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A TEM analysis of the Si_3N_4/Si_3N_4 joint brazed with a Cu-Zn-Ti filler metal

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Si_3N_4 ceramic was joined to itself using a filler alloy of (CuZn)85Ti15 at 1123–1323 K for 15 min. TEM observation showed that a reaction zone of TiN and/or Ti_2N exists at the interface between the ceramic and filler alloy, and the center of the joint is composed of Cu-Zn solid solution in which there are Cu_2TiZn and Ti_5Si_3 reaction phases. With increasing brazing temperature, both the thickness of the reaction zone and the amount and size of the Ti_5Si_3 phase increase, while the amount and size of the Cu_2TiZn phase decrease. When the brazing temperature reached 1323 K, the Cu_2TiZn phase disappeared. When the brazing temperature is lower than 1223 K, the interfacial reaction zone is mainly composed of Ti_2N, which has a cylindrical shape and orientates randomly in the zone. There is a crystal orientation relationship between the Ti_2N in the reaction zone and the Cu in the Cu-Zn solid solution, which is: $\{110\}_{Ti2N}//\{420\}_{Cu}$, $\langle 001\rangle_{Ti2N}//\langle 001\rangle_{Cu}$. When the brazing temperature is higher than 1223 K, the interfacial zone is composed of TiN, which has a plate shape crossing each other.

1. Introduction
It is well known that Si_3N_4 ceramic has high thermal and wearing resistance and is a promising material for high temperature applications. However, it is difficult to manufacture the Si_3N_4 ceramic workpieces with large dimensions and complicated shapes because the Si_3N_4 ceramic has a low ductility. In recently 20 years, many studies have been focused on the techniques of ceramic joining because it can be used not only for low-cost and high-reliability manufacturing of ceramic parts with complicated shapes but also to repair the ceramic parts with cracks. Various of methods have been adopted for ceramic joining [1–4], in which active metal brazing is widely investigated because it is a simple process to obtain high strength ceramic joints with different shapes and sizes.

Most of the current research about the active brazing of Si_3N_4 ceramic has been focused on the following three points: (1) the effect of brazing parameters on the microstructure and properties of the joints; (2) the analysis of residual stress at the joint interface; (3) the behavior of the interfacial reaction and the examination of the reaction products [5–8]. The bonding strength of the joint greatly depends on the microstructure of the joints. Therefore, this work studies the reaction behavior and microstructure of the interfaces at Si_3N_4/Si_3N_4 joint using Cu-Zn-Ti filler alloy and to observe and analyze the relationship between the different phases within the joint.

2. Materials and experimental procedures
Cu65Zn35 alloy foil with a thickness of 0.1 mm and Ti foil with a thickness of 20 μm were used as filler materials to braze the Si_3N_4 ceramic. By adjusting the amount of two kinds of foils, a filler alloy containing 15 at.% Ti will be formed at the joint between Si_3N_4 ceramic. Si_3N_4 ceramic brazing was carried out in a vacuum of 1.33–1.67 $\times$ 10^{-3} Pa for 15 min under a pressure of 2 $\times$ 10^{-3} MPa. The brazing temperatures were from 1123 to 1323 K with an interval of 50 K. Si_3N_4 ceramic samples with a size of Φ 6 $\times$ 4 mm were ground to a surface finish of Ra = 30 μm, and then were cleaned together with the metal foils in a ultrasonic bath. The cleaned metal foils were put between two pieces of Si_3N_4 ceramic and then brazed in the furnace. The microstructure of the joints was observed and analyzed by means of electron probe microanalysis

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(EPMA), X-ray diffractometer (XRD) and transmission electron microscope (TEM).

3. Results

Fig. 1 shows the morphology of the Si_3N_4/Si_3N_4 joints brazed at 1123–1323 K for 15 min using (CuZn)85Ti15 as the filler alloy. The elemental distributions across the joint are shown in Fig. 2, which was obtained by EPMA. The results shown in Figs 1 and 2 indicate that there is a reaction zone (region I) between the filler alloy and the Si_3N_4 ceramic, which contains a larger amount of titanium nitride and a small amount of compounds containing titanium and silicon. The middle of the joint is Cu-Zn solid solution (region II and IV), in which there are some new phases in the center part of the Cu-Zn solid solution (region III). With increasing brazing temperature, both the thickness of the reaction zone and the amount and size of the reactant containing Ti and Si in the Cu-Zn solid solution increase. It can be also found that the thickness of both the reaction zone and the joint layer decreases obviously when the brazing temperature reaches 1323 K.

