layer 1	64.9	31.4	1.0	1.3	—	1.4
Layer 2	6.6	27.7	43.2	7.8	8.1	6.6
Layer 3	23.4	9.5	1.0	5.7	—	60.4
Layer 4	—	46.8	—	—	—	53.2
Layer 5	5.3	29.2	51.3	12.5	—	1.7

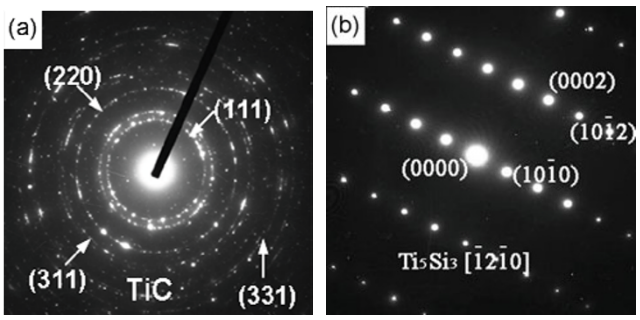

Fig. 3 Electron diffraction patterns of (a) layer 3 and (b) layer 4.

pattern is polycrystalline rings, which means that the grain size of TiC is nanoscale. Grains of layer 4 are confirmed as Ti_5Si_3 phase. Layer 5 is composed of elements Ag, Cu and Si, and a little C and Ti, which is confirmed as the filler alloy. Therefore, a representative reaction layer of SiC/SiC joints brazed by Ag–Cu–In–Ti filler alloy is In-containing layer/TiC layer/Ti_5Si_3 layer.

In-containing layer is adjacent to SiC substrate and TiC layer, containing Ag, In, Si and Ti. Some active element Ti is kept in the In-containing layer after the interfacial reaction of SiC/Ag–Cu–In–Ti. The remaining Ti does not react with SiC or transform into TiC and Ti_5Si_3, which is different from the interfacial reaction of SiC/Ag–Cu–Ti. The remainder of active Ti in In-containing layer leads to the decrease of the reaction layer's thickness. The formation mechanism of In-containing layer can probably be attributed to the crack or delamination of TiC/SiC interface. According to Iwamoto and Tanaka's research on the interfacial reaction of SiC/Ag–Cu–Ti [8], the brazing alloy melts and Ti diffuses to the boundary of SiC/Ag–Cu–Ti at brazing temperature, where Ti reacts with SiC rapidly to produce TiC and Ti_5Si_3. The interfacial reaction can be described as follows:

$$Ti + SiC = TiC + Si \quad (1)$$

$$5Ti + 3Si = Ti_5Si_3 \quad (2)$$

With the development of interfacial reaction, SiC decomposes gradually and TiC nucleates at the

boundary, accompanying with the movement from interface to SiC side. Finally, Ti is consumed completely and transformed into TiC and Ti_5Si_3. However, it is different in our work from those reported results. An In-containing layer is found between SiC substrate and TiC layer. It is speculated that during the interfacial reaction, the interface of SiC/TiC crakes or delaminates, leading to the nearby liquid brazing alloy flowing into the formed gap between SiC and TiC. When the brazing temperature cools down, the liquid brazing alloy including Ag, Cu, In, Ti and Si and C (decomposed products of SiC) freezes between SiC and TiC, which leads to the formation of In-containing layer.

3.2 Effect of reaction layer on the joining strength

Figure 4 shows the effect of reaction layer's thickness on the joining strength of SiC/SiC joints brazed using Ag–Cu–In–Ti filler alloy. It can be found that with the increase of brazing temperature, the reaction layer's thickness rises monotonously. However, the joining strength first increases then declines, and the maximum four-point bending strength of the joint reaches 234 MPa. The similar trend also can be found in the joints brazed using Ag–Cu–Ti [18], and the optimized reaction layer's thickness is about 0.8–0.9 μm. However, in this work, once the reaction layer's thickness exceeds 0.4 μm, the joining strength begins to decrease. The thickness of reaction layer has significant effect on the joining strength. On one hand, thin reaction layer resulting from insufficient interfacial reaction leads to poor joining strength. On the other hand, thick reaction layer also degrades the joining strength due to the coefficient of thermal expansion (CTE) mismatch. Before 740 ℃, interfacial reaction is the predominant factor to determine the joining strength. However, when the brazing temperature is higher than 740 ℃, the CTE mismatch of SiC and reaction layer becomes the predominant factor to determine the joining strength. In addition, the In-containing layer, comprising many metallic elements with high thermal expansion, such as In, Ag and Ti, intensifies CTE mismatch of SiC substrate and reaction layer. Therefore, the reaction layer's thickness has more important influence on the joining strength in the joints brazed by Ag–Cu–In–Ti. Figure 5 shows the fracture path of SiC/SiC joints brazed at different temperatures. The fracture occurs at SiC substrate near

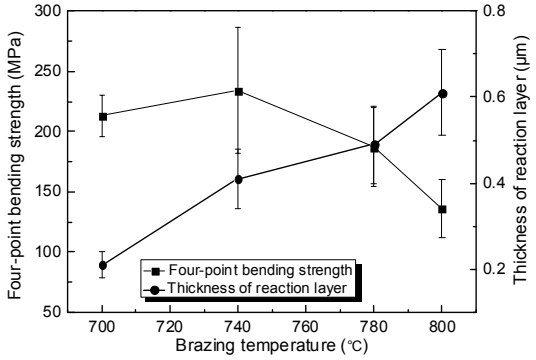

Fig. 4 Effect of the reaction layer's thickness on the joining strength of SiC/SiC joints.

