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Interfacial microstructure of the Si_3N_4/Si_3N_4 joint brazed with Cu–Pd–Ti filler alloy

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Abstract

Si_3N_4 ceramic was jointed with itself by active brazing with a Cu–Pd–Ti filler alloy. Interfacial microstructure of the Si_3N_4/Si_3N_4 joint was analyzed by EPMA, TEM and X-ray diffract meter. The results indicate that a TiN reaction layer with a thickness about 5 μm is formed at the interface between Si_3N_4 ceramic and filler alloy. The TiN reaction layer is composed of two zones: one next to the Si_3N_4 ceramic with grains of 100 nm and the other zone that connects with the filler alloy and has grains of 1 μm. The microstructure of the joint can be described as: Si_3N_4 ceramic/TiN layer with fine grains/TiN layer with coarsen grains/Cu[Pd] solid solution. Some new phases, such as Pd_2Si, PdTiSi, Ti_5Si_3 and TiN, were formed in the Cu[Pd] solid solution interlayer. With increasing brazing temperature from 1100 °C to 1200 °C, the thickness of the TiN reaction layer is not changed. Meanwhile, the amount and size of the TiN and Pd_2Si phases in the Cu[Pd] solid solution increase, while, the amount of the PdTiSi phase decreases.

Keywords: Si_3N_4; Joining; Interfaces; Microstructure

1. Introduction

Si_3N_4 ceramics, with higher strength and hardness, good corrosion and wearing resistance, excellent thermal resistance and lower coefficient of thermal expansion, have become one of the most promising structural materials for engineering applications.[1] Bonding techniques are necessary to obtain ceramic components with large size and complicated shapes. Ceramic bonding with lower cost and higher reliability can be achieved by these bonding techniques.

Various of methods have been adopted for welding Si_3N_4 ceramics, including partial transient liquid phase bonding,[2,3] refractory oxynitride joining,[4,5] diffusion bonding[6,7] and brazing.[8–10] Brazing technique is considered to be one of the most practical avenues to bond ceramics because of its advantages such as simple equipment and lower cost, higher and stable bonding strength, wide suitability for different size and shape of the joint, etc. In this research, Cu–Pd–Ti filler alloy was used to braze the Si_3N_4 ceramic. The interfacial microstructure between filler alloy and ceramic was studied and the bonding mechanism of the joint was investigated.

2. Materials and experimental procedures

The bulk Si_3N_4 ceramic used here was fabricated by hot pressure sintering. The bulk Si_3N_4 ceramic was cut and machined to a cylinder with a diameter and thickness of Ø 6 mm and 3 mm, respectively. The bonding surfaces of the ceramic were grinded to a surface finish of 30 μm with a diamond wheel. Metal foils of Cu, Ti and Pd, with thickness of 10 μm, 20 μm and 10 μm, respectively, were used as starting materials of filler alloy. In order to obtain a filler alloy with an atom ratio of Cu:Pd:Ti of 76.5:8.5:15 during brazing process, foils of Cu, Ti and Pd with a weight of 6.26 mg, 0.93 mg and 1.17 mg, respectively, were cut and ultrasonically cleaned together with the ceramic specimens in acetone for 20 min. A sandwiched ample was produced by inserting the mixed foils in between two Si_3N_4 ceramic specimens, and then put into a brazing furnace. The brazing was carried out in a vacuum atmosphere ($1.33–1.67 \times 10^{-3}$ Pa) under a pressure of 2×10^3 Pa at 1100–1200 °C for 1.8 k s. The

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heating rate during the brazing was 20–30 °C/min, and the sample was cooled in the furnace after brazing.

The microstructure of the joints was observed by EPMA, XRD and TEM. Specimens for EPMA analysis were cut from the welded sample along the direction perpendicular to the joint interface. The surface of the sample was polished to a surface finish of 0.25 μm, and then the microstructure and elemental distribution at the joint were observed and measured by using EPMA. Specimens for XRD test were cut parallel to the joint surface and then grinded to expose the filler alloy at the surface of

