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Short communication

Joining of sintered silicon carbide using ternary Ag–Cu–Ti active brazing alloy

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Abstract

Sintered silicon carbide was brazed to itself by Ag–35.25 wt%Cu–1.75 wt%Ti filler alloy at 860 °C, 900 °C and 940 °C for 10 min, 30 min and 60 min. Mechanical properties both at room temperature and high temperature were measured by flexural strength. The interfacial microstructure was investigated by electron probe microanalysis (EPMA), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The experimental results indicate that increased brazing temperature heightens the flexural strength and the maximal four-point flexural strength reaches 342 MPa at room temperature. In addition longer holding times result in thicker reaction layer, which increases mismatch of coefficients of thermal expansion (CTE) between SiC substrate and reaction layer and finally leads to poor mechanical properties due to high residual stresses. High temperature flexural strength decreases with an increase of test temperature due to softening of the filler alloy. A reaction layer composed of TiC and Ti_5Si_3 was observed at the interface of SiC/filler alloy and there is a representative microstructure: SiC/continuous fine TiC layer/discontinuous coarse Ti_5Si_3 layer/filler alloy.

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1. Introduction

Silicon carbide based advanced ceramic is an attractive material for applications in aerospace, electronics, nuclear and transportation industry because of its excellent mechanical properties, high elastic module, high thermal conductivity and corrosion resistance [1]. Engineering designs of silicon carbide components often involve large dimensions and complex shapes, which are difficult to fabricate due to the process limit and high cost. Joining of simple or small components to build up complex or large ones is an effective method to overcome the difficulty. Therefore some technologies of joining ceramics have been developed, such as solid state bonding, brazing, preceramic polymer joining, glass oxide joining and gluing method [2–6]. Among these techniques, active brazing, especially using Ti as the active element, triggers the great interests. Ag–Cu–Ti system wets nearly all the ceramics and shows good joints strength [7–9]. In previous work [10,11] Ag–Cu–Ti filler alloy which was used to braze SiC ceramic was often in the form of paste or combination of Ag–Cu foil and Ti foil, and most researches were concentrated on the strength at room temperature [11,12]. Compared with paste and combination of two foils, the thickness and composition of ternary Ag–Cu–Ti foil are more uniform. In this paper, attention was focused on the mechanical properties of SiC/SiC joints brazed by ternary Ag–Cu–Ti foil both at room temperature and high temperature. In addition the microstructures of the interface and reaction layer, including composition, morphology were studied.

2. Experimental procedure

Sintered silicon carbide employed in the experiment was home-made, which consists of a little carbon black and boron carbide as sintering aids. The average flexural strength of SiC at room temperature is over 400 MPa and relative density

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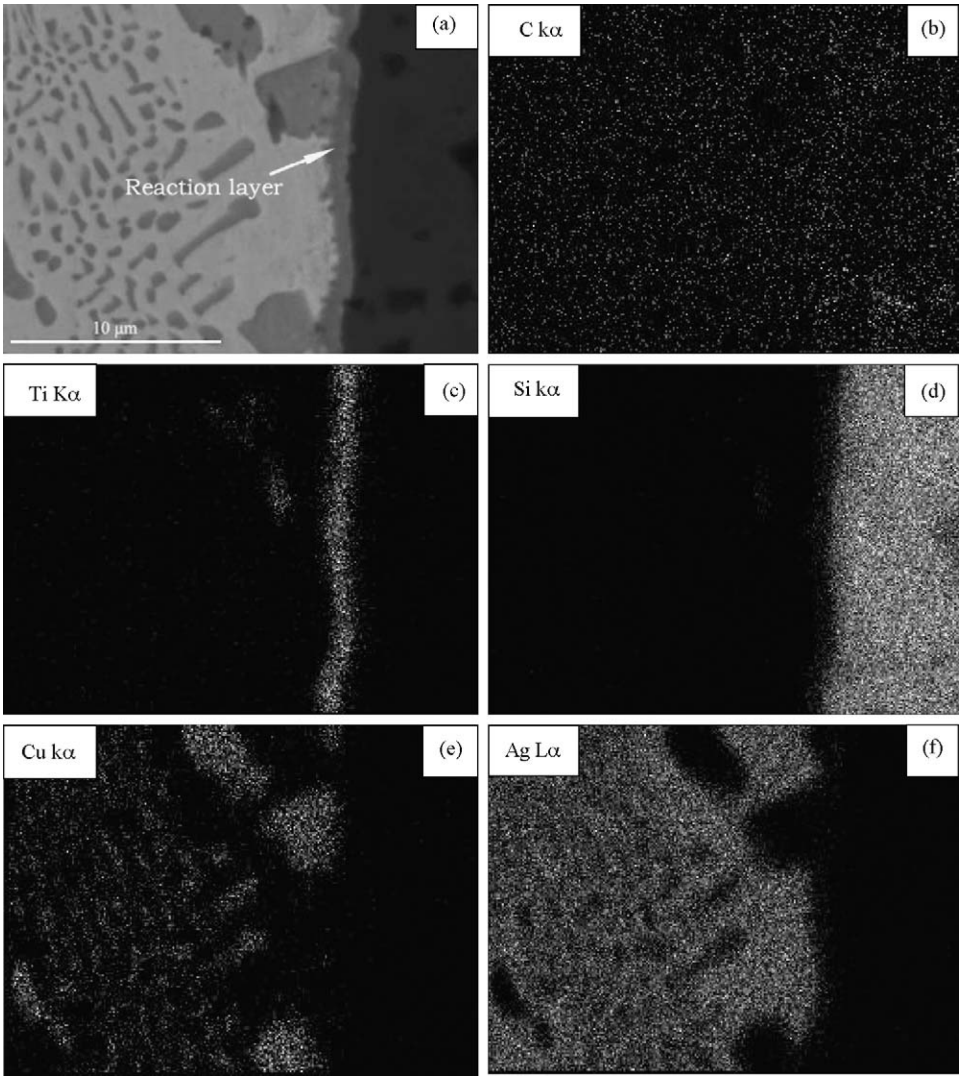

