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Microstructure and reaction phases in Si_3N_4/Si_3N_4 joint brazed with Cu–Pd–Ti filler alloy

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Abstract

Si_3N_4 ceramic was self-jointed using a filler alloy of Cu–Pd–Ti, and the microstructure of the joint was analyzed. By using a filler alloy of Cu76.5Pd8.5Ti15 (at.%), a high quality Si_3N_4/Si_3N_4 joint was obtained by brazing at 1100–1200 °C for 30 min under a pressure of 2×10^{-3} MPa. The microstructure of the Si_3N_4/Si_3N_4 joint which was observed by EPMA, XRD and TEM, and the results indicated that a reaction layer of TiN existed at the interface between Si_3N_4 ceramic and filler alloy. The center of the joint was Cu base solid solution containing Pd, and some reaction phases of TiN, PdTiSi and Pd_2Si found in the Cu [Pd] solid solution.

Keywords: A. Joining; B. Microstructure; C. Si_3N_4

1. Introduction

Si_3N_4 ceramic is a special and attractive material in engineering applications because of its lower density, higher thermal resistance and excellent wearing resistance without lubricants. It has become an ideal material for manufacturing the rotor of jet turbines. However, it is difficult to manufacture the Si_3N_4 ceramic workpieces with lager dimensions and complicated shapes due to its poor workability and lower ductility. Therefore, the engineering application of the Si_3N_4 ceramic greatly depends on the development of the bonding techniques of the Si_3N_4 ceramic. In recent 30 years, many studies have been focused on the joining techniques of the Si_3N_4 ceramic.

Active metal brazing has been widely investigated and used for joining the Si_3N_4 ceramic because it is a simple process to obtain high strength ceramic joints with different shape and size [1–3]. For active brazing of the Si_3N_4 ceramic, filler alloys containing some active metals such as Ti, Zr, Hf, etc. are usually used, and a high strength ceramic joint can be obtained by reaction between the active metals and the Si_3N_4 ceramic. Cu–Ag based alloys containing various amount of Ti have been widely adopted as the filler alloy for the brazing of Si_3N_4 ceramic [4,5]. This kind of filler alloys has a good wettability to almost all the ceramics. However, the ceramic joints using these filler alloys have lower thermal and oxidation resistance, and cannot be used at temperatures above 500 °C. Therefore the Cu–Ag–Ti filler alloys are not suitable for brazing the Si_3N_4 ceramic which is usually used at high temperature environment.

In order to improve the thermal and oxidation resistance of the Si_3N_4 ceramic joint, it is important to develop new filler materials with higher melting point and oxidation-resistance. It has been reported that by using Y–Al–Si–O–N glass filler a Si_3N_4/Si_3N_4 joint with the microstructure and properties similar to the bulk Si_3N_4 ceramic was obtained, and such a joint is suitable for high temperature applications [6–8]. It was also reported that the Si_3N_4/Si_3N_4 joints with high thermal and oxidation resistance have been obtained using active filler alloys with higher melting point and oxidation-resistance, which were developed by adding metals such as Au, Pd, Pt, V, Co, etc. into the filler alloys [9–13]. In this investigation, a Cu–Pd–Ti alloy was used as the filler alloy for brazing the Si_3N_4 ceramic. Tillmann [9,10] reported that Pd improves the heat resistance of the active filler alloy. However, the influence of Pd in the filler alloy on its microstructure still has not been clarified. In the present work, the reaction between the filler alloy and the Si_3N_4 ceramic and the resulting microstructure of

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the Si_3N_4/Si_3N_4 joint were investigated and the metallurgical behavior and bonding mechanism of the joint were analyzed.

2. Materials and experimental procedures

The Si_3N_4 ceramic used in this investigation was made by a hot-pressure sintering process. The content of MgO and Al_2O_3 in the ceramic is less than 5 wt.%. The raw materials of the filler alloy are Cu, Ti and Pd foils with the thickness of 10, 20 and 10 μm, respectively. By adjusting the amount of the three kinds of foils, an alloy with a composition of 76.5Cu–8.5Pd–15Ti (at.%) is formed during brazing.