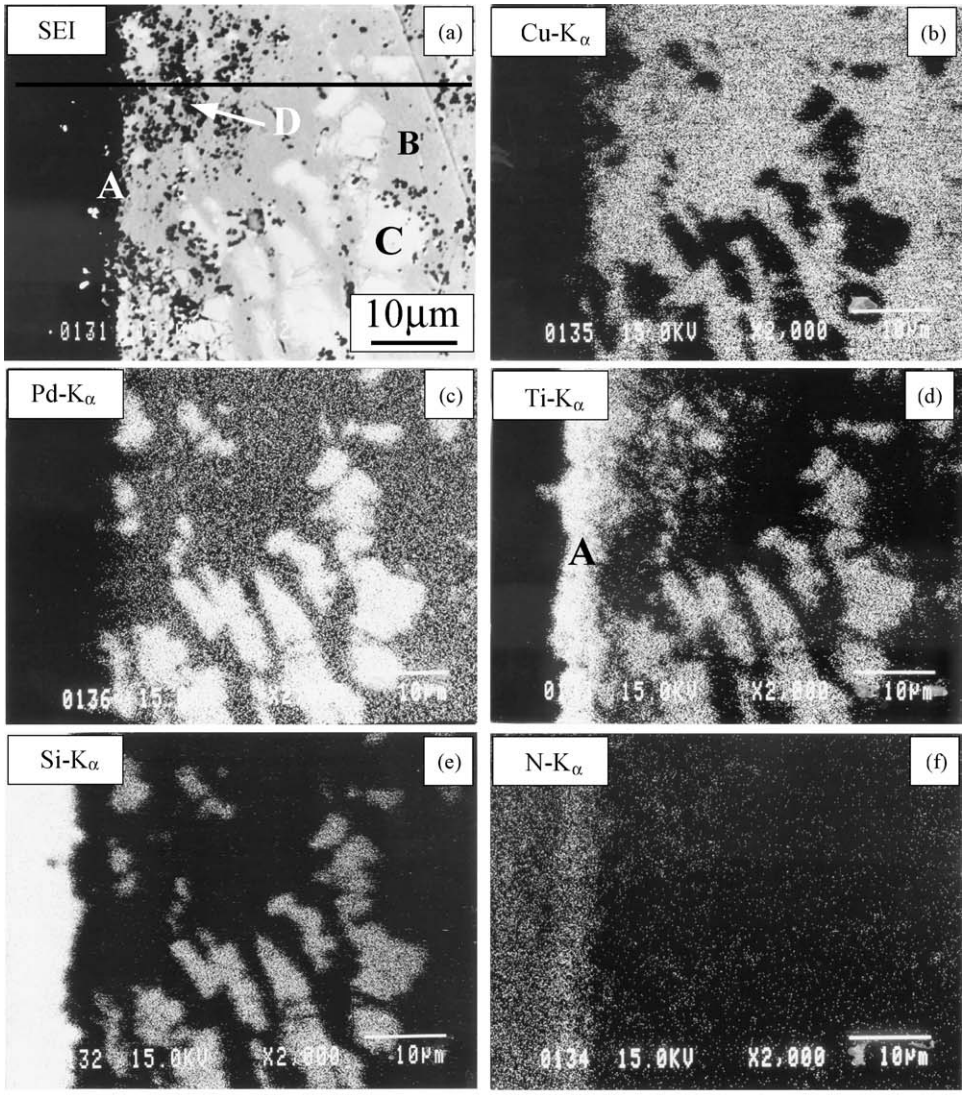

Fig. 1. Morphology (a); elemental analysis (b–f); and line profiles of elements (g) of the Si_3N_4/Si_3N_4 joint brazed at 1100 °C for 30 min.

the specimen. Phase composition of the joint was measured and analyzed by XRD. TEM Specimens with a thickness of 0.5 μm were made by a Focus Ion Beam (FIB) technique.

3. Results

Fig. 1 shows the morphology and elemental distribution of Cu, Pd, Ti, Si and N of the Si_3N_4/Si_3N_4 joint brazed at 1100 °C for 30 min. A continuous reaction layer with a thickness about 5 μm exists between Si_3N_4 ceramic and filler alloy (zone A in Fig. 1(a)). This reaction layer is mainly composed of Ti and N as shown in Fig. 1(d and f). Fig. 1(b and c) show the distribution of Cu and Pd, respectively, indicating that the matrix in the core of the joint is Cu base solution containing Pd. Two kinds of reactants are found in the Cu[Pd] solution matrix (marked by C and D in Fig. 1(a)). Compared with phase D, phase C is larger in size and distributes in the core of the joint. The results of elemental distribution analysis indicate that phase C contains Pd, Ti and Si (Fig. 1(c–e)) and phase D contains Ti and N (Fig. 1(d and f)). Fig. 1(g) shows line-scanning results of Cu, Pd, Ti, Si and N in the area shown in Fig. 1(a). In the Si_3N_4 ceramic zone, only Si and N exist and no other element in the filler alloy can diffuse into the ceramic. The area nearby the ceramic contains mainly Ti and N, corresponding to the TiN continuous reaction layer as shown in Fig. 1(d). The area nearby the TiN reaction layer contains Ti, N and Cu, and is considered to be discontinuous TiN phases in the Cu base solution. The core of the joint contains mainly Cu and Pd, corresponding to the Cu[Pd] solution. However, in some area, the content of Cu decreases and the content of Pd, Ti and Si increases, indicating the appearance of PdTiSi phase in this area. In Fig. 1(a), in order to obtain higher contrast of the phase C and D, the TiN reaction layer is not clear. However, the TiN reaction layer can be clearly observed in Fig. 1(d and f).

