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Microstructural and mechanical characterization of the Si_3N_4/Si_3N_4 joint brazed using Au–Ni–V filler alloys

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Abstract

In this study, two Au–Ni–V filler metals were used to braze Si_3N_4 ceramic in the form of foils. The effects of brazing temperature and V content in the filler alloy on microstructure and bonding strength of the joint were studied. The results reveal that a VN reaction layer with a thickness about 4 μm was formed at the interface between Si_3N_4 substrate and filler alloy. With increasing brazing temperature or V content the thickness of VN reaction layer increased. A maximum joint bending strength of 242 MPa was achieved when the joint was brazed at the temperature of 1423 K for 30 min using Au58.7Ni36.5V4.8 filler alloy. The bonding mechanism was discussed with reference to the discovered phases and brazing parameters.

Keywords: Si_3N_4; Joining; Au–Ni–V filler alloy; Microstructure; Mechanical properties

1. Introduction

Si_3N_4 ceramic has been widely used in aerospace and automobile industries because of its excellent thermal and oxidation resistance as well as outstanding high-temperature mechanical properties. However, Si_3N_4 ceramic is extremely difficult to machine due to its brittle natures. Thus, development of joining technologies is essential, in particular for joining ceramic components with complex shapes and lager size. To date several techniques for joining ceramics have been developed.[1–3] Among them, active metal brazing has been proven to be effective in joining Si_3N_4 ceramic because of its simplicity and flexibility in the joining process.[4] For active brazing of Si_3N_4 ceramic, filler alloys containing active metals such as Ti, Zr, and Hf have been used, and high bonding strength of the joint has be achieved by reaction between the active metals and the Si_3N_4 ceramic. In particular, Cu–Ag based alloys containing Ti have been adopted as the filler alloy for brazing Si_3N_4 ceramic. Such filler alloys have a good wettability to almost all ceramics. However, the drawbacks of using these filler alloys are (1) lower thermal and oxidation resistance and (2) lower service temperature below 773 K. In order to improve the thermal and oxidation resistance of the Si_3N_4 ceramic joint, it is of critical importance to develop new filler metals with higher melting points as well as thermal and oxidation-resistance. Previous studies showed that the Si_3N_4/Si_3N_4 joints with high thermal and oxidation resistance can be achieved by adding metals such as Au, Pd, Ni, and V into the filler alloys.[5–7] In this study, two Au–Ni–V metals in the form of foils were used as filler alloys for brazing Si_3N_4 ceramic. The microstructure and mechanical properties of the Si_3N_4/Si_3N_4 joint were studied, and the bonding mechanism was discussed with reference to the discovered phases in the joint and brazing parameters. The results reported here are expected to provide guidelines for brazing materials development and brazing parameter selection.

2. Materials and experimental procedures

The Si_3N_4 ceramic used in this research was synthesized by hot-pressed sintering. The raw Si_3N_4 ceramic was sawed by diamond discs into the samples of 3 mm × 4 mm × 17 mm for bending test and 3 mm × 4 mm × 2 mm for microstructure observation. The bonding surface (3 mm × 4 mm) of the Si_3N_4 ceramic was polished with diamond powder down to a surface roughness of 1 μm. The raw filler metals between the Si_3N_4 specimens to be joined are foils of pure Au, Ni and V with thicknesses of 20 μm for each. Prior to brazing, the Si_3N_4 spec-

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imens and metal foils were degreased and cleaned with acetone in an ultrasonic bath. Then the filler foils were sandwiched in between the two Si_3N_4 specimens in the order of Au/Ni/V and butted by cyanacrylate adhesives. By varying the amount of the three kinds of metal foils, two alloys with compositions of Au58.7Ni36.5V4.8 and Au55.5Ni34.5V10.0 (at.%) can be obtained during brazing process.