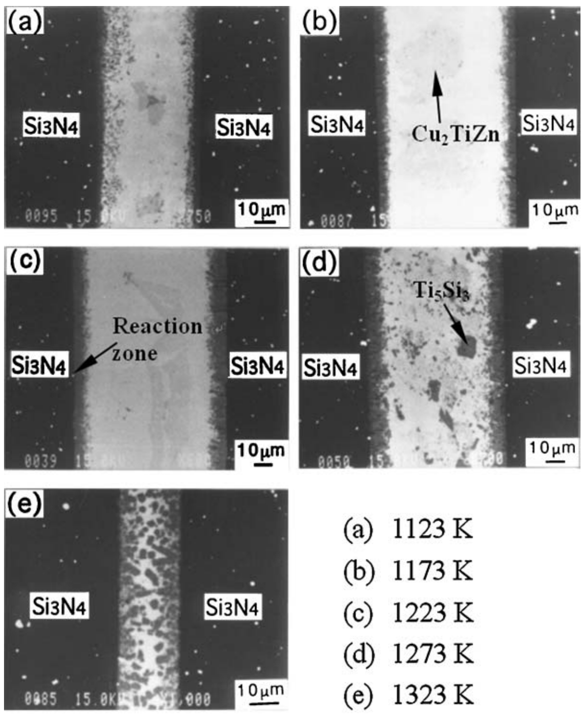

Figure 1 Microstructure of the Si_3N_4/Si_3N_4 joint brazed at different temperatures.

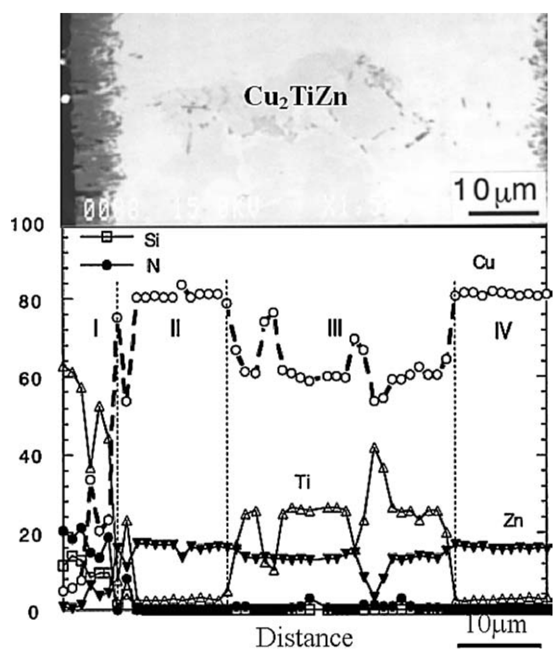

Figure 2 Elemental distributions in the filler alloy across the Si_3N_4/Si_3N_4 joint brazed at 1173 K for 15 min.

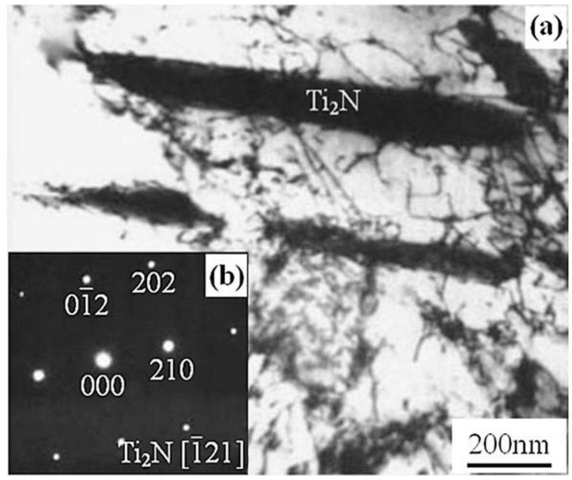

Figure 3 TEM image showing the morphology of Ti_2N in the reaction zone obtained during brazing at 1173 K for 15 min: (a) morphology of the Ti_2N and (b) diffraction patterns of the Ti_2N.