Morphology of the Si_3N_4/Si_3N_4 joint brazed at 1200 °C for 30 min is shown in Fig. 2. A phase (marked by E) containing Pd, Si and Cu is found in Fig. 2.

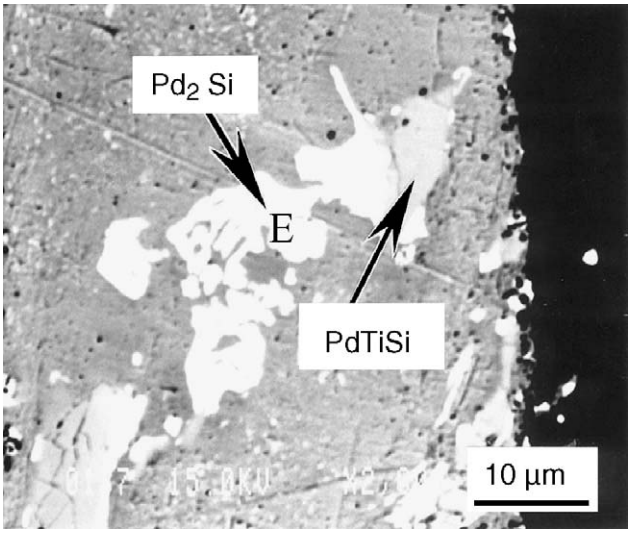

Fig. 2. Morphology of the Si_3N_4/Si_3N_4 joint brazed at 1200 °C for 30 min.

Table 1
Quantitative composition analysis results of the phases in the Si_3N_4/Si_3N_4 joint

Position	Composition (at%)				
	Si	Ti	Cu	Pd	N
A	0.5	50.0	2.6	0.3	46.7
B	3.7	0.3	90.7	5.3	–
C	30.4	30.1	15.0	24.5	–
D	1.2	34.6	18.2	2.1	44.0
E	26.2	2.4	21.6	49.8	–

Quantitative composition analysis results of the position A, B, C, D and E are shown in Table 1. It indicates that: (1) the reaction layer is supposed to be TiN; (2) the matrix of the joint is supposed to be Cu based solid solution containing 5 at% Pd; (3) there are three kinds of reactants in the Cu based solid solution: PdTiSi phase as marked by C in Fig. 1(a), TiN phase as marked by D in Fig. 1(a) and Pd_2Si phase as marked by E in Fig. 2. Because Pd_2Si and Cu are eutectic, a large amount of Cu is measured in the position E. The existence of Pd_2Si phase in the joint has been proved in the previous work.[11] These phases in the joint are also determined by X-ray diffraction results as shown in Fig. 3. It can be seen from Fig. 3 that besides the phases mentioned above, a Ti_5Si_3 phase is determined which is not found in the EPMA images.

The existence of these phases in the Si_3N_4/Si_3N_4 joints is also proved by TEM observations and analysis. Fig. 4(a) is a TEM image showing the morphology of the reaction layer next to the

