

Joining of $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ with CuNiTiB paste brazing filler metals and interfacial reactions of the joints

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The joining of $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ was carried out using CuNiTiB paste brazing filler metals. The maximum room-temperature three-point bend strength of the joints is 338.8 MPa. The cross-section microstructures of the joints and the element area distribution were examined by scanning electron microscope (SEM) equipped with wave dispersive X-ray spectroscopy (WDS). The phases appeared on the fracture surfaces of the joints were determined by means of X-ray diffraction analysis (XRDA) method. A model is established of the interfacial reactions between Si_3N_4 and the CuNiTiB brazing filler metals. With this model, the relationship between the joint strength and the interfacial reactions is discussed. © 1999 Kluwer Academic Publishers

1. Introduction

Silicon nitride (Si_3N_4) is an engineering ceramic material with superior properties and widely used in industries. However, it may be easy to produce defects inside the great or sophisticated ceramic parts, and these ceramic parts also may be expensive. Thus joining of ceramic to ceramic and ceramic to metal has been becoming very important. AgCuTi active brazing alloys are commonly used as the brazing filler metals [1, 2]. Such brazing alloys contain rather high quantity of silver (about 57 at % Ag) therefore are expensive as well as possess rather good properties. So it is necessary to develop a new brazing alloy with similar properties but without silver and other expensive metals. On the other hand, although the interfacial reactions of $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joints brazed using different brazing filler metals have been greatly studied [2–7], the investigation on the relationship between the interfacial reactions and the joint strength is still insufficient.

Recently the wettability of CuNiTi alloys on the Si_3N_4 has been investigated [8]. Based on the previous experimental results, this article studied on the joining of $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ using the new brazing alloys of CuNiTiB. The brazing alloys were used in paste form. In order to understand well the joining mechanism of $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joints brazed using such new brazing alloys, the interfacial reactions in the joints were investigated in detail in this study, and their effects on the joint strength were discussed with the help of an established model of the interfacial reactions between Si_3N_4 and the CuNiTiB brazing filler metals.

2. Materials and experimental procedures

The hot-pressed sintered Si_3N_4 used in this study was supplied by Shanghai Institute of Ceramics, Academia Sinica. The size of the Si_3N_4 bars was 3 mm × 4 mm ×

20 mm and the faying surface of the bars was mechanically polished. Before brazing experiments, the Si_3N_4 specimens were ultrasonically cleaned in acetone, and then dried by air blowing. The paste brazing filler metals were designed of four compositions, that is, HTB1 (Cu5-25Ni12-16Ti), HTB2 (Cu5-25Ni16-28Ti), HTB3 (Cu5-25Ni28-33Ti) and HTB4 (Cu5-25Ni33-42Ti) (at %). Trace of B was added to reduce the melting point of the alloys when necessary. The Ni content of the four brazing alloys was kept constant. The purities of the used Cu, Ni, Ti and B powders are 99.7%, 99.8%, 99.0% and 97.1% (wt %) respectively. The powders of about 2 gram with certain proportion were mixed in a mortar, blended for 15 min to make them homogeneous. A kind of organic liquid, ethandiol, was added into the mixture, then, to make it into the paste brazing filler metal which was used to join the $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$. The specimens were installed into an iron jig with the butt joint. Finally, they were put into a vacuum furnace together. During the succeeding heating process, the organic liquid would vaporize and no pollutant substance would be remained. The heating rate was 15 K/min, the cooling rate after brazing was 15 K/min above 673 K, and then 1.5 K/min to room temperature. The vacuum was kept $3.0\text{--}6.5 \times 10^{-3}$ Pa during the heating and cooling.

The room-temperature three-point bend strength of the joints was measured with a cross-head speed of 0.5 mm/min. The phases appeared on the fracture surfaces of the tested specimens were determined by means of X-ray diffraction analysis (XRDA) method. The cross-section microstructures of the joints were observed by scanning electron microscopy (SEM), and the element area distribution and the compositions across the joint, brazed using brazing filler metal HTB2, were determined by wave dispersive X-ray spectroscopy (WDS) and energy dispersive X-ray spectroscopy (EDS).