Fig. 1. Interface BEI image of SiC/SiC joints brazed by Ag–Cu–Ti filler alloy at 900 °C/10 min and element distribution. (a) Interface BEI image, (b) distribution of element C, (c) distribution of element Ti, (d) distribution of element Si, (e) distribution of element Cu, and (f) distribution of element Ag.

reaches 99.8% of the theoretical density. The sintered SiC bars were ground into dimensions of 3 mm × 4 mm × 25 mm and the surfaces of 3 mm × 4 mm (joining surfaces) were ground with 180 mesh diamond wheel which ensures $R_a < 30$ μm. The ternary Ag–Cu–Ti filler alloy foil, with composition of Ag–35.25 wt%Cu–1.75 wt%Ti was provided by Wesgo metal division, Morgan Advanced Ceramics Inc USA and its thickness is 50 μm. The filler alloy was also cut into the dimensions of 3 mm × 4 mm. Before joining, the SiC bars and filler alloy foils were ultrasonically cleaned in acetone for 15 min and were assembled into a stainless steel jig after drying. The joining was carried out at 860 °C, 900 °C and 940 °C for 10 min, 30 min and 60 min in a vacuum furnace with a vacuum better than 5×10^{-3} Pa. The samples were heated to brazing temperature at a rate of 8 °C/min and cooled naturally after holding times. The joints strength at room temperature was measured by four-point flexural test on an Instron 5566 mechanical testing system with a displacement rate of 0.5 mm/min. Strength at high temperature was measured by three-point flexural test on an Instron 5500R testing system with a displacement rate of 0.5 mm/min. The high temperature strength test was carried out in air with a heating rate of 6 °C/min and the specimens were kept at testing temperature for 10 min. For each set of test, at lease five specimens were involved. The reaction products were confirmed by X-ray diffraction (D/max-2500 V) and the microstructure of interface was observed by electron probe microanalysis (JXA-8100) and transmission electron microscope (JEM-2010). One face of brazed SiC bars which includes interface was ground and polished to a surface finish of 0.05 μm as specimens for EPMA test. Specimens for XRD test were cut from the brazed SiC bars along the direction parallel to the joining face and then ground to expose the filler alloy. Specimens of about 0.5 mm thick for TEM test were made by Focus Ion Beam (FIB). The thickness of reaction layers was measured at 20 different sites on the EPMA photographs by Image-Pro Plus software and average value was adopted.

3. Results and discussion

3.1. Interfacial microstructures of SiC/SiC joints brazed by Ag–Cu–Ti filler alloy

Fig. 1 presents the backscattered image of interface of SiC/Ag–Cu–Ti/SiC joints brazed at 900 °C/10 min and the corresponding elemental distribution. It is shown that the interface is composed of three parts: filler alloy zone, reaction layer and SiC zone. In Ag–Cu–Ti filler alloy zone, there exist two distinct phases: dark phase and grey phase, which distribute discretely. They were confirmed as Cu and Ag respectively by the elemental distribution in Fig. 1(e) and (f). An obvious continuous compact reaction layer is adjacent to filler alloy and SiC ceramic, which combines SiC and filler alloy tightly and shows no crack. It can be seen from Fig. 1(c) that Ti distribution coincides with the shape of reaction layer very well, which means that nearly all the active element Ti concentrated on the reaction layer. It also can be found from the Si distribution, as seen in Fig. 1(d), that Si exists not only in SiC zone but also in reaction layer. XRD result indicates that new phases TiC and Ti_5Si_3 formed in the interface, as shown in Fig. 2. The formation of interfacial microstructure is attributed to the addition of active element Ti, which diffused at the SiC/filler alloy interface and reacted with SiC. According to the thermodynamic data manual [13], the Gibbs free energy of SiC and TiC formation are represented as below