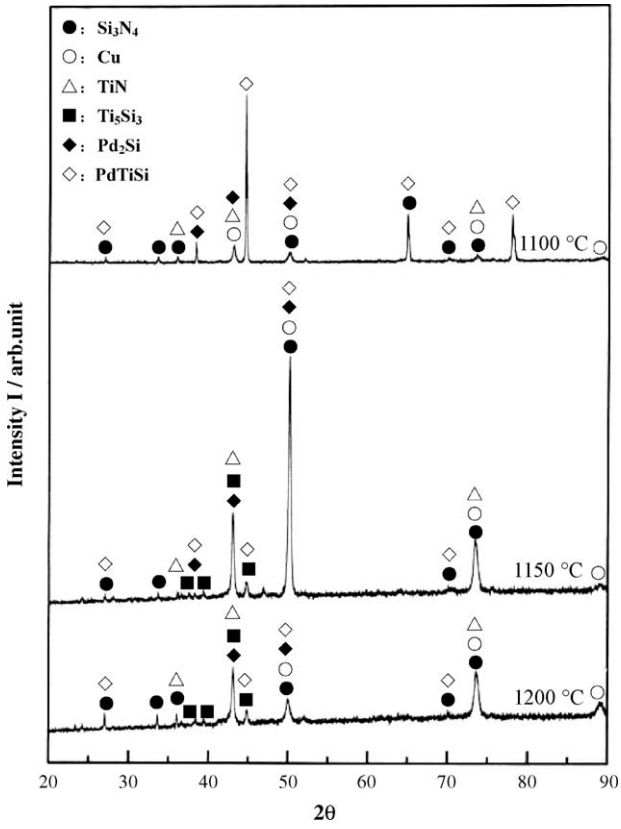

Fig. 3. X-ray diffraction results of the Si_3N_4/Si_3N_4 joints brazed at different temperatures for 30 min.

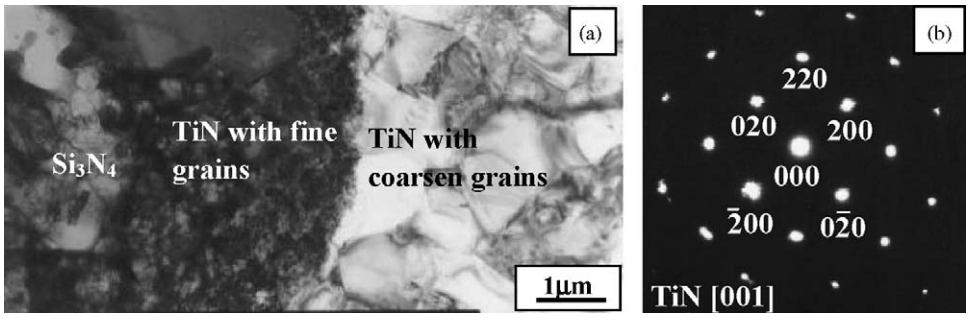

Fig. 4. TEM observation and analysis results of the TiN reaction layer: (a) TEM image of the TiN reaction layer; (b) electron diffraction pattern of the coarsen grain TiN layer.

Si_3N_4 ceramic. It indicates that a fine-grained TiN interlayer with a thickness of 2–3 μm exists besides the Si_3N_4 ceramic, and another interlayer connecting the fine-grained TiN layer is a coarsen grain TiN layer with an average grain size of 1 μm. Fig. 4(b) is an electron diffraction pattern of the coarsen grain layer indicating that it is TiN phase. Fig. 5(a) shows the TEM image of the fine-grain TiN layer. It indicates that the average grain size of this layer is 150 nm. Electron diffraction pattern (shown in Fig. 5(b)) and electron energy loss spectrum analysis results (shown in Fig. 5(c)) indicate that the fine-grained layer is TiN phase.

Fig. 6 shows the TEM observation and analysis results of the interlayer core. The electron diffraction patterns shown in Fig. 6(b and c) indicate the existence of TiN and Pd_2Si phases. Fig. 7 also shows the TEM observation and analysis results of a different area in the same region. The electron diffraction patterns shown in Fig. 7(b and c) indicate the existence of Ti_5Si_3 and PdTiSi phases.

The experimental and analysis results shown above indicate that the microstructure of the Si_3N_4/Si_3N_4 joint brazed at 1100–1200 °C for 30 min using Cu76.5Pd8.5Ti15 filler alloy is: Si_3N_4 ceramic/fine-grain TiN reaction layer/coarsen grain TiN reaction layer/Cu–Pd solid solution containing TiN, PdTiSi, Pd_2Si and Ti_5Si_3 phases/coarsen grain TiN reaction layer/fine-grain TiN reaction layer/Si_3N_4 ceramic. Fig. 8 shows the microstructure of the Si_3N_4/Si_3N_4 joints brazed at different temperatures. It is measured that the thickness of the TiN reaction layer in the joints brazed at 1100 °C, 1150 °C and 1200 °C is 5.16 μm, 5.08 μm and 5.42 μm, respectively. It indicates that the brazing temperature between 1100 °C and 1200 °C does not affect the thickness of the TiN reaction layer. However, when the brazing temperature is 1100 °C, the TiN particles distribute only nearby the TiN reaction layer as shown in Fig. 8(a), and when the brazing temperature surpasses 1150 °C, the amount of the TiN particle increases and they distribute in all the interlayer as shown in Fig. 8(b and c). X-ray diffraction results as