TABLE I Effect of different compositions of the brazing filler metals on the three-point bend strength of the joints ($T = 1353 \text{ K}$, $t = 10 \text{ min}$)

Brazing filler metals	Joint strength σ_b (MPa)		
	σ_{maximum}	σ_{average}	σ_{minimum}
HTB1	112.0	82.4	60.2
HTB2	364.4	338.8	308.0
HTB3	272.0	244.8	215.0
HTB4	200.0	177.2	151.0

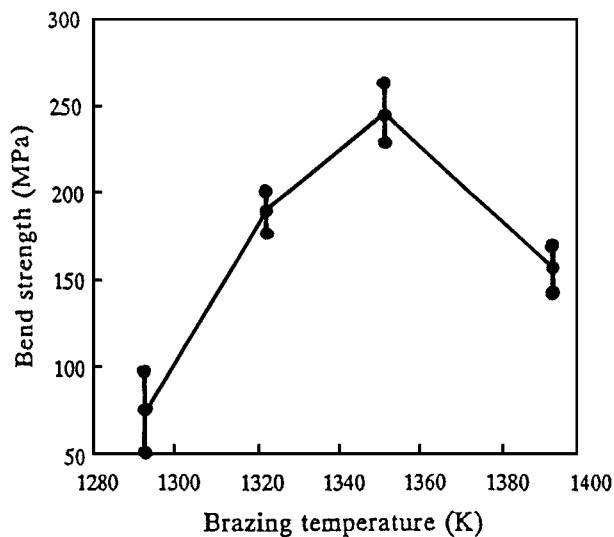


Figure 1 Effects of the brazing temperature on the room-temperature three-point bend strength of $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joints (brazed using the brazing filler metal HTB3).

3. Results and discussion

3.1. Strength of the $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joints

The previous research results show that, when using the CuNiTi system alloys as brazing filler metals to join $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$, the holding time of 10 min at the brazing temperature is adequate [9]. Fig. 1 shows the variation of three-point bend strength of $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joints with brazing temperatures when using the brazing filler metal HTB3, with the holding time fixed at 10 min. The experimental data reveal that the joint strength was increased at first with the increase of the brazing temperature. The strength of the joints brazed at 1353 K presented a maximum value (244.8 MPa). Then the strength was decreased with the increase of the temperature.

Table I shows the effect of different compositions of the brazing filler metals on the joint strength. As shown in the table, the maximum joint strength was achieved with the brazing filler metal HTB2.

3.2. Interfacial reactions between Si_3N_4 and the brazing filler metals

3.2.1. Microstructures of the $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joints and the element area distribution

Fig. 2 shows the cross-section microstructures of the $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joints obtained with the four brazing filler metals, i.e. HTB1, HTB2, HTB3 and HTB4. The thickness of the brazing filler metal layers varied in a narrow range from approximate 48 to 58 μm (shown in

Fig. 2), assuring the comparability of the joint strength. Fig. 3 shows the cross-section microstructure of the joint brazed with HTB2 and the corresponding element area distribution images. The element Si diffused from Si_3N_4 to the brazing filler metal, while elements Ni and Ti diffused conversely from the brazing filler metal to Si_3N_4 and accumulated at the interfaces. As the principal element in the brazing filler metal, Cu was rich in the middle of the joint. The fact that the diffusion distance (of 9 μm) of Si is almost as same as that of Ti indicates that during the brazing process the active element Ti diffused bilaterally to the interfaces and led to the decomposition of Si_3N_4 into Si and N.

The distribution of Ni is similar to that of Ti but the bands rich in Ti are wider and nearer to Si_3N_4 than those rich in Ni (refer to Fig. 3c and d). That is, the narrow reaction bands “a” (labeled in Fig. 3a) neighbored to Si_3N_4 do not contain Ni. At the first place it was only active element Ti in brazing filler metal that participated in the interfacial reactions. Then, Ni also participated in the reactions at the region “e” (labeled in Fig. 3a). The composition analysis results of the joint (shown in Fig. 4) are in agreement with the previous element distribution. For all four brazing alloys, the narrow reaction bands were formed in the joints. But there exists a difference in the width of the narrow reaction bands, that is, for brazing alloy HTB4, the width is about 4–6 μm , while, it is about 2 μm for HTB1, 2 and 3 (refer to Fig. 2).