$$\Delta G^0(\mathrm{SiC})\,(\mathrm{kJ/mol}) = -53.4 + 0.0069T \tag{1}$$

$$\Delta G^0(\mathrm{TiC})\,(\mathrm{kJ/mol}) = -183.1 + 0.01T \tag{2}$$

It can be found that the free energy for formation of SiC and TiC are both negative at brazing temperature from 860 °C to 940 °C; however the free energy of TiC is lower than SiC at the same temperature, which means that TiC is more stable than SiC. So Ti atoms which concentrate at the interface react with SiC at brazing temperature and form TiC. At the same time Si atoms are released from SiC, which react with Ti atoms and form Ti_5Si_3. The reaction layer is composed of TiC and Ti_5Si_3 which is consistent with the result of Ti and Si distribution in the reaction layer. With regards to filler alloy, Ag and Cu separate each other after the filler alloy solidifies from liquid phase.

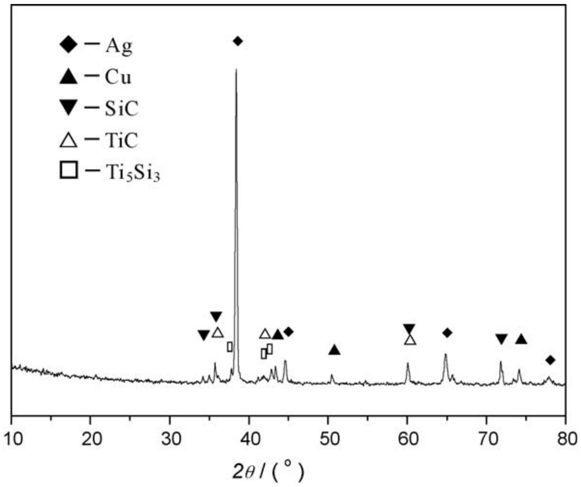

Fig. 2. XRD pattern of interface of SiC/SiC joints brazed by Ag–Cu–Ti filler alloy.

3.2. Morphology of the reaction products

Fig. 3 presents TEM image of reaction products TiC and Ti_5Si_3 and their diffraction pattern. There is a representative microstructure of SiC/continuous fine TiC layer/discontinuous coarse Ti_5Si_3 layer/filler alloy. TiC layer adheres to SiC and is continuous; its diffraction pattern shows polycrystalline rings. The HRTEM image of TiC, as shown in Fig. 3(b) reveals that the grain size of TiC is about 10 nm. However the grain size of Ti_5Si_3 varies from 100 nm to 500 nm and the Ti_5Si_3 layer is discontinuous. This structure is similar to the

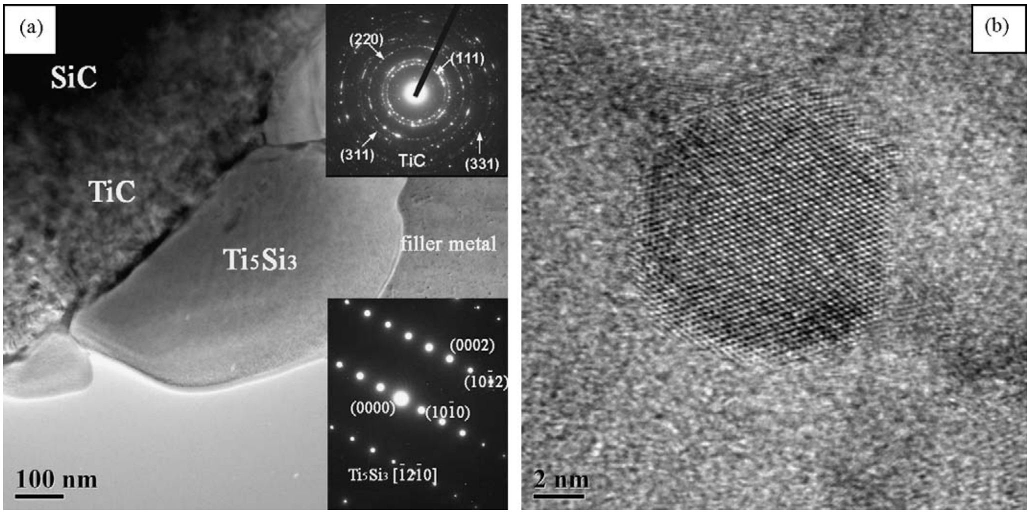

Fig. 3. Microstructure of interfacial reaction layer and HRTEM image of TiC. (a) Microstructure of reaction layer and diffraction pattern and (b) HRTEM image of TiC grain.