The Si_3N_4 ceramic sample with a size of Ø6 mm × 4 mm was polished to a surface finish of $R_a = 30$ μm, and then was cleaned together with the metal foils in a super sonic device. The cleaned metal foils were placed between two pieces of Si_3N_4 ceramic samples and a small weight was put on the upper ceramic sample to obtain a pressure of 2×10^{-3} MPa. The brazing of the Si_3N_4 ceramic was carried out in a vacuum of 1.33×10^{-3} Pa at 1100–1200 °C for 30 min. The microstructure of the joints was observed and analyzed by EPMA, XRD and TEM.

3. Results

Fig. 1 shows the morphology and elemental analysis results of the joint brazed at 1100 °C. It can be seen that a continuous TiN reaction layer with an average thickness of 5 μm exists between the Si_3N_4 ceramic and filler alloy as shown in Fig. 1(d) and (f). The matrix in the central part of the joint is Cu base solid solution containing 5 at.% Pd. There are two phases in the Cu [Pd] solid solution as shown in Fig. 1(a). It was determined by the elemental analysis results that the white, large, is PdTiSi phase as shown in Fig. 1(c)–(e), and the small black one is TiN phase as indicated for the results shown in Fig. 1(d) and (f).

Fig. 2(a) shows the morphology of the joint brazed at 1200 °C. Two phases were found in the Cu [Pd] solid solution. Elemental analysis results indicated that one of them with the grey phase is PdTiSi and white one is Pd_2Si. From the results of Figs. 1 and 2(a), the microstructure of the Si_3N_4/Si_3N_4 joint brazed using the 76.5Cu–8.5Pd–15Ti filler alloy at the brazing conditions of this work is schematically shown in Fig. 2(b). It shows that the microstructure of the joint is ''Si_3N_4 ceramic/TiN reaction layer/filler alloy''. The base of the filler alloy is Cu [Pd] solid solution, in which there are TiN, Pd_2Si and PdTiSi phases.