3.2.2. Interfacial reaction model between Si_3N_4 and CuNiTiB brazing filler metals

Fig. 4 shows the X-ray diffraction patterns of the fracture surfaces of the joints after three-point bend strength tests. It can be seen from the patterns that there always exists TiN in the four joints, while the Ti-Si compounds are different from each other. With the change of the brazing filler metals, the Ti-Si compounds varied from TiSi_2 (Fig. 5a) to TiSi (Fig. 5c), until to Ti_5Si_3 (Fig. 5d). In addition, for the HTB2 and HTB3, there exists NiTiSi tribasic compound at the interface.

When liquid brazing filler metals of CuNiTiB reacted with Si_3N_4 , Ti, as an active element, could directly participate in the interfacial reactions. In fact, when at the liquid state, the dissolution enthalpy of Ti in Ni (−170 kJ/mol) is far lower than that in Cu (−78 kJ/mol), therefore the combining ability of Ni-Ti is much stronger than that of Cu-Ti [8, 10]. Thus, before participating in the interfacial reactions, part Ti would prefer to combine with Ni to become Ni-Ti atomic clusters. Undoubtedly, these clusters are less active than the free Ti atoms. Based on the previous thought, an interfacial reaction model is established to explain the reactions occurred at the interfaces of the four joints. The whole reaction process is divided into four steps by the model, as shown in Fig. 6a–d. During the brazing process, after the brazing filler metal is melted, the free Ti atoms diffuse more easily to the surfaces of Si_3N_4 and then accumulate there (the first step, Fig. 6a). According to the reference [11], the free energy of formation of Si_3N_4 and TiN for one

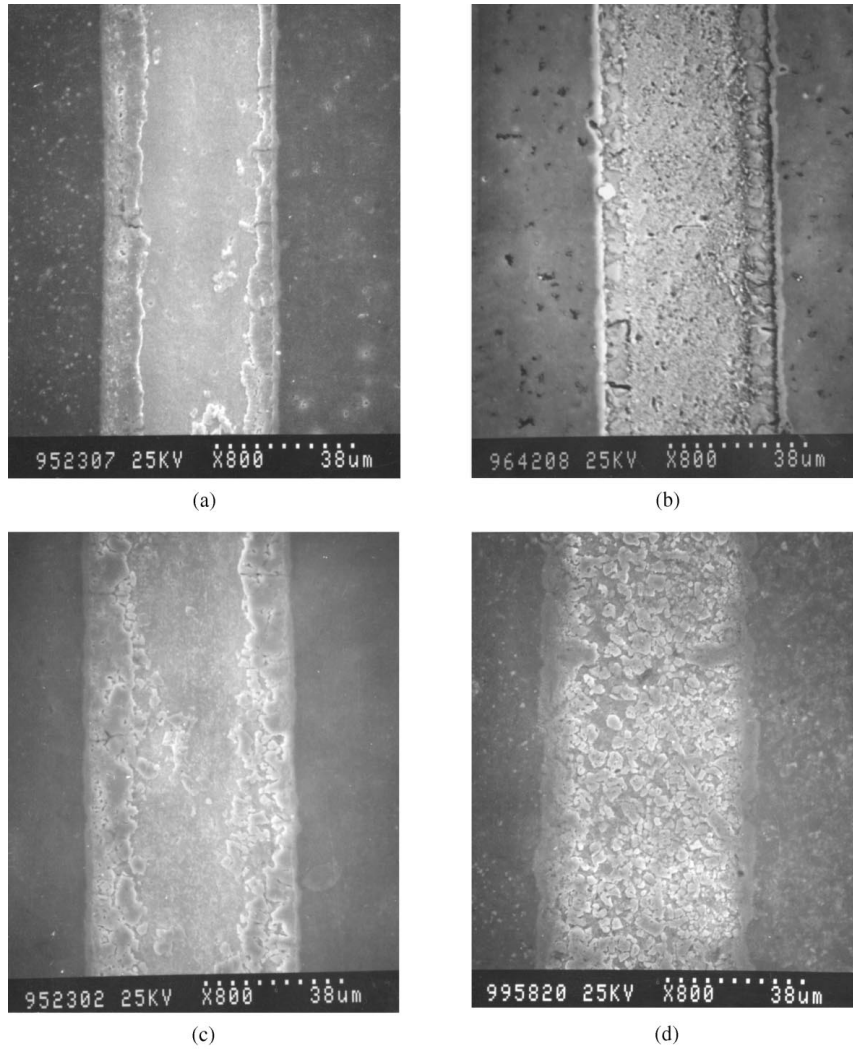


Figure 2 Cross-section microstructures of the joints brazed at 1353 K for 10 min using the brazing filler metals HTB1 (a), HTB2 (b), HTB3 (c) and HTB4 (d). Etched first by water solution of (HF + HNO₃) and then by 5% FeCl₃ solution.