structure of Si_3N_4/Si_3N_4 joints brazed by Cu–Zn–Ti filler alloy [14].

The morphology difference of the reaction products is attributed to the different growth kinetics. Nomura [15] found that the nucleating size of TiC grain was only about 10 nm when investigating the SiC/Ag–Cu–Ti system with TEM method, and even about 1 nm size of nucleated TiC has been observed in Iwamoto's research [16]. The small nucleating size means nucleation of TiC grain is easy, so lots of TiC nucleate and grow in a short time when Ti enrich in the boundary of SiC/filler alloy and react with SiC at brazing temperature. Nucleation rate is predominant for TiC growth kinetics. However, growth will be retarded once the TiC grains contact each other, which results in continuous fine TiC grain layer. With regard to Ti_5Si_3, its growth is different from TiC. Some studies [17,18] reported that the critical nucleation size of Ti_5Si_3 is about 20 nm in Ti/SiC system, Ag–Cu–Ti/SiC system and Ag–Cu–Ti/Si_3N_4 system, which far exceeds the expectation of Ti_5Si_3 nucleation size. Large nucleation size means high energy fluctuation and abundant elements supply need to be met, so Ti_5Si_3 nucleates only on the position where energy and composition conditions are met. Growth of individual grain is predominant for Ti_5Si_3 growth kinetics. Separated nucleated Ti_5Si_3 grains grow gradually with the more supply of Si, which results in the discontinuous coarse Ti_5Si_3 layer.

3.3. Mechanical properties

Table 1 demonstrates the effects of brazing temperature and holding times on the joints strength at room temperature and high temperature flexural strength at different testing temperature. The thickness of reaction layer and crack path are also listed in the table to explain the dependence of joints strength on the microstructure of interface.

Table 1 reveals that the joints strength at room temperature increases rapidly with an increasing of brazing temperature and the maximal four-point flexural strength reaches 316 MPa at 940 °C/10 min when holding time is 10 min. At the same time the thickness of reaction layer shows the same trend as the joints strength. The thickness of reaction layer has a significant effect on the joints strength at room temperature, which is consistent with previous studies [19–21]. On one hand, appropriate thickness of reaction layer can improve the joints strength, which can be found from the effects of brazing temperature on the joints strength for short holding time. Lower brazing temperature results in insufficient interface reaction, which leads to poor joints strength. As a result fracture occurs along the interface of ceramics/reaction layer, such as the joints brazed at 860 °C. While higher brazing temperature results in sufficient interface reaction and joints strength, which causes mixed fracture from interface to ceramics and fracture generating on the ceramics near the interface, such as the joints brazed at 900 °C and 940 °C. Fig. 4 shows the different fracture modes schematics. On the other hand, with an increase of thickness of reaction layer, the CTE mismatch between SiC substrate and reaction layer increase and residual stress rises, which cause the decline of joints strength. For example the strength of joints brazed for 60 min holding time generally decreases compared with that of joints brazed for 30 min holding time at all brazing temperature. The change of joints

Table 1
Effects of brazing temperature and holding times on joints strength at room temperature and high temperature joints strength at different testing temperature.

Condition	Thickness (μm)	Flexural strength (MPa) at testing temperature (°C)			
	Reaction layer	20	300	400	500
10 min					
860 °C	0.5	[a]109 ± 8			
900 °C	0.69	[b]219 ± 48			
940 °C	0.73	[b,c]316 ± 38			
860 °C					
10 min	0.5	[a]109 ± 8			
30 min	0.67	[a]114 ± 24			
60 min	0.79	[a]110 ± 27			
900 °C					
10 min	0.69	[b]219 ± 48			
30 min	0.85	[c]342 ± 69			
60 min	1.01	[b]263 ± 38			
940 °C					
10 min	0.73	[b,c]316 ± 38			
30 min	1.19	[b]284 ± 41			
60 min	1.37	[b]250 ± 61			
[d]900 °C					
10 min		[e,b]339 ± 29	[e,a]155 ± 22	[e,a]139 ± 30	[e,a]88 ± 29

[a] Fracture at the interface of ceramics and reaction layer.
[b] Mixed fracture from interface to ceramics.
[c] Fracture on the ceramics near the interface.
[d] Samples were brazed at 900 °C/10 min, then cooled from 900 °C to 500 °C at 5 °C/min.
[e] Three-point flexural strength.