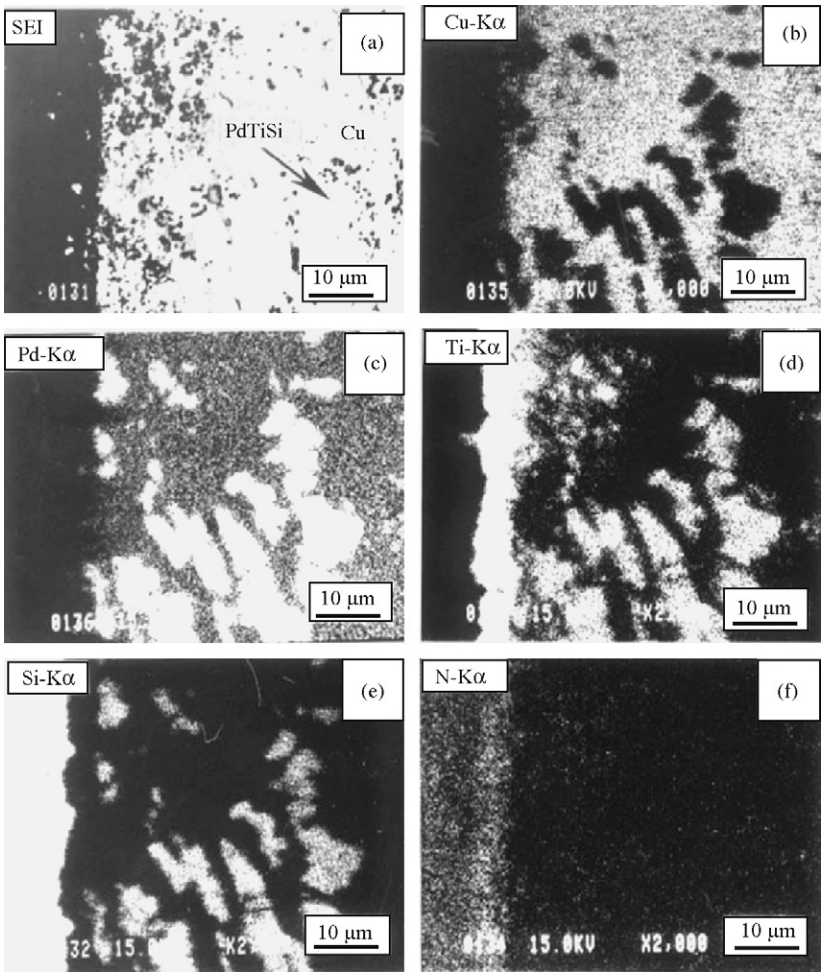

Fig. 1. Morphology and elemental analysis results of the Si_3N_4/Si_3N_4 joint brazed using Cu76.5Pd8.5Ti15 filler alloy at 1100 °C for 30 min.

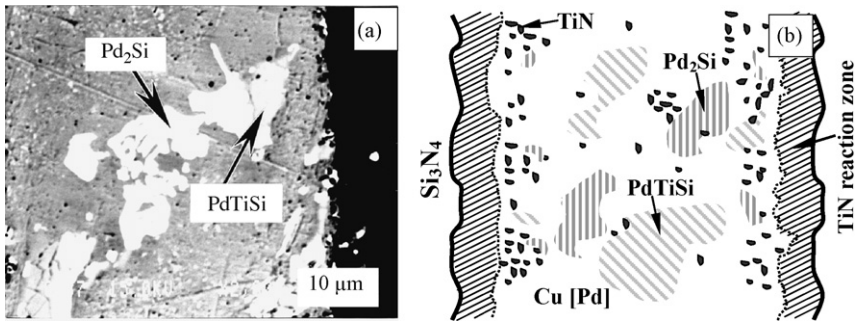

Fig. 2. Morphology and schematic drawing of the Si_3N_4/Si_3N_4 joint brazed using Cu76.5Pd8.5Ti15 filler alloy at 1200 °C for 30 min: (a) morphology and (b) schematic drawing.

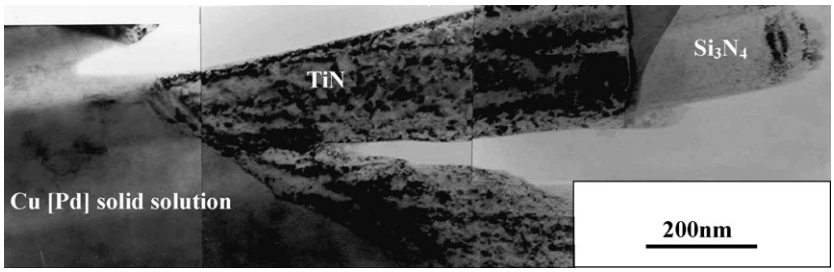

Fig. 3. TEM image showing the Si_3N_4/Si_3N_4 joint brazed at 1150 °C for 30 min.

Fig. 3 is a TEM image showing the existence of the TiN layer between Cu [Pd] solid solution and Si_3N_4 ceramic. It can be seen that the TiN layer has a clear interface with the Si_3N_4 ceramic and the Cu [Pd] solid solution. The TEM image also indicates that the grain size of the TiN layer is only about 100 nm in diameter as shown in Fig. 4(a). Both the electron diffraction pattern (Fig. 4(b)) and the electron energy loss spectrum (Fig. 4(c)) show that the reaction layer between filler alloy and Si_3N_4 ceramic is TiN.

Fig. 5(a) is a TEM image of the filler alloy. It shows that all the phases, such as PdTiSi, Pd_2Si and TiN, in the Cu [Pd] solid solution appear simultaneously. Fig. 5(b) and (c) show the diffraction patterns of the TiN in [0 0 1] direction and the PdTiSi in $[3\,7\,\bar{1}]$ direction, respectively. They further prove the existence of these two phases. Fig. 5(a) also shows that the grain size of the TiN in the Cu [Pd] solid solution is much larger than that of the reaction layer as shown in Fig. 4(a).