The brazing process was carried out at temperatures between 1373 K and 1473 K for 60 min in a vacuum (1.33×10^{-3} Pa). In order to keep the filler alloy in good contact with Si_3N_4 ceramic, a pressure of 1.63×10^3 Pa was exerted on the brazing specimen. During the heating process, the brazing specimen was firstly heated to 573 K at a heat rate of 30 K/min and kept at this temperature for 15 min to make the organic glue volatilize from the brazing surfaces. Then the specimen was heated to the target brazing temperatures at rate of 10 K/min. After holding the specimen at the brazing temperature for 60 min, the specimen was cooled down to 573 K at a cooling rate of 10 K/min, and then to room temperature in the furnace without power.

The microstructure of the joints was examined using Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS). The phases and crystal structures in the joints were determined by X-ray Diffraction (XRD). The specimens for XRD analysis were cut parallel to the joint surface and then grinded to expose the filler alloy at the surface of the specimens. The morphology and diffraction pattern of interfacial reaction layer were analyzed by transmission electron microscopy (TEM) at 200 kV accelerating voltage for studying the bonding mechanism. TEM specimen with thickness of 0.2 μm was prepared by focused ion beam (FIB) technique. Flexural tests were carried out under 3-point-bend loading conditions using a displacement rate of 0.5 mm/min. At least three specimens were tested for each brazing parameter.

