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Joining of silicon nitride with a Cu76.5Pd8.5Ti15 filler alloy

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Abstract

Si_3N_4 ceramic has been joined successfully to itself by brazing in a vacuum at 1373–1573 K holding for 1.8 ks using a Cu76.5Pd8.5Ti15 alloy filler. By observation and analysis of the microstructure of the joints, it is found that the joints comprise three parts: (1) a continuous reaction layer of TiN between Si_3N_4 and filler alloy, (2) a discontinuous reaction layer containing TiN, Pd_2Si and Ti_5Si_3 connecting the continuous reaction layer, and (3) the Cu-based solid solution in the mid of the joint and some reaction products (TiN, Pd_2Si, PdTiSi and Ti_5Si_3) in the solution. With increasing brazing temperature, both the thickness of the continuous reaction layer and amount of reaction phases increase, which improves the bending strength of the joints. When the brazing temperature surpasses 1473 K, voids are formed in the joint because of the decomposition of the Si_3N_4 ceramic, leading to a decrease of the bond strength. The room-temperature bending strength of the joint brazed at 1423 K reaches a maximum value of 155.8 MPa.

Keywords: A. Joining; B. Interface; D. Si_3N_4; Cu–Pd–Ti filler alloy

1. Introduction

Silicon nitride ceramic with superior heat resistance, corrosion resistance and wearability has been widely used. However, it is not only difficult but also expensive to manufacture ceramic work pieces with large dimensions and complicated shapes due to the bad workability and low ductility of the ceramics. Therefore, many studies have focused on ceramic joining to solve these problems [1–11]. Some progress has been made towards obtaining reliable brazing joint [1–6]. Previous results indicated that when the Si_3N_4 ceramic was brazed with the commonly used Ag–Cu–Ti filler alloy, the resulted joint had a lower thermal resistance and was usually used below 800 K [12], by which the superior properties of Si_3N_4 ceramics could not be taken full advantage. Therefore, it is necessary to develop new kinds of brazing filler alloys to meet the high temperature requirement for many of the applications of ceramics. The addition of palladium, which has a high melting point, can increase the melting point of common brazing alloys, and moreover, Pd possesses good thermal and oxidation resistance. So the development and application of palladium-containing filler alloys are expected to improve the resistance to high temperature and oxidization of the ceramic joint. In recent years, several alloys containing palladium have been considered for use in brazing Si_3N_4 ceramic [12–15], but more researches paid attention to the joining strength while less was performed to study the microstructure of the joint.

In this study, attentions were focused on the usefulness of Pd–Cu–Ti alloys as interlayer materials in which the role of the Ti was to promote wettability to the ceramic by forming reaction products with the ceramic. The room-temperature strength and the nature of the microstructure of the brazed joint were investigated, which will provide a reference to the study on the high temperature applications of the joint brazed with the Cu–Pd–Ti filler alloy.

2. Experimental procedure

Hot-sintering Si_3N_4 ceramics (density, 3.3 g/cm^3) were used for the bonded materials, in which there are no open porosities. A small amount of MgO and Y_2O_3 were used as sintering additives. The bending strength of Si_3N_4 at room temperature is over 700 MPa. A hot-sintered Si_3N_4 ceramic was cut into bars with the dimension of 3.8 mm × 5.0 mm × 16 mm by diamond cutting machine. Cu, Ti and Pd foils with the thickness of 20, 20

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and 100 μm, respectively were cut by scissors into the corresponding sizes according to the composition of fillers (Cu76.5Pd8.5Ti15 (at.%)). The brazing surfaces of the ceramic bars were coarsely ground on SiC sand papers and then polished using diamond paste of 0.5 μm. Before joining, the brazing fillers and the ceramic bars were cleaned ultrasonically in acetone and dried by air blowing. The brazing fillers were placed between two Si_3N_4 bars in the form of Cu/(Ti, Pd)/Cu and butted by a kind of organic glue, and then the assembly was put into a graphite jig. During the brazing process, a weight was put on the brazing bars to form a pressure of 6.7×10^{-5} MPa and to ensure them to contact each other closely. A vacuum was kept at $(1.3–1.7) \times 10^{-3}$ Pa. At the beginning of brazing process, the temperature was increased to 573 K at a rate of 30 K/min and held for 0.3 ks to make organic glue volatilize in order to clean the brazing surfaces. Then the temperature continued to rise at 40 K/min to 1373–1573 K with an interval of 50 K and held for 1.8 ks at each temperature. At last, the workpiece was cooled down at a rate of 5 K/min to 473 K and then cooled down spontaneously in the furnace. The strength of the butt joint was measured by the three-point bend test with a cross-head speed of 0.5 mm/min. The microstructure of the joint was observed and examined by electron probe micro-analysis (EPMA).