mole of N₂ can be described respectively as follows:

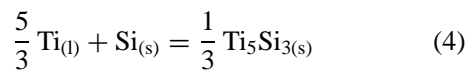
$$\Delta G_{f(\text{Si}_3\text{N}_4)}^0 = -396.48 + 0.207T \text{ (kJ/mol)} \quad (1)$$

$$\Delta G_{f(\text{TiN})}^0 = -679.14 + 0.193T \text{ (kJ/mol)} \quad (2)$$

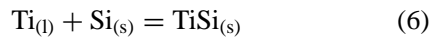
At 1353 K, Si₃N₄ is less stable than TiN. So the following reaction can take place to form TiN on the surface of Si₃N₄:



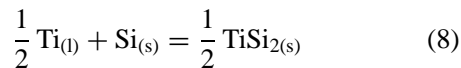
Meanwhile the Si atoms are released (the second step, Fig. 5b). Afterwards, Ti can react with Si to form Ti-Si compounds (the third step, Fig. 5c), for example [12]:



$$\Delta G^0 = -220.4 + 0.0265T \quad (5)$$



$$\Delta G^0 = -163.6 + 0.0270T \quad (7)$$



$$\Delta G^0 = -91.1 + 0.0055T \quad (9)$$

At 1353 K, ΔG^0 (Equations (5), (7), and (9)) for reactions (4), (6), and (8) are respectively -184.5 kJ/mol, -127.7 kJ/mol, and -83.7 kJ/mol. The negative values of ΔG^0 signify that these reactions can take place spontaneously. The reactions through this step may be accompanied with the continuous growth of TiN. Then the residual free Ti atoms as well as the atomic clusters of Ni-Ti concurrently participate in the interfacial reactions to form TiN, Ti-Si compounds and even NiTiSi compound (the fourth step, Fig. 6d). In accordance with the model, the narrow reaction bands described above are formed factually through all three steps (Fig. 6a–c). The fourth step (Fig. 6d) is the last interfacial reaction step. If the reactions through the last step are not controlled, the thickness of the reaction layer would be far greater than that through the other three steps (refer to Fig. 2a–c).

Concerned with each of the four brazing filler metals, during the brazing process, the reactions relevant to the first two steps all take place, resulted in the compound TiN. But the reactions corresponding to the third and fourth step are different from each other. For brazing alloys HTB2 and HTB3, the reactions of the third and fourth step take place evidently, forming the compounds of Ti-Si that take in principal the two forms of Ti₅Si₃ and TiSi, and the NiTiSi compound resulted from