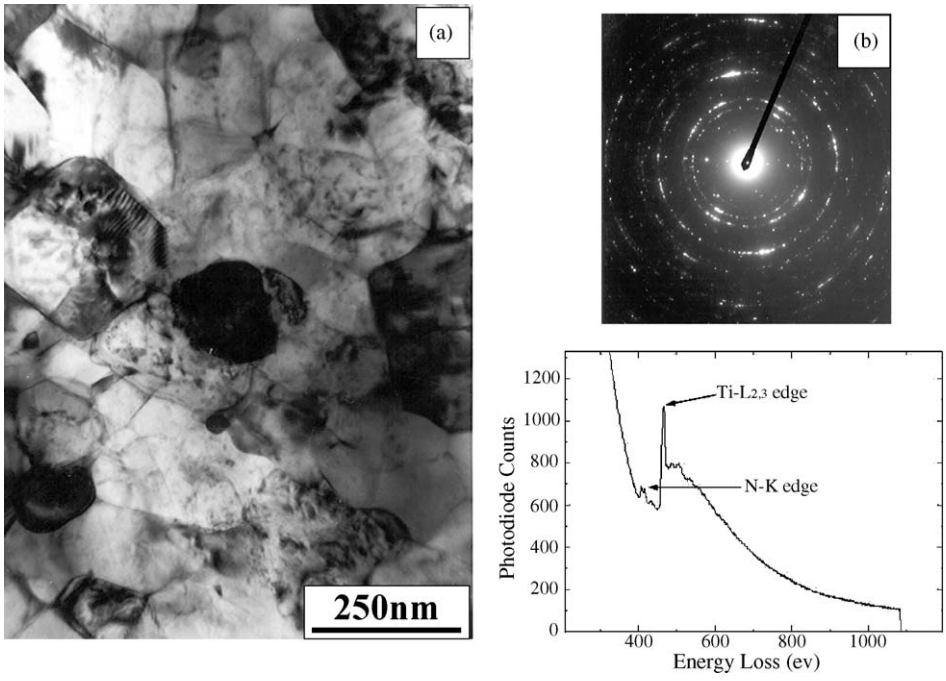

Fig. 5. TEM observation and analysis results of the fine-grain TiN layer: (a) TEM image of the fine-grain TiN layer; (b) electron diffraction pattern of the fine-grain TiN layer; (c) EELS analysis result of the fine-grain TiN layer.

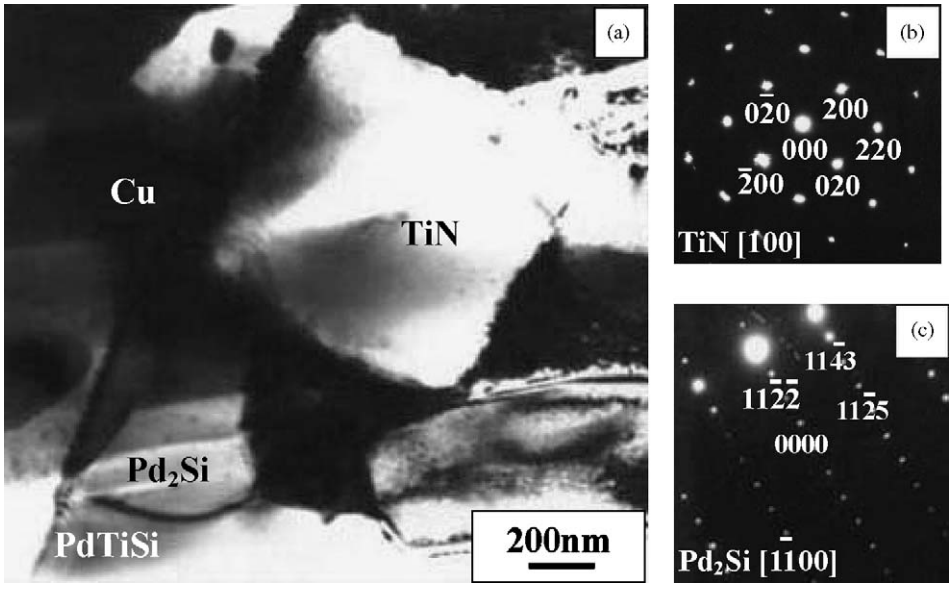

Fig. 6. Microstructure of the center part of the Si_3N_4/Si_3N_4 joint: (a) TEM image; (b) electron diffraction pattern of the TiN phase; (c) electron diffraction pattern of the Pd_2Si phase.