3. Results and discussion

3.1. Microstructures of the Si_3N_4/Si_3N_4 joints

Durability of brazed blocks when being cut and polished revealed that Si_3N_4 ceramic can be joined to itself successfully using Cu76.5Pd8.5Ti15 alloy filler. The microscopic examination revealed the typical morphology and the elemental distribution in the observed area of Ti, Cu, Pd and Si of the Si_3N_4/Si_3N_4 joint brazed with Cu76.5Pd8.5Ti15 (at.%) at 1423 K/1.8 ks as shown in Fig. 1. It is found that the joint consists of three parts: (1) continuous reaction layer next to ceramic (A); (2) discontinuous reaction layer connecting the continuous reaction layer (B); and (3) solid-solution in the mid of the joint (C) where some reaction phases exist.

Fig. 1(b) shows that Ti distributes mainly in the reaction layers, indicating that Ti as an active element has diffused towards the Si_3N_4 ceramic and richened at the interface between Si_3N_4 ceramic and filler alloy. According to reaction thermodynamic data [16] which will be elucidated in Section 3.4 in detail, the stability of TiN is superior to that of Si_3N_4. Therefore, Ti is ready to react with the Si_3N_4 to form a reaction layer at high temperature. The continuous reaction layer does not contain Si as indicated in Fig. 1(e), implying that the continuous layer may be composed of only TiN. Simultaneously, during the formation of the TiN reaction layer, Si is released from the Si_3N_4 ceramic and diffuses through the continuous reaction layer into the area between the continuous reaction layer and filler alloy as shown in Fig. 1(e). Wei et al. [17] investigated the reaction of Ti-coating and Si_3N_4 and indicated that Ti can wet and react with Si_3N_4. The possible products include TiN and Ti_5Si_3 due to the different reactions. But the calculation of Gibbs free energy revealed that the reaction to form products of TiN and Si is easier to perform. This conclusion is consistent with the microscopic examination in present work.

When the filler alloy melts, the element Pd is dissolved in the whole of filler alloy, but richens where Si is richer as shown in Fig. 1(d). According to the corresponding phase diagrams and the elemental analysis results, it is considered that the discontinuous reaction layer may be composed of TiN, Pd_2Si and Ti_5Si_3 phases. Fig. 1(c) shows that the element of Cu distributes uniformly at the center of the joint, indicating that the center of the joint is a Cu based solution. It is also found from Fig. 1 that a small amount of reaction phases containing the elements of Ti, Pd and Si exist in the center part of the joint.

3.2. Effect of brazing temperature on the microstructure of joint

Fig. 2 shows the microstructure of the joint brazed at different temperatures. At lower brazing temperature (1373 K),

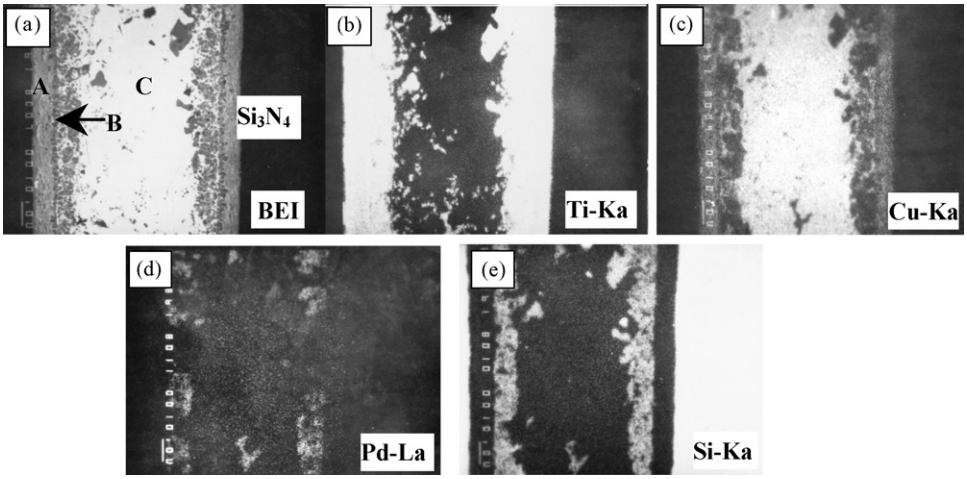

Fig. 1. Typical morphology and elemental distribution of the Si_3N_4/Si_3N_4 joint brazed using Cu76.5Pd8.5Ti15 filler alloy at 1423 K holding for 1.8 ks. (a) BEI image of the joint, (b) distribution of Ti, (c) distribution of Cu, (d) distribution of Pd, and (e) distribution of Si.