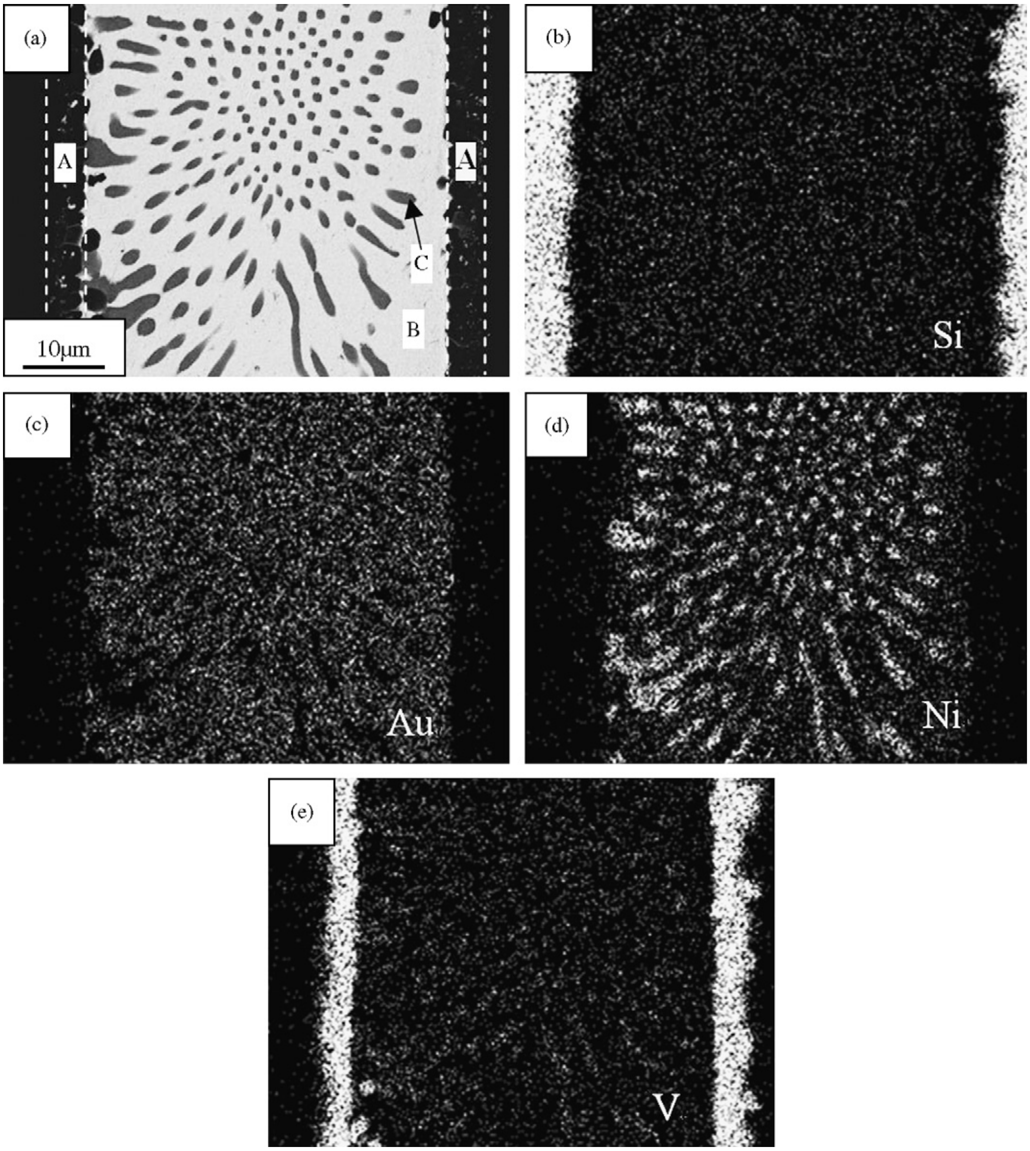

Fig. 1. Microstructure and elemental distribution of the joint brazed at 1423 K for 60 min using the filler alloy of Au58.7Ni36.5V4.8: (a) morphology; (b), (c), (d) and (e) distribution of Si, Au, Ni and V, respectively.

3. Results and discussion

Based on the Au–Ni binary phase diagram,[8] it is known that the solidus temperature of the Au58.7Ni36.5V4.8 and Au55.5Ni34.5V10.0 alloys is 1228 K and the liquidus temperatures of the two alloys are about 1273 K and 1293 K, respectively. During the brazing process, liquid phase appeared between Au and Ni foils when the temperature was above 1228 K. As the temperature increase to brazing temperature (1373–1473 K), both alloys (Au58.7Ni36.5V4.8 and Au55.5Ni34.5V10.0) became liquid. Chemical reactions took place between the melt filler alloy and Si_3N_4 ceramic during the holding time, resulting in a complicated microstructure of the Si_3N_4/Si_3N_4 joint.

Fig. 1 shows the microstructure and elemental distribution of the Si_3N_4/Si_3N_4 joint brazed at 1423 K for 60 min using the Au58.7Ni36.5V4.8 filler alloy. There are two different regions in the seam: one is a continuous reaction layer with a thickness of about 4 μm close to the Si_3N_4, as shown by label A in Fig. 1(a), and the other is in the center of the seam containing matrix phase B and particle phase C in the matrix. Fig. 1(b) reveals that Si distributes mainly in the area of Si_3N_4 ceramic but a small amount of Si distributes in the central region of the seam. It is also found that almost no Si exists in the reaction layers. The matrix of the central region contains mainly Au and a small amount of Ni, as shown in Figs. 1(c) and (d). The particle phase C contains mainly Ni and a small amount of Si and V, as shown in Fig. 1(b), (d) and (e). Fig. 1(e) shows that a great amount of V exists in the reaction layer.