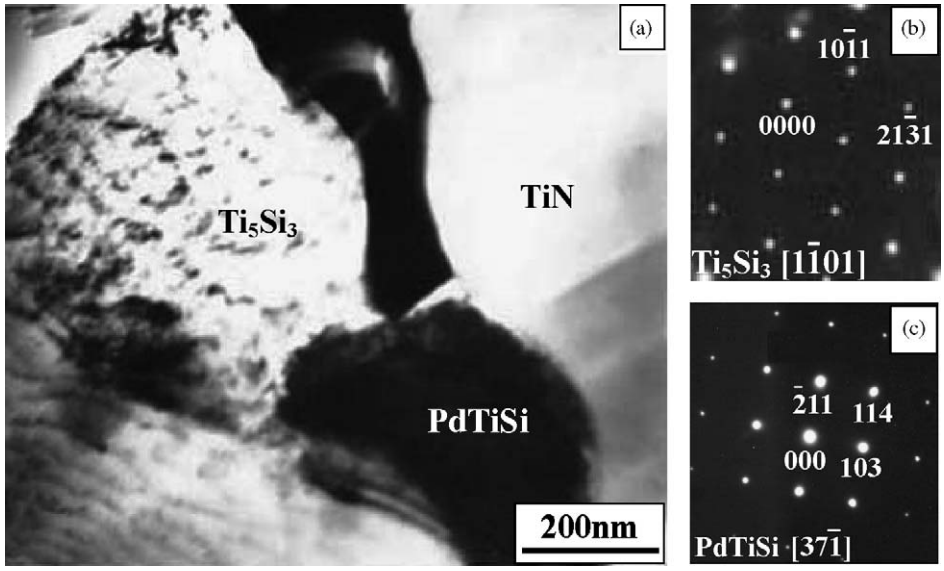

Fig. 7. Microstructure of the center part of the Si_3N_4/Si_3N_4 joint: (a) TEM image; (b) electron diffraction pattern of the Ti_5Si_3 phase; (c) electron diffraction pattern of the PdTiSi phase.

shown in Fig. 3 indicate that with increasing brazing temperature from 1100 °C to 1200 °C, the diffraction peaks of TiN and Pd_2Si increase, while that of PdTiSi phase decreases, indicating that the amount of the TiN and Pd_2Si phases in the Cu–Pa solid solution increases and that of the PdTiSi phase decreases. It is also found from Fig. 3 that Ti_5Si_3 phase appears in the joint for the brazing temperature of 1150 °C and 1200 °C.

4. Discussions

Previous researches on the active brazing of the Si_3N_4 ceramic using filler alloys containing Pd indicate that brazing temperature increases because of the high melting point of the filler alloy. When the brazing temperature surpasses 1100 °C, voids are found at the surface of the Si_3N_4 ceramic because of the decomposition of the Si_3N_4 ceramic. It is also found that the thickness of the TiN reaction layer formed in the Si_3N_4/alloy joint is less than 1 μm.[13–15] Peteves and Paulasto[15] reported that the activity between Ti and Si_3N_4 ceramic decreases by the existence of Pd in the filler alloy, resulting in the decreasing thickness of the TiN reaction layer. Tillmann and co-workers,[13–15] and Selverian and Kang[12] found that a good Si_3N_4/Si_3N_4 joint is obtained if a TiN reaction layer (2–3 μm in thickness) is formed at the Si_3N_4 surface before brazing. The pre-formed TiN reaction layer improved the bonding of the joint and prevented the decomposition of the Si_3N_4 ceramic.