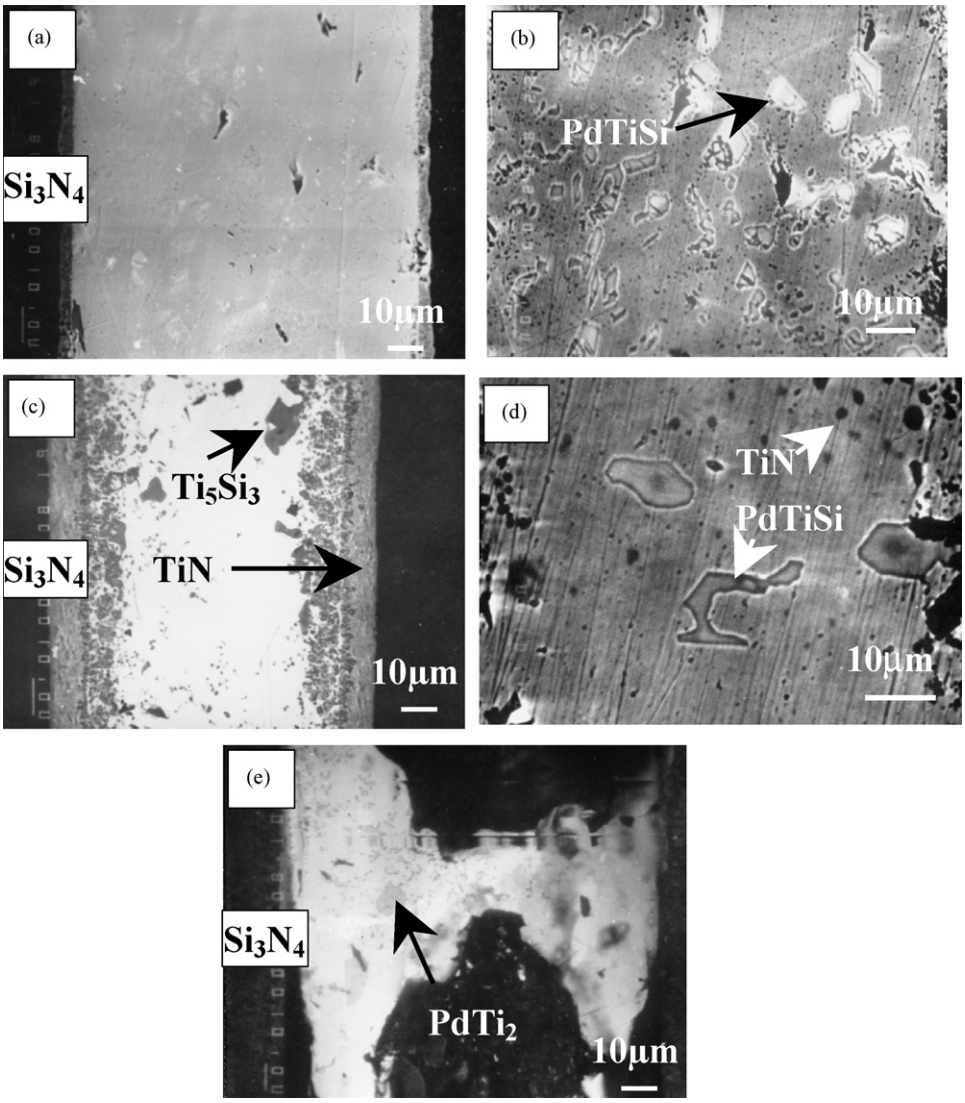

Fig. 2. The morphologies of Si_3N_4/Si_3N_4 joints brazed using a Cu76.5Pd8.5Ti15 filler alloy at different temperature for 1.8 ks. (a and b) Brazing at 1373 K, (c and d) brazing at 1423 K, and (e) brazing at 1573 K.