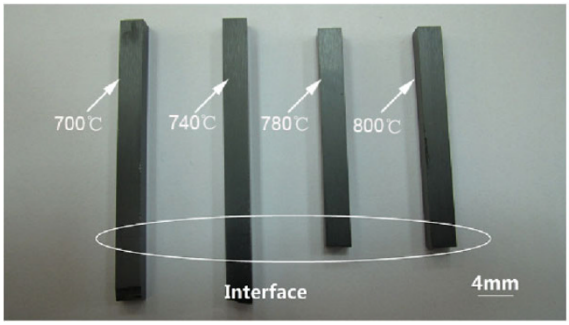

Fig. 5 Optical image of fracture path for the SiC/SiC joints.

the interface for the joints brazed at 700 ℃ and 740 ℃. However, the fracture is observed at the interface of SiC and reaction layer for the joints brazed at 780 ℃ and 800 ℃, indicating that residual stress caused by the CTE mismatch of SiC and reaction layer is responsible for the fracture.

4 Conclusions

Compared with Ag–Cu–Ti filler alloy, Ag–Cu–In–Ti active filler alloy not only decreases the brazing temperature, but also changes the reaction layer's microstructure of SiC/SiC joints. A representative reaction layer's microstructure: In-containing layer/ continuous TiC layer/discontinuous Ti_5Si_3 layer is found. The formation of In-containing layer can be attributed to the crack or delamination of SiC/TiC interface. With the increase of reaction layer's thickness, the joining strength first raises, then declines, and the maximum four-point bending strength reaches 234 MPa. The In-containing layer with higher CTE intensifies CTE mismatch of SiC and reaction layer, leading to the deterioration of the joining strength.

Acknowledgements

The authors gratefully acknowledge the financial support from Chinese Academy of Sciences.

References

[1] Wang J, Guo Q, Liu L, *et al*. The preparation and performance of high-temperature adhesives for graphite bonding. *Int J Adhes Adhes* 2005, **25**: 495–501.

[2] Halbig MC, Coddington BP, Asthana R, *et al*. Characterization of silicon carbide joints fabricated using SiC particulate-reinforced Ag–Cu–Ti alloys. *Ceram Int* 2013, **39**: 4151–4162.

[3] Cockeram BV. Flexural strength and shear strength of silicon carbide to silicon carbide joints fabricated by a molybdenum diffusion bonding technique. *J Am Ceram Soc* 2005, **88**: 1892–1899.

[4] Katoh Y, Kotani M, Kohyama A, *et al*. Microstructure and mechanical properties of low-activation glass-ceramic joining and coating for SiC/SiC composites. *J Nucl Mater* 2000, **283–287**: 1262–1266.

[5] Luo Z, Jiang D, Zhang J, *et al*. Development of SiC–SiC joint by reaction bonding method using SiC/C tapes as the interlayer. *J Eur Ceram Soc* 2012, **32**: 3819–3824.

[6] Tian W, Kita H, Hyuga H, *et al*. Reaction joining of SiC ceramics using TiB_2-based composites. *J Eur Ceram Soc* 2010, **30**: 3203–3208.

[7] Nomura M, Ichimori T, Iwamoto, *et al*. Structure of wetting front in the Ag–Cu–Ti/SiC reactive system. *J Mater Sci* 2000, **35**: 3953–3958.

[8] Iwamoto C, Tanaka S-I. Atomic morphology and chemical reaction of the reactive wetting front. *Acta Mater* 2002, **50**: 749–755.

[9] Xiong J, Li J, Zhang F, *et al*. Joining of 3D C/SiC composites to niobium alloy. *Scripta Mater* 2006, **55**: 151–154.

[10] Li J, Liu L, Wu Y, *et al*. A high temperature Ti–Si eutectic braze for joining SiC. *Mater Lett* 2008, **62**: 3135–3138.

[11] Mao Y, Li S, Yan L. Joining of SiC ceramic to graphite using Ni–Cr–SiC powders as filler. *Mat Sci Eng A* 2008, **491**: 304–308.

[12] Mao Y, Mombello D, Baroni C. Wettability of Ni–Cr filler on SiC ceramic and interfacial reactions for the SiC/Ni–51Cr system. *Scripta Mater* 2011, **64**: 1087–1090.

[13] Singh M, Asthana R, Shpargel TP. Brazing of ceramic-matrix composites to Ti and Hastealloy using Ni-base metallic glass interlayers. *Mat Sci Eng A* 2008, **498**: 19–30.

[14] Xiong H-P, Mao W, Xie Y-H, *et al*. Control of interfacial reactions and strength of the SiC/SiC joints brazed with newly-developed Co-based brazing alloy. *J Mater Res* 2007, **22**: 2727–2736.

[15] Iseki T, Yano T, Chung Y-S. Wetting and properties of reaction products in active metal brazing of SiC. *J Ceram Soc Jpn* 1989, **97**: 710–714.

[16] López-Cuevas J, Rendón-Angeles JC, Rodríguez-Galicia JL, *et al*. High temperature chemical interaction between SSiC substrate and Ag–Cu based liquid alloys in vacuo. *Mater Sci Forum* 2006, **509**: 111–116.

[17] Iwamoto C, Tanaka S-I. Reactive wetting of Ag–Cu–Ti on SiC in HRTEM. *Acta Mater* 1998, **7**: 2381–2386.

[18] Liu Y, Huang ZR, Liu XJ. Joining of sintered silicon carbide using ternary Ag–Cu–Ti active brazing alloy. *Ceram Int* 2009, **35**: 3479–3484.