Previous researches about the active brazing of the Si_3N_4 ceramic have indicated that when Cu–Ti base alloys are used as filler alloy, the typical microstructure is "Si_3N_4 ceramic/TiN reaction layer/Ti_5Si_3 reaction layer/filler alloy", and some Ti_5Si_3 phases also exist in the filler alloy [1,3,14,15]. In this

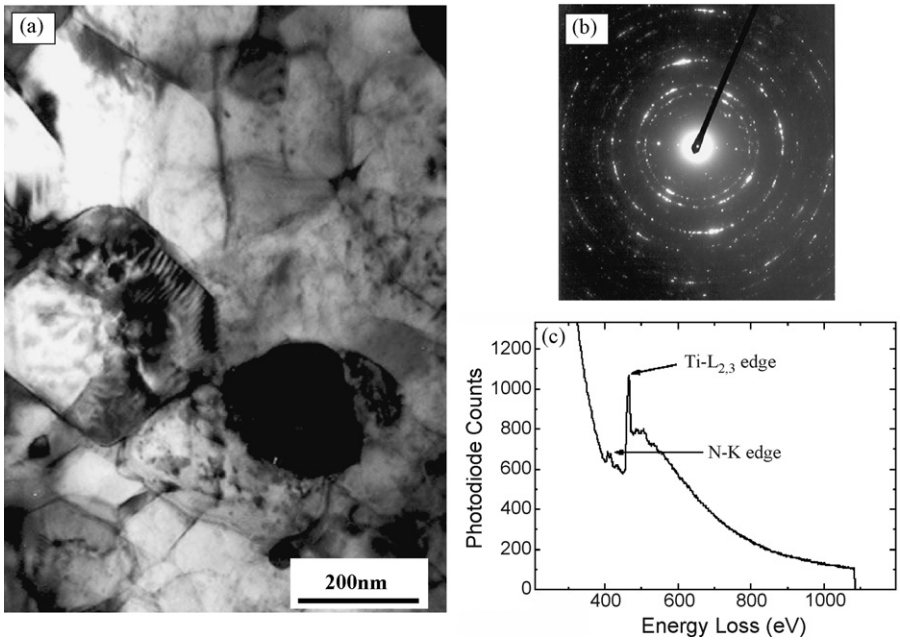

Fig. 4. TEM analysis results of the TiN reaction layer: (a) TEM image, (b) diffraction pattern, and (c) electron energy loss spectrum.

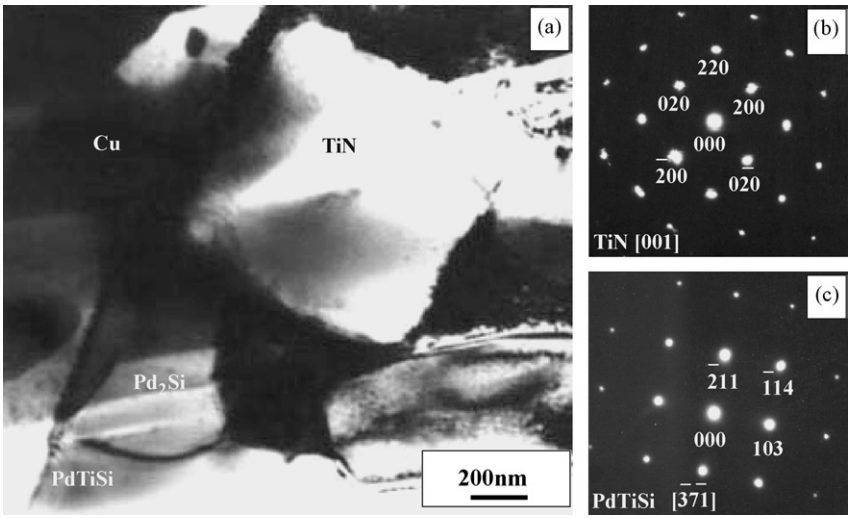

Fig. 5. TEM analysis results of the filler alloy nearby the TiN reaction layer in the Si_3N_4/Si_3N_4 joint brazed at 1150 °C: (a) TEM image, (b) and (c) diffraction pattern of the TiN and PdTiSi phases.

investigation, when the Cu–Pd–Ti alloy is used as filler alloy and the brazing temperature is 1100 °C, there is no Ti_5Si_3 reaction layer and no Ti_5Si_3 phase cannot be found in the filler alloy as shown in Fig. 1. When the brazing temperature is higher, a small amount of Ti_5Si_3 phases is found in the filler alloy as shown in Fig. 6; however, the Ti_5Si_3 reaction layer cannot be found.