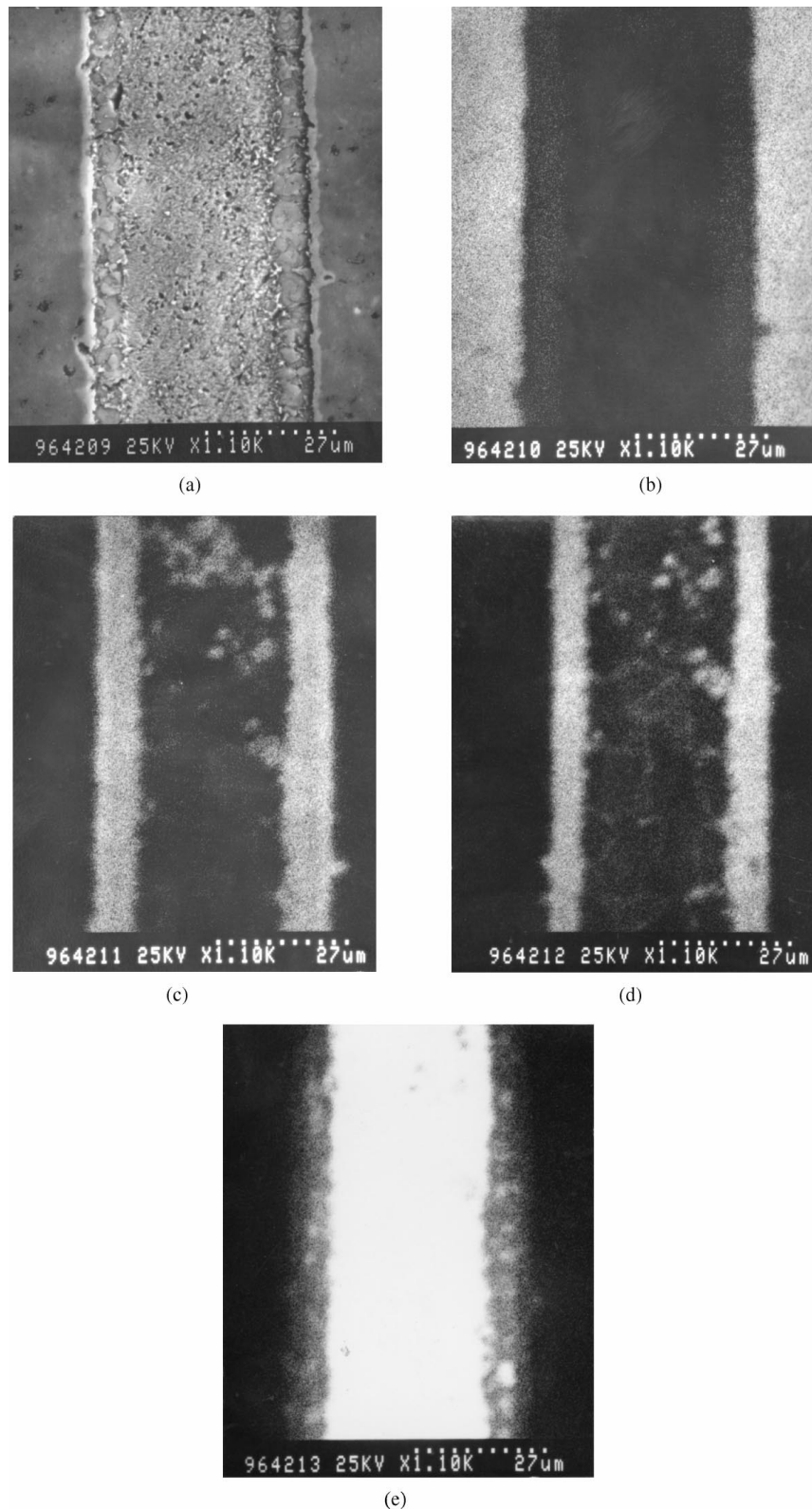


Figure 3 Cross-section microstructure (a) and element area distribution images of Si (b), Ti (c), Ni (d) and Cu (e) for the joint brazed at 1353 K for 10 min using HTB2.

the combination of Ni-Ti clusters and Si atoms (refer to Fig. 5b and c). Concerned with the brazing alloy HTB1 of less quantity of Ti, in light of the Equations 4–9, after the reaction of Equation 3, it is only accomplishing the reaction of Equation 8 that needs the least Ti atoms but consumes Si atoms most rapidly, with the compound of $TiSi_2$ formed. When the reaction reaches the fourth step, there is hardly chance for the Ni-Ti clusters to

combine with Si atoms to form $NiTiSi$ compound (refer to Fig. 5a). For the brazing alloy HTB4 with the highest quantity of Ti, in the beginning, the number of Ti atoms per unit area accumulating on the Si_3N_4 surfaces is much greater, so the reaction of Equation 3 is accomplished rapidly, producing a large number of TiN. The released Si atoms reacted with abundant Ti atoms in vicinity. In such a case, it is easier to produce