Fig. 3 is the TEM image showing the morphology of titanium nitride in the reaction zone obtained during brazing at 1173 K for 15 min. Both composition analysis (Fig. 2) and diffraction patterns (Fig. 3b) indicate that the titanium nitride in the reaction zone obtained at lower temperature is Ti_2N. Fig. 4a also shows the morphology of the Ti_2N in the reaction zone obtained with the same brazing condition. From Figs 3a and 4a it can be seen that the Ti_2N in the reaction zone obtained during brazing at 1173 K for 15 min has a cylindrical shape with the length and diameter of 0.4–0.8 μm and 0.1–0.2 μm, respectively. Fig. 3a shows the morphology of the Ti_2N in the longitudinal direction, and Fig. 4a shows the cross section of the Ti_2N. Fig. 4b shows the electron energy loss spectrum (EELS) result of the Ti_2N shown in Fig. 4a, indicating the existence of Ti and N in the new phase in reaction zone.

Figs 3a and 4a also show that there is high density of dislocations around the Ti_2N in the Cu-Zn solid solution. Because of the large difference of the coefficient of thermal expansion (CTE) between Ti_2N and Cu-Zn solid solution, interfacial stress will be formed during the cooling from brazing temperature, resulting in not only internal residual stress at the interface between Ti_2N and Cu-Zn solid solution but also local plastic deformation in the Cu-Zn solid solution and the formation of dislocations around the Ti_2N phases as shown in Figs 3a and 4a.

Fig 4c shows the diffraction patterns, which contain the patterns of both Cu-Zn solid solution in [001] direction and Ti_2N in [001] direction. Calculating and

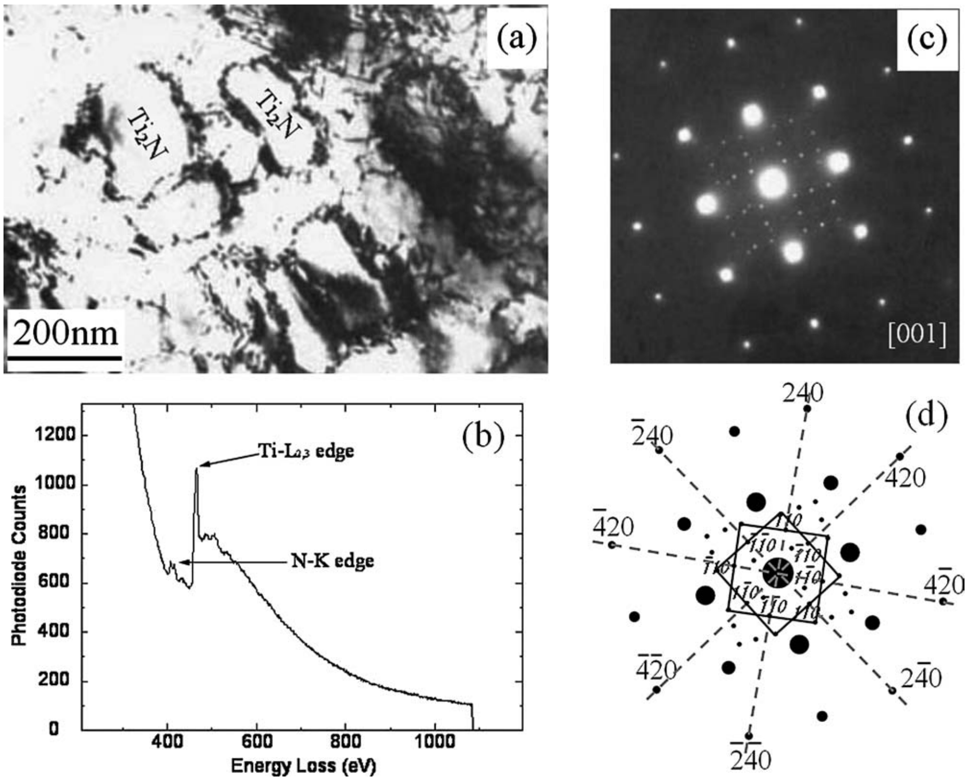

Figure 4 TEM results showing the morphology and composition of the Ti_2N phase and the crystal orientation relationship between Ti_2N and Cu-Zn solid solution: (a) morphology of the cross section of the Ti_2N phase, (b) EELS results showing the existence of Ti and N in the Ti_2N phase, (c) diffraction patterns of both Ti_2N and Cu matrix, and (d) indexing of the patterns.

analyzing the result indicate that the pattern with larger spots corresponds to the Cu-Zn solid solution and that with smaller spots is attributed to the Ti_2N phase. The indexing results are shown in Fig. 4d, which clearly shows a crystal orientation relationship between Cu matrix and Ti_2N phase. The orientation relationship is $\{110\}_{Ti2N}//\{420\}_{Cu}$, $\langle 001\rangle_{Ti2N}//\langle 001\rangle_{Cu}$.