Fig. 7 is the X-ray diffraction results of the Si_3N_4/Si_3N_4 joints brazed at different temperatures. When the brazing temperature is lower (1100 °C), there are diffraction peaks of TiN, PdTiSi, Pd_2Si, Cu and Si_3N_4. With increasing brazing temperature, the intensity of the PdTiSi peak decreases and that of the TiN and Pd_2Si peaks increases, meanwhile, the Ti_5Si_3 peaks appear. All the results here indicate that with increasing brazing temperature from 1100 to 1200 °C, the thickness of the TiN reaction layer in the interface between Si_3N_4 and filler alloy increases, meanwhile, the amount of the Pd_2Si phase increases and that of the PdTiSi phase decreases. Titanium silicide appears in the filler alloy when the brazing temperature is higher than 1100 °C.

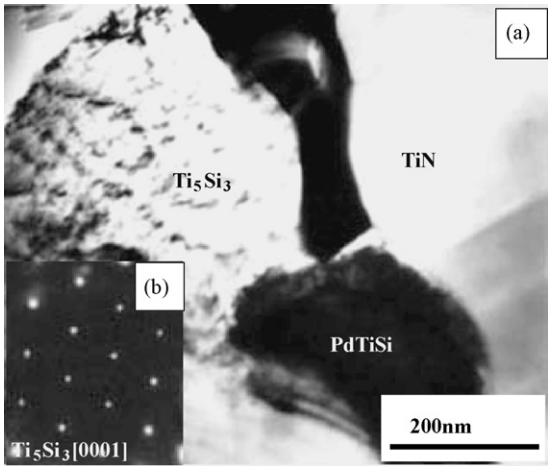

Fig. 6. TEM analysis results of the filler alloy in the Si_3N_4/Si_3N_4 joint brazed at 1150 °C: (a) TEM image and (b) diffraction pattern of the Ti_5Si_3 phase.

The shear strength of the Si_3N_4/Si_3N_4 joint brazed with the Cu76.5Pd8.5Ti15 filler alloy at 1150 °C for 30 min was measured at 400, 600 and 700 °C, respectively. As a comparison, the shear strength of the joints brazed with the Cu85Ti15 filler alloy at 1000 °C for 15 min was also measured at the same temperatures, and the results are shown in Fig. 8. It was found that the shear strength at room temperature of the joint brazed with the Cu–Ti filler alloy is a little higher than that brazed with the Cu–Pd–Ti filler alloy. However, with increasing