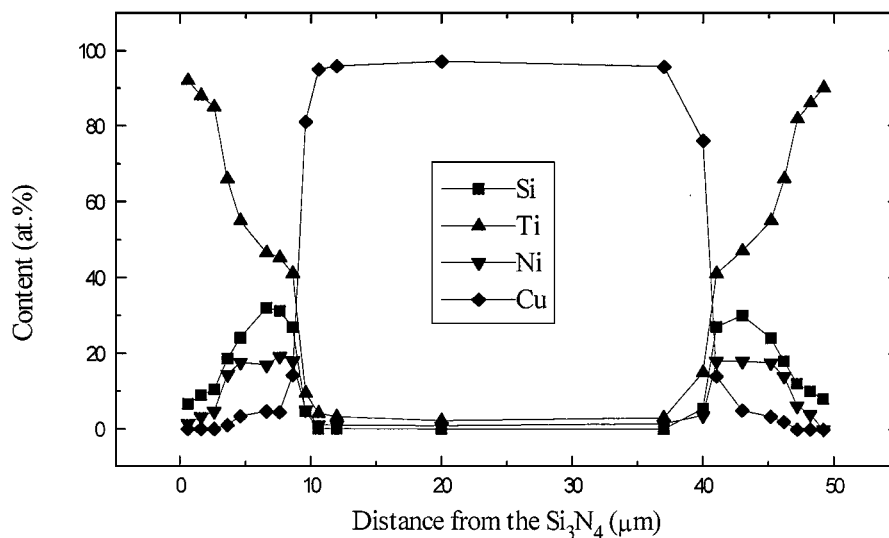


Figure 4 Compositional profile across the $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joint brazed at 1353 K for 10 min using HTB2.

the compound like Ti_5Si_3 , with a higher proportion of $X_{\text{Ti}}/X_{\text{Si}}$ (X presents atomic number). The abundant Ti atoms also reduce the diffusion time of Ti atoms to Si_3N_4 surface and the reaction time. As a consequence, through the reactions of the first three steps, a thick reaction band (mixture of TiN and Ti_5Si_3) is formed rapidly on the Si_3N_4 surface (shown in Fig. 2d). The thick reaction band would inhibit the continuous diffusion of Ti to Si_3N_4 [3], therefore it is difficult for Si_3N_4 to be further decomposed, so the reaction of Step 4 is restrained (refer to Figs 5d and 6d).

3.3. Relationship between the joint strength and interfacial reactions

The different compositions of the four brazing alloys result in not only different interfacial reaction extent but also different interfacial reaction products in the $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joints, therefore making the difference in the joint strength. According to ASTM cards, the type of crystal systems and the crystal lattice parameters a_0 , b_0 and c_0 of Si_3N_4 , Ti_5Si_3 , TiSi and TiSi_2 can be described as followings: Si_3N_4 , hexagonal: $a_0 = 7.604$, $c_0 = 2.908$; Ti_5Si_3 , hexagonal: $a_0 = 7.444$, $c_0 = 5.143$; TiSi, orthorhombic: $a_0 = 6.544$, $b_0 = 3.638$, $c_0 = 4.997$; TiSi_2 , orthorhombic, $a_0 = 3.62$, $b_0 = 13.76$, $c_0 = 3.605$. It is only Ti_5Si_3 that belongs to the same hexagonal system as Si_3N_4 does, and their a_0 values are very similar to each other, so Ti_5Si_3 and Si_3N_4 can match well each other, indicating that the formation of Ti_5Si_3 rather than TiSi or TiSi_2 is favorable to the joint strength.

When using the brazing filler metals HTB2 and HTB3 to join $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$, the reaction products of Ti-Si compounds at the interfaces are Ti_5Si_3 and TiSi. With interfacial reaction layers of thickness $9 \mu\text{m}$, the joints brazed with HTB2 exhibited the maximum strength of 338.8 MPa. While, for HTB3, due to containing more quantity of Ti, the excessive interfacial reactions occurred in the joint, resulting in thicker interfacial reaction layers (about $15 \mu\text{m}$). In general, in-

terfacial reaction layers described previously belong to brittle layers, and this increases the possibility of producing micro-default in the reaction layers. On the other hand, the thicker interfacial reaction layers also cause the increase of the residual thermal stress [13], which is resulted from the difference of thermal expansion coefficients between the Si_3N_4 and the interfacial reaction layers. Thus the joint strength is decreased. According to the analysis results of the phases formed on the fracture surface (shown in Fig. 5c), there do not exist phases of Cu and Ni_3Ti etc., which were formed in the brazing filler metal layer. This reveals that when tested the samples fractured at the interfacial reaction layers.