the continuous reaction layer is extremely thin, while the discontinuous one is relatively thicker and a thickness about 2.4 μm is observed, as shown in Fig. 2(a). Fig. 2(b) shows the microstructure of the center part of the joint brazed at 1373 K, indicating that many block-like phases, which are determined to be PdTiSi by elemental analysis results of EPMA, exist in the Cu-based solid solution. When elevating the temperature to 1423 K, the continuous and discontinuous reaction layers grow to a thickness of 8.0 and 12.0 μm, respectively as shown in Fig. 2(c). It can also be seen that Ti_5Si_3 phases with larger size appear in the discontinuous reaction layer. Fig. 2(d) shows the microstructure of the center part of the joint brazed at 1423 K, indicating that the size of the block-like phase PdTiSi increases, while its amount decreases, with increasing brazing temperature. Increasing the brazing temperature favors the diffusion of Ti and reaction of Ti and Si_3N_4, thus the amount of nitrogen and silicon available for interaction increase. Furthermore, the reduction of Ti content in the center part of the filler alloy accounts for the decreasing amount of the PdTiSi phase with increasing brazing temperature. At higher brazing temperature, the ability to diffusion of elements is enhanced, so much nitrogen diffuse into the center seam and react with Ti to form the reaction product TiN (as shown in Fig. 2(d)), which was further determined by electron diffraction results of TEM. Further increasing brazing temperature to 1573 K, no reaction layer can be found at the interface between Si_3N_4 ceramic and filler alloy, and Pd–Ti phase is seen instead of the PdTiSi phase in the central part of the joint. Therefore, the joint brazed at 1573 K is characterized by the $PdTi_2$ phase distributing in the Cu-based solution. At 1573 K, the decomposition of the Si_3N_4 ceramic leads to the formation of N_2. And that N_2 escapes from the ceramic results in holes remained in the surface of Si_3N_4 ceramic. In terms of the wetting theory [18], the wetting between filler alloy and ceramic is bad when they do not interact with each other in either liquid or solid state, but the liquid filler alloy can wet ceramic better if they can dissociate into each other or form compounds. Besides, the adsorption behavior of the active atoms at the interface of solid ceramic

and liquid alloy is also very important to obtain a good wetting. The adsorption extent is proportional to the thickness of adsorption layer formed at the solid–liquid interface. Therefore, the N_2 escaping from Si_3N_4 ceramic not only prohibits forming a wettable reaction product (TiN) with the ceramic but also impedes the development of an absorption layer. Consequently, the wetting between the liquid filler alloy and Si_3N_4 ceramic is decreased. Moreover, the higher brazing temperature also leads to the overflow of liquid filler alloy. As a result, the welding seam is filled with porosities.

3.3. Effect of brazing temperature on bond strength of the joint

Bond strength of the Si_3N_4 joints brazed at the temperatures from 1373 to 1573 K for 1.8 ks was measured in room temperature, and the results are shown in Fig. 3. It can be seen that the bond strength of the joint brazed at 1423 K has a maximum value of 155.8 MPa. When the brazing temperature is 1373 or 1473 K and above, bond strength of the joint is only 60–80 MPa. The samples failed invariably along one of the two ceramic/interlayer interfaces implying that either the reaction product layer is of very brittle nature, or that the reaction layer is not thick enough.

In the light of the Cu–Ti phase diagram [18], when the temperature reaches 1243 K, Cu–15Ti alloy becomes in liquid state. With increasing the temperature, Pd will dissolve into the Cu–Ti melt. When the temperature is increased to 1373 K, Cu–Pd–Ti alloy becomes liquid state completely. However, because of the lower flowability of the liquid filler alloy at 1373 K, Ti diffuses slowly, leading to a very thin reaction layer of TiN at the ceramic/filler interface. The thin TiN reaction layer cannot transfer enough load and results in lower bond strength of the joint brazed at 1373 K. With an increase in temperature, the TiN reaction layer becomes thicker and more continuous because Ti diffuses more rapidly and reacts with ceramic more sufficiently, consequently, bond strength of the joint increases. But at the temperature of 1473 K and above, the decomposition of Si_3N_4 not only decreases the interfacial reaction but also reduces properties of the ceramic, thereby the bonding strength of the joint decreases. It has been pointed out that premetallizing the surface of Si_3N_4 with AgCuInTi for 0.6 ks at 1173 K would form a TiN layer which could both restrain the decomposition of Si_3N_4 and improve the wetting of active filler on the surface of Si_3N_4, thus an excellent joint would be obtained [12]. Therefore, the pretreatment of the ceramic surface is a key route to increase bond strength of the joint brazed with thermal-resistant filler alloys.

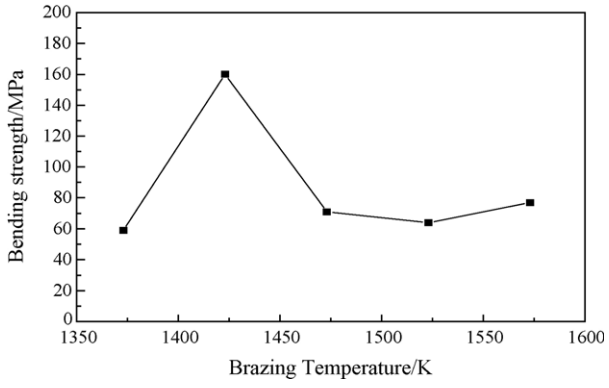

Fig. 3. The effect of brazing temperature on bending strength of the joint.