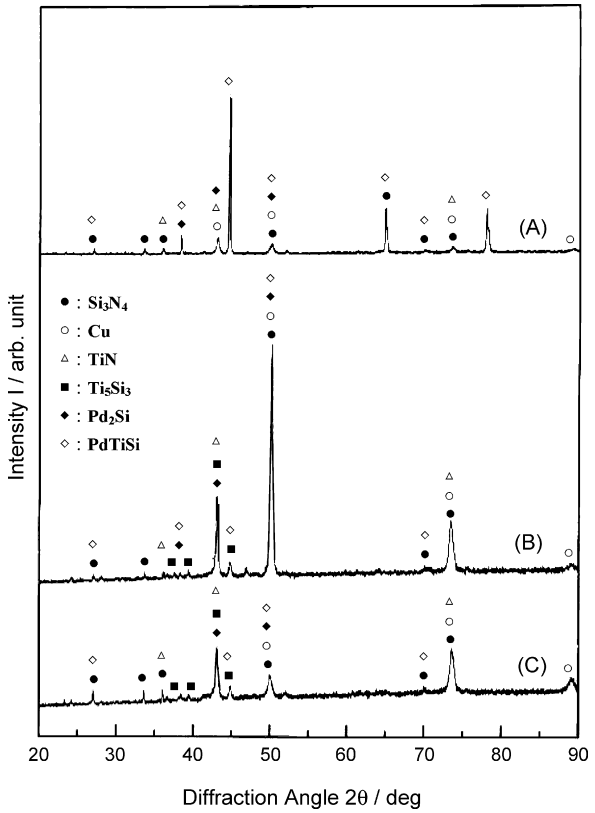

Fig. 7. X-ray diffraction results of the Si_3N_4/Si_3N_4 joints brazed at 1100 °C (A), 1150 °C (B) and 1200 °C (C).

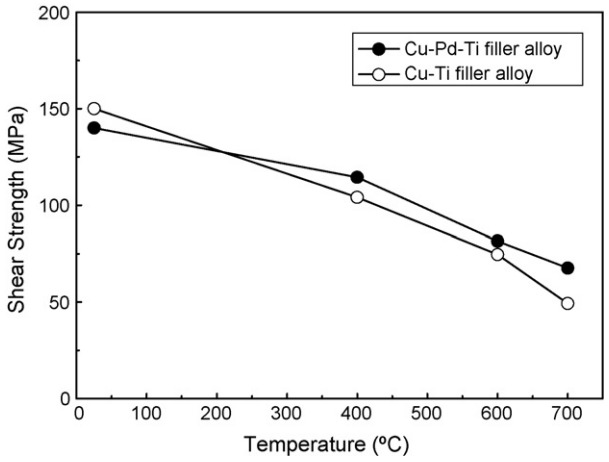

Fig. 8. Effect of test temperature on the shear strength of the Si_3N_4/Si_3N_4 joints brazed using different filler alloy.

test temperature, the decreasing rate of the shear strength of the joint brazed with the Cu–Pd–Ti filler alloy is lower than that brazed with the Cu–Ti alloy. At the test temperature of 700 °C, the shear strength of the joint brazed with the Cu–Pd–Ti filler alloy is 67.62 MPa, while that brazed with the Cu–Ti filler alloy is only 42.94 MPa, indicating that the joint brazed with Cu–Pd–Ti filler alloy has a hither thermal resistance.

4. Discussion

During the heating process of the joint, with increasing temperature, the deformability of the filler alloy increases and the contact among Cu, Ti and Pd foil is improved, leading to the diffusion between each neighboring foil. According to the phase diagram [16–18], the eutectic temperature of the Cu–Ti alloy is 870 °C, and liquid phase appears when the temperature reaches 870 °C. With increasing temperature, the amount of the liquid phase increases, and when the temperature reaches 950 °C, the entire Cu–15Ti alloy is in the liquid state. With further increasing temperature, Pd will diffuse into the Cu–Ti melt.

At the brazing temperatures (1100–1200 °C) used in this work, the Cu–8.5Pd–15Ti alloy is in the liquid state.

The analysis above indicates that the Cu–Ti alloy is melted below the brazing temperature, at which Pd is dissolved. During the heating process, the Ti in the Cu–Ti melt diffuses to the Si_3N_4 ceramic/filler alloy interface and concentrates near the interface, leading to the reaction (1). A TiN reaction layer is then formed, while, the Si released from the decomposition of the Si_3N_4 ceramic diffuses into the melt filler alloy. Because, the heating rate is low and the reaction speed between Ti and Si_3N_4 is very high, a TiN reaction layer with a certain thickness is formed when the brazing temperature is reached. The reaction to form the TiN layer is:

$$Si_3N_4\,(s) + 4Ti\,(l) = 4TiN\,(s) + 3Si\,(s) \quad (1)$$

$$\Delta G^\circ = -1356 + 0.199T\,(kJ/mol)$$

Previous results have indicated that during the brazing of the Si_3N_4 ceramic the activity of Ti in the filler alloys containing Pd is lower than that in the filler alloys without Pd, which results in a decreasing thickness or disappearance of the TiN and a decrease of the joint properties [11–13]. The experiments presented here show different results from the previous results. A TiN reaction layer was formed and observed in the joint brazed using a filler alloy containing Pd. This result is due to the different states of the filler alloy. In the previous research, the filler material is a ternary alloy. The filler alloy containing Pd has a higher melting point, so that when the filler alloy is molten, Ti reacts with other elements in the filler alloy before it reacts with the Si_3N_4 ceramic, resulting in a decreasing amount of the TiN reactant at the interface between the filler alloy and the Si_3N_4 ceramic.