Fig. 5 is the TEM image showing the morphology of titanium nitride in the reaction zone obtained during brazing at 1223 K for 15 min. Comparing with the Ti_2N shown in Fig. 3a, the titanium nitride formed at 1223 K is much more coarser than Ti_2N. The titanium nitride shown in Fig. 5a has a plate shape with a thickness of 0.5–1.0 μm, and they cross each other and oriented randomly in the Cu-Zn solid solution. The diffraction patterns of the titanium nitride shown in Fig. 5b indicate that the titanium nitride formed at 1223 K is actually TiN. Because the Cu-Zn solid solution has been removed during the preparation of the TEM sample, it could not be confirmed if there is crystal orientation relationship between TiN and Cu-Zn solid solution.

The results above indicate that Ti_2N is formed in the reaction zone during the brazing at lower temperatures ($\leq$1173 K), while TiN is formed during brazing at higher temperature ($\geq$1223 K). X-ray diffraction results shown in Fig. 6 also indicate that with increasing brazing temperature, the peak value of the Ti_2N phase decreases and that of the TiN phase increases.

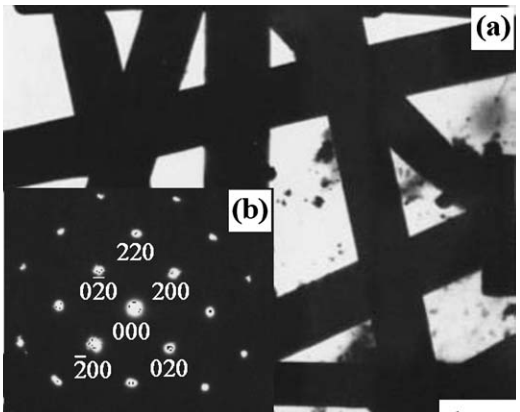

Figure 5 TEM image showing the morphology of TiN in the reaction zone obtained during brazing at 1233 K for 15 min: (a) morphology of the TiN and (b) diffraction patterns of the TiN.

4. Discussion

According to the thermodynamic data [9], the free energy of formation of Si_3N_4 and TiN is

$$\Delta G^0(Si_3N_4) = -361.9 + 0.1575T\ (kJ/mol) \quad (1)$$

$$\Delta G^0(TiN) = -672.6 + 0.1865T\ (kJ/mol) \quad (2)$$

respectively, indicating that TiN is more stable than Si_3N_4 within the temperature range employed here. Therefore, during the brazing process, with increasing temperature, filler alloy is molten gradually and the Ti in the melt will diffuse to the interface between Si_3N_4 and filler alloy and concentrate near the surface of the Si_3N_4 ceramic, and then following reaction will take

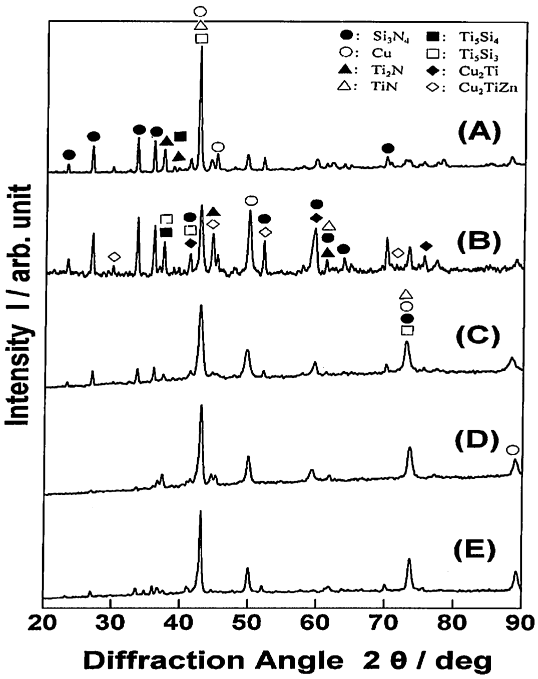

Figure 6 XRD spectrums of the reaction products at the Si_3N_4/Si_3N_4 joints brazed at different temperatures: (A) 1123 K, (B) 1173 K, (C) 1223 K, (D) 1273 K, and (E) 1323 K.

place to form titanium nitride [10]:

$$Si_3N_4\,(s) + 8Ti\,(l) = 4Ti_2N\,(s) + 3Si\,(s) \quad (3)$$

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

According to the Ti-N binary alloy phase diagram [11], the Ti_2N phase is stable until 1373 K when the N content is 32.4–34 at.%. With increasing temperature, the TiN phase becomes stable. The transformation temperature between Ti_2N and TiN decreases with increasing N content. In the brazing temperature range used in this investigation (1123–1323 K), Ti_2N phase will be formed according to reaction (3) at the interface between Si_3N_4 and filler alloy when the brazing temperature is lower. When the temperature surpasses 1223 K, TiN phase will be formed at the interface instead of Ti_2N phase.