For HTB1, the formed Ti-Si compound is TiSi_2 (Fig. 5a), which is less favorable to the joint strength. In addition, HTB1 contains the least quantity of the active element Ti, thus its ability of wetting Si_3N_4 is feeble. In fact, it was found that the joint gap was not well filled by HTB1. Because of the previous two reasons, the joint strength for HTB1 is very low.

For the brazing alloy HTB4, the compound of Ti-Si in the interfacial reaction layer takes the form of Ti_5Si_3 . Though Ti_5Si_3 can better match Si_3N_4 , there exist a great number of brittle compounds such as Cu-Ti and Ni-Ti in the brazing filler metal layer (shown in Figs 2d and 5d), the strength of the brazing filler metal itself is weakened. Consequently, the joint strength value is also very low.

4. Conclusions

The joining of $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ was carried out using the paste brazing filler metals of four different compositions. The maximum room-temperature three-point bend strength of 338.8 MPa was achieved with the brazing filler metal HTB2 at 1353 K for 10 min. During the brazing process, Si_3N_4 is decomposed into Si and N at the interface, while the Ti and Ni in the brazing filler metal diffuse to Si_3N_4 and accumulate there, because Ni prefers to combine with Ti to form Ni-Ti clusters. At the interface the bands rich in Ti are wider and nearer to