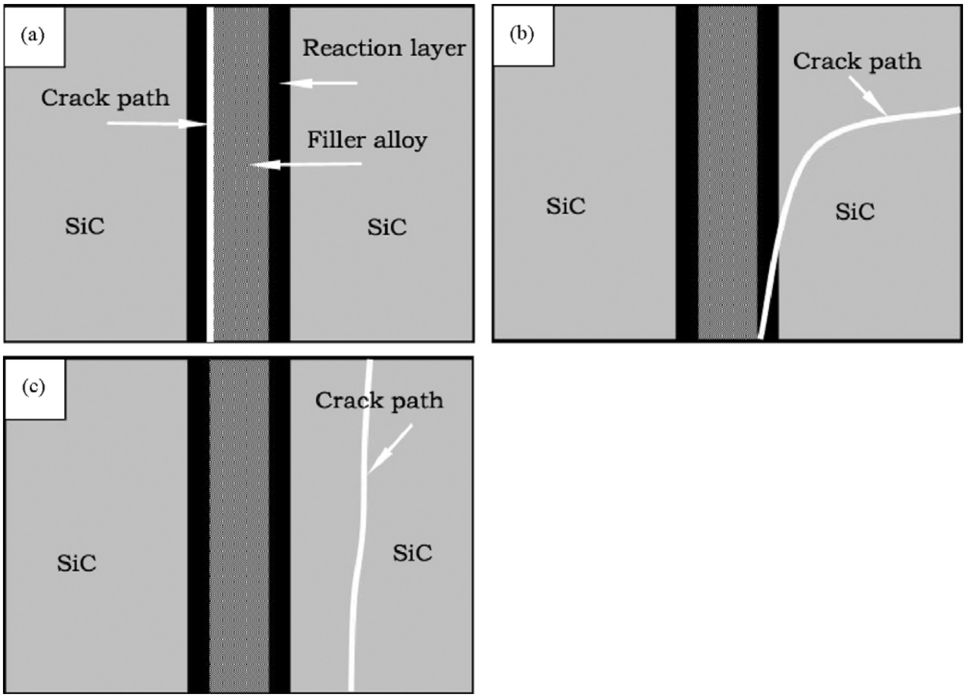

Fig. 4. Schematic diagram of fracture modes for the SiC/SiC joints brazed by Ag–Cu–Ti filler alloy. (a) Fracture at the interface of ceramics and reaction layer, (b) mixed fracture from interface to ceramics, and (c) fracture on the ceramics near the interface.

strength and fracture route is attributed to the combination of the increase of the reaction layer thickness and residual stresses generated by the CTE mismatch between SiC and TiC/Ti_5Si_3 reaction layer. The maximal joints strength at room temperature can be obtained only at appropriate brazing temperature and holding times. The proper thickness of reaction layer has an important role for the joint strength. Thinner reaction layer lead to poor joints strength because of insufficient interface reaction, whereas thicker reaction layer also decrease joints strength because of the residual stresses caused by CTE mismatch between SiC and reaction layer. In this research a optimum brazing condition 900 °C/30 min was obtained at which joints strength at room temperature can reach 342 MPa.

The high temperature joints strength decreases with an increase of testing temperature, as shown in Table 1. The flexural strength at 300 °C is 46% of that at room temperature, while the strength decreases to 26% at 500 °C. With an increase of testing temperature, the morphology of fractured surfaces change from sinuation to straight. The softening of filler alloy layer at high temperature is the main reason for the decreasing of joints strength.

4. Conclusions

Silicon carbide was brazed to itself by ternary Ag–Cu–Ti filler alloy foil successfully. The joint strength at room temperature increases with an increase of brazing temperature for short holding times because the reaction layer become thicker. However, too longer holding times lead to poor joints strength because too thick reaction layer cause the increase of CTE mismatch between SiC substrate and reaction layer and residual stress rises. High temperature joints strength decreases with an increase of testing temperature due to the softening of filler alloy. The reaction layer formed at SiC/filler alloy is composed of TiC and Ti_5Si_3. There is a representative microstructure: SiC/continuous fine TiC layer/discontinuous coarse Ti_5Si_3 layer/filler alloy in the reaction layer.

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