In this research, the filler materials are the foils of Cu, Ti and Pd, but not the Cu–Pd–Ti alloy. During the heating process, Cu–Ti alloy is formed and molten before the brazing temperature is reached. In this case, Ti diffuses to the interface between ceramic and filler alloy and reacts with the ceramic forming a TiN layer at the interface. Because, the reaction rate between Ti and Si_3N_4 is very fast, a reaction layer with a certain thickness has been formed when Pd begins to diffuse into the melt Cu–Ti alloy at the brazing temperature. The TiN reaction layer not only improves the bonding of the interface, but also limits the decomposition of the Si_3N_4 ceramic.

When the TiN reaction layer with a certain thickness is formed, it becomes a barrier-layer of the further reaction between Ti and Si_3N_4, and in this case, the growth rate of the TiN reaction layer is controlled by the diffusion rate of Ti in the TiN layer [3]. During the formation of the TiN layer, some Si and N elements released from the decomposition of the Si_3N_4 ceramic also diffuse to the filler alloy. The Ti in the filler alloy will reacts with N to form some TiN particles in the filler alloy nearby the TiN reaction layer. Only a small amount of Ti_5Si_3 was observed in the Si_3N_4 joint. Instead, Pd_2Si and PdTiSi silicides were observed in the Si_3N_4 joint. The formation of the Pd_2Si and PdTiSi suppresses the formation of Ti_5Si_3 in the filler alloy. Because, Pd is a strong silicide forming element and can react easily with Si to form various compounds, most of the Si released from the decomposition of the Si_3N_4 ceramic will preferentially react with Pd to form Pd_2Si by the reaction:

$$2Pd\,(l) + Si\,(l) = Pd_2Si\,(s) \quad (2)$$

Some of the Si released from the decomposition of the Si_3N_4 ceramic also reacts with Pd and Ti by the following reaction:

$$Pd\,(l) + Ti\,(l) + Si\,(l) = PdTiSi\,(s) \quad (3)$$

Because of the lack of thermodynamic data about the Pd element, the free energy of reaction (2) and (3) cannot be obtained. However, the experimental exults of composition and structure analysis have indicated the existence of the PdTiSi phase.

5. Conclusions

The Si_3N_4 ceramic was jointed to itself successfully using a Cu76.5Pd8.5Ti15 filler alloy at 1100–1200 °C for 30 min under a pressure of 2×10^{-3} MPa. A TiN reaction layer is formed

between the Si_3N_4 ceramic and the filler alloy. The center of the joint is composed of Cu [Pd] solid solution and some reaction phases such as Pd_2Si, PdTiSi and TiN. The processes of the formation of the Si_3N_4/Si_3N_4 joint is: (1) when the heating temperature surpasses 950 °C, the Ti in the melt Cu–Ti alloy diffuses to the interface between the Si_3N_4 ceramic and the filler alloy; (2) Si_3N_4 ceramic reacts with the Ti forming a TiN layer at the interface; (3) with further increasing the brazing temperature, Pd is dissolved into the melt Cu–Ti alloy, and all the filler alloy becomes molten when the brazing temperature reaches 1100 °C; (4) Si arise from the reaction between the Si_3N_4 ceramic and Ti diffuses into the melt and reacts with Pd and Ti forming Pd_2Si and PdTiSi, and the formation of the Pd silicides suppresses the formation of Ti_5Si_3. Meanwhile, N released from the decomposition of the Si_3N_4 ceramic diffuses into the melt and reacts with Ti nearby the TiN reaction layer where the content of Ti is higher; forming dispersed TiN particles in this area.

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