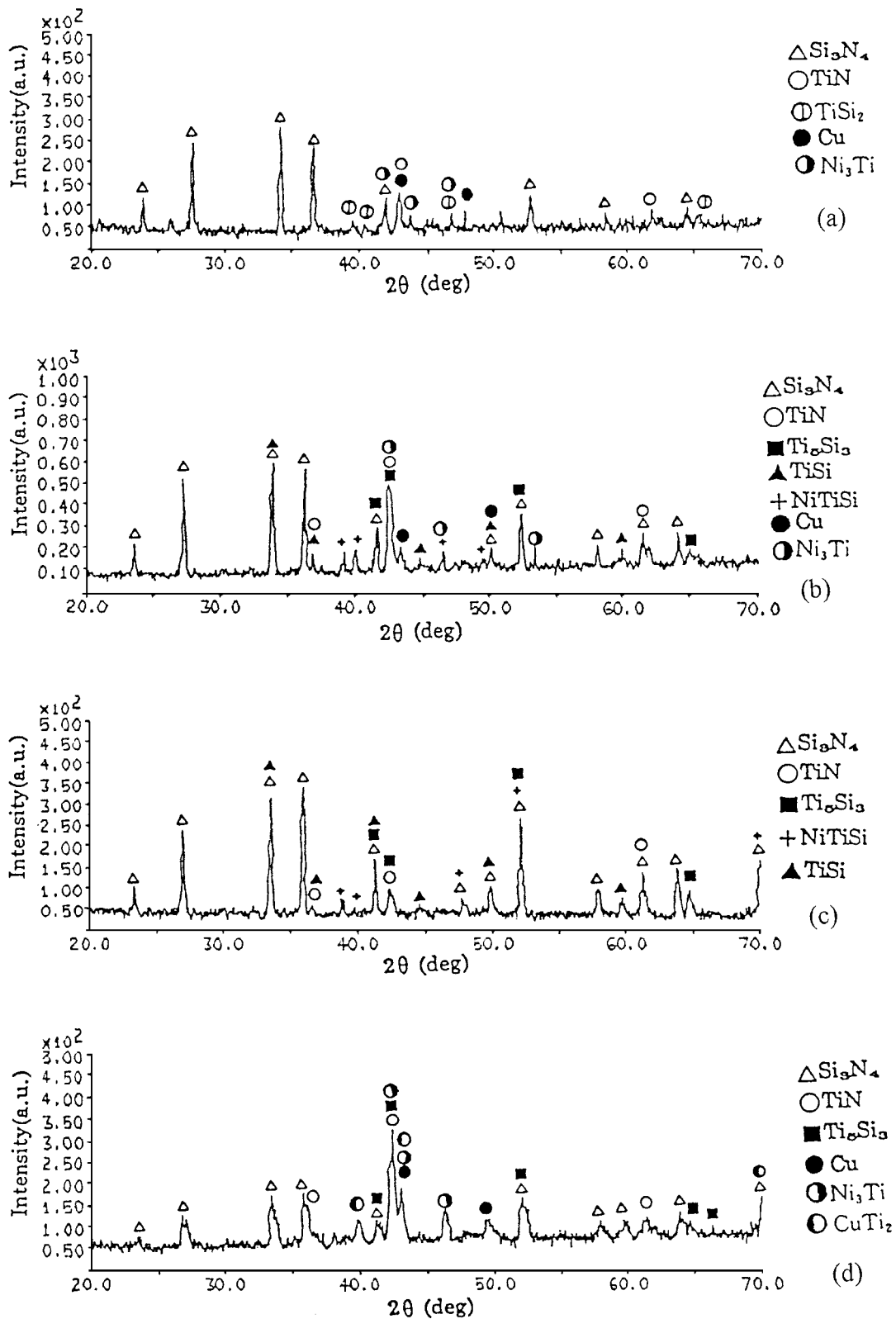


Figure 5 X-ray diffraction patterns of the fracture surfaces of the joints brazed using brazing filler metals HTB1 (a), HTB2 (b), HTB3 (c) and HTB4 (d).

Si_3N_4 than those rich in Ni, indicating that the free Ti atoms reacted preferentially with N and Si decomposed from Si_3N_4 to form TiN and Ti-Si compounds, then, for HTB2 and HTB3, Ni-Ti clusters also participated in the interfacial reactions to form NiTiSi compound. With the increase of Ti content in the brazing filler metals, the interfacial reaction extent of the joints was increased, and the reaction products varied evidently from TiSi_2 , TiSi

to Ti_5Si_3 , having an evident effect on the joint strength. In general, the formation of Ti_5Si_3 rather than TiSi or TiSi_2 at the interface is favorable to the joint strength. But excessive interfacial reactions will produce unduly-thick brittle reaction layer, which may reduce the joint strength. The relationship between the joint strength and the interfacial reactions are clearly explained by the established interfacial reaction model.

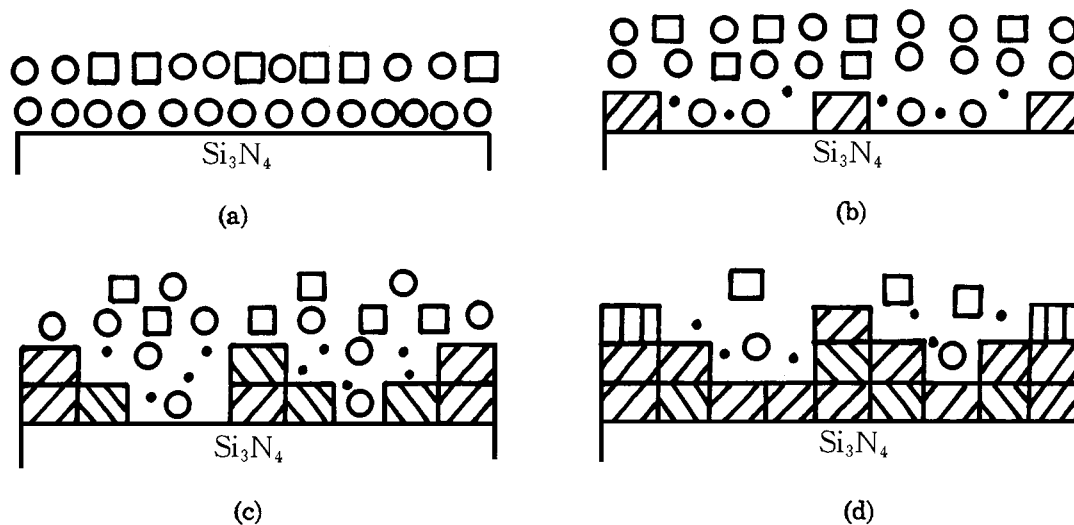


Figure 6 Interfacial reaction model between Si_3N_4 and CuNiTiB brazing filler metals (○ Ti atom; □ atomic cluster of Ni-Ti; ● Si atom; ▨ TiN; ▩ Ti-Si compound; ▤ NiTiSi).

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