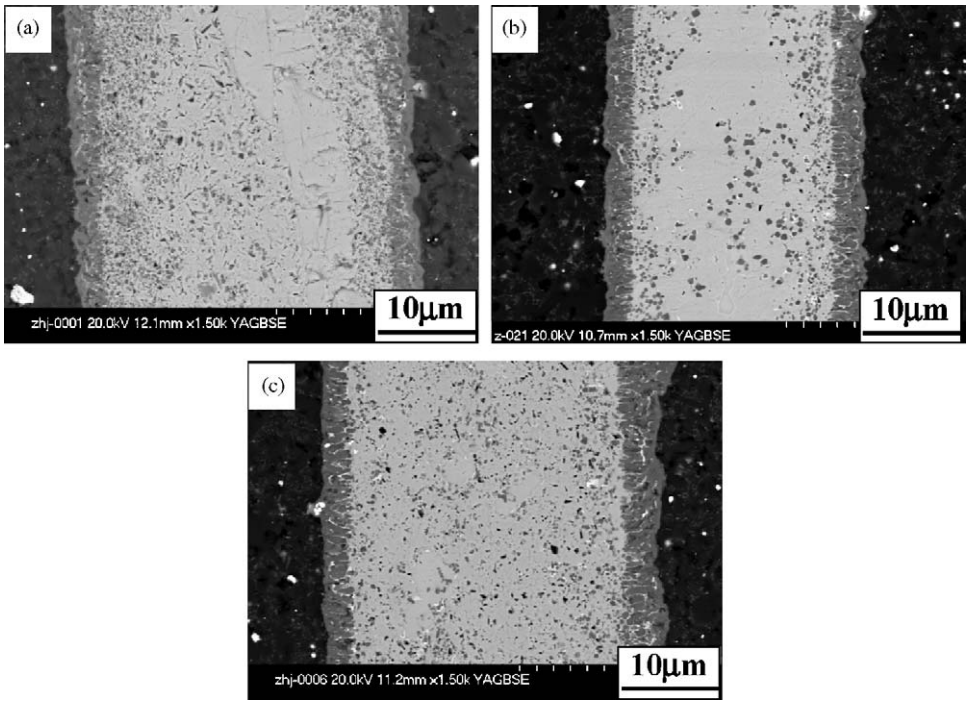

Fig. 8. EPMA microstructure of the Si_3N_4/Si_3N_4 joint brazed at: (a) 1100 °C; (b) 1150 °C; and (c) 1200 °C.

In this research, although the surface of the Si_3N_4 ceramic is not modified before brazing, a TiN reaction layer with a thickness of about 5 μm is formed at the interface between Si_3N_4 ceramic and Cu–Pd–Ti filler alloy, meanwhile, no voids can be found in the interface. This accounts for the special way to use the filler alloy. In this research, metal foils of Cu, Pd and Ti are used to form in situ the Cu–Pd–Ti filler alloy during brazing. In the heating process, with increasing temperature, plasticity of the metal foils increases, leading to a tight connection and mutual diffusion among Cu, Pd and Ti foils. When the temperature reaches 875 °C, liquid phase of Cu–Ti alloy appears. The amount of the liquid Cu–Ti phase increases with increasing temperature. For the Cu–15Ti composition, all the alloy becomes melted when the temperature reaches 950 °C. Pd is re-dissolved into the melted Cu–15Ti alloy gradually with increasing temperature. When the temperature reaches 1100 °C, the Cu–Pd–Ti alloy becomes melted.

When the temperature surpasses 875 °C, Cu–Ti alloy becomes melted and Ti in the melted alloy diffuses to the Si_3N_4/filler interface and reacts with Si_3N_4 ceramic, resulting in the formation of TiN reaction layer at the interface. Because the reaction rate is very high, the TiN layer has been formed before the brazing temperature of 1100 °C is reached. With further increasing temperature, the content of Pd in the Cu–Ti melted alloy increases. Because of the interaction between Pd and Ti in the melted filler alloy, the activity of Ti decreases, and the growth of the TiN reaction layer stops. Therefore, the thickness of the TiN reaction layer does not change with increasing brazing temperature above 1100 °C, as shown in Fig. 8

Si_3N_4 ceramic at the Si_3N_4/filler interface decomposes because of the enrichment of Ti. Most of the N atoms react with Ti, forming the TiN reaction layer at the interface. Some of the N atoms diffuse into the melted filler alloy and react with the Ti atoms, forming the TiN particles in the Cu–Pd solid solution. Si atoms from the decomposition of the Si_3N_4 ceramic diffuse into the melted filler alloy and react with the Pd and Ti atoms, forming PdTiSi and Pd_2Si phases.

With increasing brazing temperature, more and more N and Si atoms diffuse into the melted filler alloy and react with Ti and Pd, forming TiN and Pd_2Si phases, respectively. Therefore, the size and amount of the TiN and Pd_2Si phases increase with increasing brazing temperature, meanwhile, the size and amount of the PdTiSi phase decrease with increasing brazing temperature because more and more Ti atoms are consumed by the formation of the TiN particles.

The formation processes of the interfacial structure of the joint between Si_3N_4 ceramic and filler alloy are shown in Fig. 9.

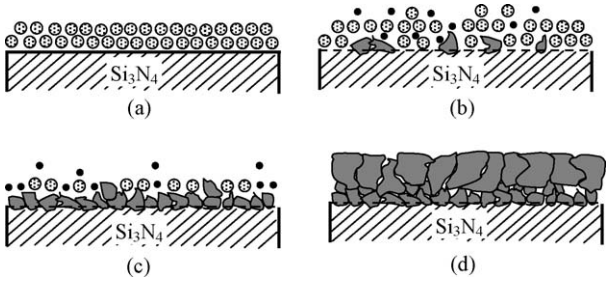

Fig. 9. Schematic drawing of the formation processes of the interfacial structure of the joint between Si_3N_4 ceramic and Cu–Pd–Ti filler alloy: (a) enriched Ti atoms at the interface; (b) fine TiN grains formed at the interface; (c) fine-grain TiN reaction layer formed at the interface; (d) coarsen grain TiN reaction layer contacting with the fine-grain TiN layer.