During the process of the reaction (3) and/or (4), Si will be released from the Si_3N_4 ceramic and diffuses to the middle of the filler alloy and reacts with Ti to form Ti_5Si_3 according to the following reaction [10]:

$$5Ti\,(l) + 3Si\,(s) = Ti_5Si_3\,(s) \quad (5)$$

With increasing brazing temperature and holding time, more and more Ti_2N and/or TiN phases are formed and the thickness of the reaction zone increases. The reaction zone will act as a barrier to the diffusion of Ti and Si and reduce the reaction rate. Kim [12] pointed out that the thickness growth kinetics obey the parabolic rate law, and when the Ti content surpasses 15 at.%, the reaction rate will be controlled by Ti diffusion in the reaction zone of the joint.

Zn in the filler alloy does not react with the Si_3N_4 ceramic, however, it decreases the melting temperature of the filler alloy [13], enabling the brazing process be carried out at lower temperatures. From Fig. 2 it can be found that a phase with large size and grey color exists in the Cu-Zn solid solution at the center of the joint. The composition of this phase was determined to be Cu56.43Ti23.45Zn19.40. Based on the Cu-Zn-Ti ternary phase diagram [14] and the composition analysis results, this phase is suggested to be Cu_2TiZn. The X-ray diffraction results shown in Fig. 6 also indicate the existence of the Cu_2TiZn phase, although the only one unique peak is a little weak because the amount of the Cu_2TiZn phase is comparably lower. Fig. 6 also indicates several overlapping lines, which makes it difficult to identify the presence of the Cu_2TiZn phase. With increasing brazing temperature and holding time, more and more Zn is evaporated, leading to a decreasing content of Zn in the filler alloy. When the brazing temperature surpasses 1223 K, Cu_2TiZn phase could not be formed, as shown in Fig. 6, due to the decreasing content of Zn in the filler alloy.

From the experimental results and above analysis, it is clear that the new phases in the center part of the Cu-Zn solid solution are Ti_5Si_3 and/or Cu_2TiZn. With increasing brazing temperature, the size and amount of the Ti_5Si_3 phase increase, while that of the Cu_2TiZn phase decrease. The viscosity of the melt filler alloy decreases and its flowability increases with increasing brazing temperature, which leads to more and more liquid filler alloy flowing out of the joint, resulting in a decrease thickness of both the reaction zone and the joint layer.

5. Conclusions

Si_3N_4 ceramic was successfully joined to itself using a filler alloy of (CuZn)85Ti15 at 1123–1323 K for 15 min. Following conclusions were drawn:

(1) A reaction zone of TiN and/or Ti_2N exists at the interface between the ceramic and filler alloy, and the center of the joint is composed of Cu-Zn solid solution in which there are some reaction phases of Cu_2TiZn and/or Ti_5Si_3.

(2) With increasing brazing temperature, the thickness of the reaction zone increases. When the brazing temperature surpasses 1223 K, the thickness of both reaction zone and joint layer decrease with increasing brazing temperature, because the melt filler alloy flows out of the joint more easily at higher temperature.

(3) When the brazing temperature is lower than 1223 K, the interfacial reaction zone is mainly composed of Ti_2N, which has a cylindrical shape and orientates randomly in this zone. There is a crystal orientation relationship between the Ti_2N in the reaction zone and the Cu in the Cu-Zn solid solution, which is: $\{110\}_{Ti2N}//\{420\}_{Cu}$, $\langle 001\rangle_{Ti2N}//\langle 001\rangle_{Cu}$. When the brazing temperature is higher than 1223 K, the interfacial zone is composed of TiN, which has a criss-cross plate morphology.

(4) With increasing brazing temperature, the amount and size of the Ti_5Si_3 phase increase, while, the amount and size of the Cu_2TiZn phase decrease. When the brazing temperature reached 1223 K, the Cu_2TiZn phase could not be formed.

Acknowledgments

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