3.4. Bonding mechanism of the ceramic/filler alloy interface

According to the literature [16], the free energy of formation for Si_3N_4 and TiN, when one mole N_2 participates in the reactions, is represented by the following, respectively,

$$\Delta G_f^{\circ}\,(\mathrm{Si_3N_4})\,(\mathrm{kJ\,mol^{-1}}) = -361.9 + 0.1575T \quad (1)$$

$$\Delta G_f^{\circ}\,(\mathrm{TiN})\,(\mathrm{kJ\,mol^{-1}}) = -672.6 + 0.1865T \quad (2)$$

It can be found that the free energy of formation for Si_3N_4 and TiN are both negative at the brazing temperature ranging from 1373 to 1573 K. Moreover, the free energy for TiN is lower than that for Si_3N_4. It indicates that TiN is more stable than Si_3N_4, so Ti will react with Si_3N_4 to form titanium nitride immediately after they contact with each other at high temperature. And accordingly, the systematic free energy is decreased. Based on the theory, a Ti foil was added into the brazing filler to form reaction layer, thus a reliable joint can be achieved.

Because the eutectic point of Cu–Ti is 1153 K [18], liquid appears between Cu and Ti foils during heating process. The amount of the liquid phase increases with increasing temperature. The Cu–Ti alloy dissolves completely when the temperature reaches 1223 K. With further increasing the temperature, Pd dissolves into the Cu–Ti melt. According to the Cu–Pd phase diagram [19], Cu76.5Pd8.5Ti15 alloy has been in liquid at the brazing temperatures used in this study. During the heating process, Ti, as an active element, diffuses towards the Si_3N_4 ceramic and reacts with Si_3N_4 to form TiN at the Si_3N_4/filler alloy interface by the following reaction:

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

$$\Delta G^{\circ}\,(\mathrm{kJ\,mol^{-1}}) = -1356 + 0.199T$$

Due to the negative free energy, the reaction will proceed continuously until a certain thickness of TiN reaction layer has been obtained, which will impede Ti diffusing any further towards Si_3N_4. During the reaction above, Si is released and diffuses through the TiN reaction layer, leading to the formation of Ti_5Si_3 phase between the TiN reaction layer and the filler alloy according to the following reaction:

$$5\mathrm{Ti\,(s)} + 3\mathrm{Si\,(s)} = \mathrm{Ti_5Si_3\,(s)} \quad (4)$$

$$\Delta G^{\circ}\,(\mathrm{kJ\,mol^{-1}}) = -194.14 + 0.0167T$$

During the holding process at the brazing temperatures, Pd dissolves into the Cu–Ti alloy and distributes in the whole of welding seam, but richens where Si was richer because of the strong binding force between Pd and Si to form Pd_2Si phase.

Experimental results also indicate that Pd, Ti and Si in the filler alloy react to form PdTiSi phase. The two reactions above can be represented by the following equations:

$$2\mathrm{Pd}\,(\mathrm{l}) + \mathrm{Si}\,(\mathrm{s}) = \mathrm{Pd_2Si}\,(\mathrm{s}) \quad (3)$$

$$\mathrm{Pd}\,(\mathrm{l}) + \mathrm{Ti}\,(\mathrm{l}) + \mathrm{Si}\,(\mathrm{s}) = \mathrm{PdTiSi}\,(\mathrm{s}) \quad (4)$$

However, since there is a lack of thermodynamic data, a detailed calculation for the two reactions can hardly be made at present stage, but the experiments have proved the existence of Pd_2Si and PdTiSi.

4. Conclusions

Si_3N_4 ceramic has been joined to itself using a Cu–Ti–Pd filler alloy by brazing at 1373–1573 K holding for 1.8 ks. The joint comprises three parts, that is (1) a continuous reaction layer of TiN between Si_3N_4 and filler alloy, (2) a discontinuous reaction layer containing TiN, Pd_2Si and Ti_5Si_3 connecting the continuous reaction layer, and (3) the Cu-based solid solution in the mid of the joint and some reaction products (TiN, Pd_2Si, PdTiSi and Ti_5Si_3) in the solution. A maximum bending strength of 155.8 MPa has been reached from the joint brazed at 1423 K for 1.8 ks.

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