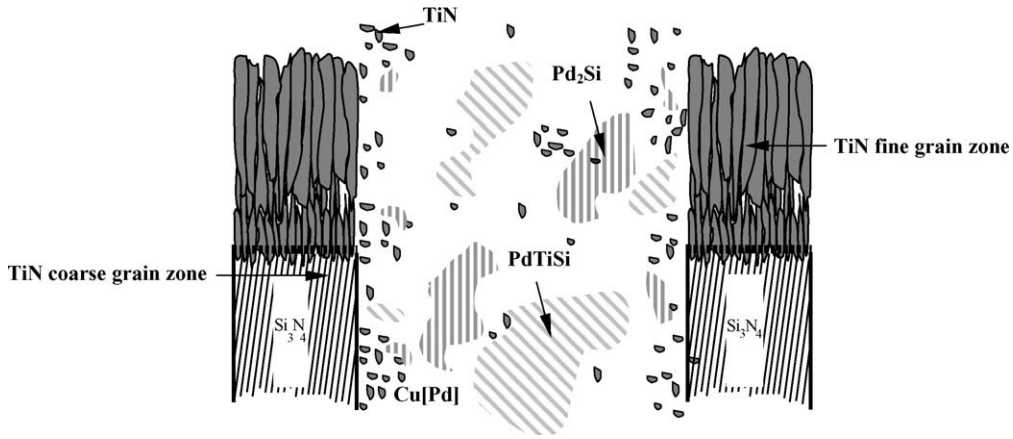

Fig. 10. Schematic draw showing the microstructure of the Si_3N_4/Si_3N_4 joint brazed with Cu–Zn–Ti filler alloy.

With increasing temperature, melted state Cu–Ti alloy appears and then Ti in the melted alloy diffuses and enriches at the Si_3N_4/filler interface as shown in Fig. 9(a). The enriched Ti atoms react with Si_3N_4 ceramic, resulting in the formation of the TiN reaction layer and the decomposition of the Si_3N_4 ceramic. Some of the Si and N atoms from the decomposition of the Si_3N_4 ceramic diffuse into the melted filler alloy as shown in Fig. 9(b). Because the nucleation rate of the TiN phase is very high, a fine-grain TiN reaction layer is formed as shown in Fig. 9(c). When the thickness of the fine-grain TiN layer reaches a certain value, it becomes difficult for the N atom to diffuse across this layer, meanwhile, the content of Ti atom decreases at the interface, leading to a decrease of the nucleation rate of the TiN phase. With increasing temperature and time, the TiN grains grow and contact each other, resulting in the formation of the coarsen grain TiN reaction layer as shown in Fig. 9(d).

Based on the analysis and observation results, the microstructure of the Si_3N_4/Si_3N_4 joint brazed with Cu–Pd–Ti filler alloy is shown in Fig. 10. It indicates that a fine-grain TiN reaction layer is formed neighboring the Si_3N_4 ceramic, and the next layer contacting this fine-grain TiN layer is a coarsen grain TiN reaction layer. The center of the joint is Cu based solid solution containing Pd. PdTiSi, Pd_2Si, TiN and Ti_5Si_3 phases distribute in the solid solution.

5. Conclusions

(1) A perfect bonding between Si_3N_4 ceramics is achieved by brazing at 1100 °C and 1200 °C with Cu–Pd–Ti filler alloy.
(2) A TiN reaction layer of about 5 μm in thickness is formed at the interface between Si_3N_4 ceramic and filler alloy. This layer contains a fine-grain (about 100 nm in diameter) TiN reaction layer neighboring the Si_3N_4 ceramic and a coarsen grain (about 1 μm in diameter) TiN reaction layer.
(3) The microstructure of the Si_3N_4/Si_3N_4 joint is as follows: Si_3N_4 ceramic/fine-grain TiN reaction layer/coarsen grain TiN reaction layer/Cu–Pd solid solution containing TiN, PdTiSi, Pd_2Si and Ti_5Si_3 phases/coarsen grain TiN reaction layer/fine-grain TiN reaction layer/Si_3N_4 ceramic.
(4) With increasing brazing temperature from 1100 °C to 1200 °C, the thickness of the TiN reaction layer is not changed, however, the size and amount of the TiN and Pd_2Si phases in the Cu [Pd] solid solution increase, while, the amount of the PdTiSi phase decreases.

Acknowledgment

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