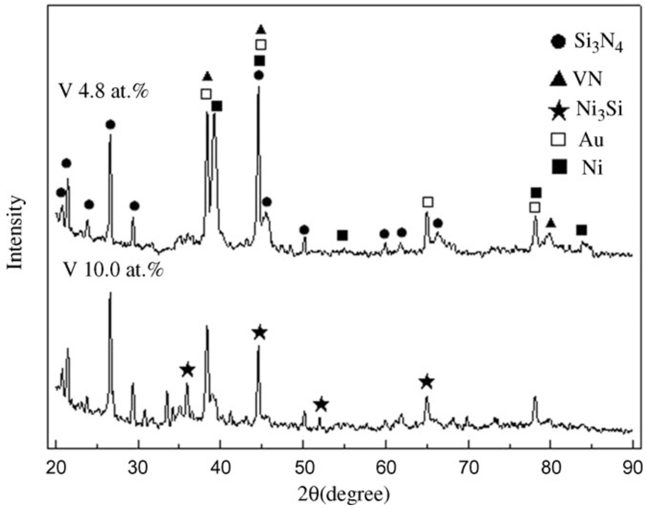

Fig. 2. X-ray diffraction results of the Si_3N_4/Si_3N_4 joints brazed at 1423 K for 60 min using the filler alloys of Au58.7Ni36.5V4.8 and Au55.5Ni34.5V10.0.

Table 1
Composition of different zones in Fig. 1(a).

Position	Composition (at.%)				
	Au	Ni	V	Si	N
A	0.9	–	68.1	1.0	30.0
B	84.4	15.6	–	–	–
C	2.5	81.1	8.6	7.8	–

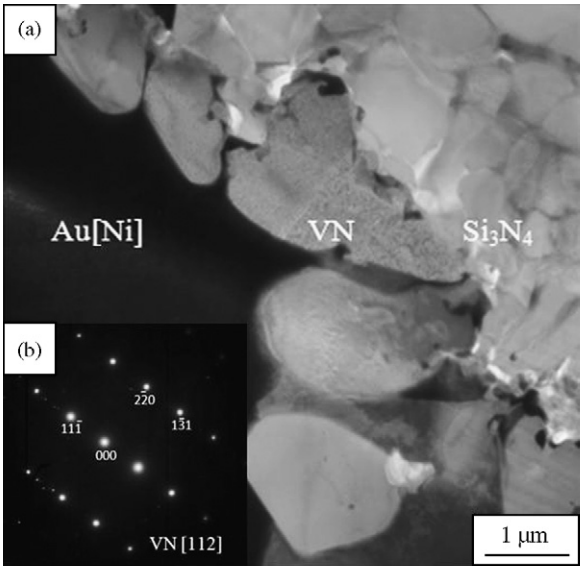

Fig. 3. TEM results of the reaction layer of the joint: (a) the morphology of the reaction interlayer between the Si_3N_4 ceramic and filler alloy; (b) electron diffraction pattern of VN.

XRD results of the joint shown in Fig. 2 indicate that VN, Au and Ni exist in the seam as the V content in the filler is 4.8 at.%. In order to determine the phases in the seam, the composition of the reaction layer marked by A at the ceramic/filler interface, the matrix phase B, and particle phase C in the central region was measured by EDS. The result shown in Table 1 indicates that the reaction layer contains 68.1 at.% V and 30.0 at.% N, respectively. According to the V–Si–N triple phase diagram and corresponding thermodynamic calculations, both VN and V_2N phases are stable at 1273 K. Thermodynamic calculations on the effects of the nitrogen gas pressure on the V–N phase suggest that the nitrogen pressure of 10^{-9} bar N_2 in the vacuum furnace is insufficient to form VN phase.[9,10] In order to further confirm the reaction layer, the joint was analyzed by TEM, which is shown in Fig. 3. The result testifies that the reaction layer between the Si_3N_4 ceramic and filler alloy is the face-center cubic lattice VN but not V_2N.

It also can be seen from Table 1 that the matrix of the seam (position B) contains mainly Au and a small amount of Ni. By comparing with the XRD results in Fig. 2, it can be confirmed that the matrix phase B shown in Fig. 1(a) is Au[Ni] solid solution which was formed during cooling process. In the same way, the particle phase C shown in Fig. 1(a) is Ni[Si,V] solid solution.

Table 2
Composition of different zones in Fig. 4(a).

Position	Composition (at.%)				
	Au	Ni	V	Si	N
A	–	–	71.5	–	28.5
C	–	74.3	–	25.7	–
B	83.4	16.6	–	–	–
D	–	–	75.6	–	24.4

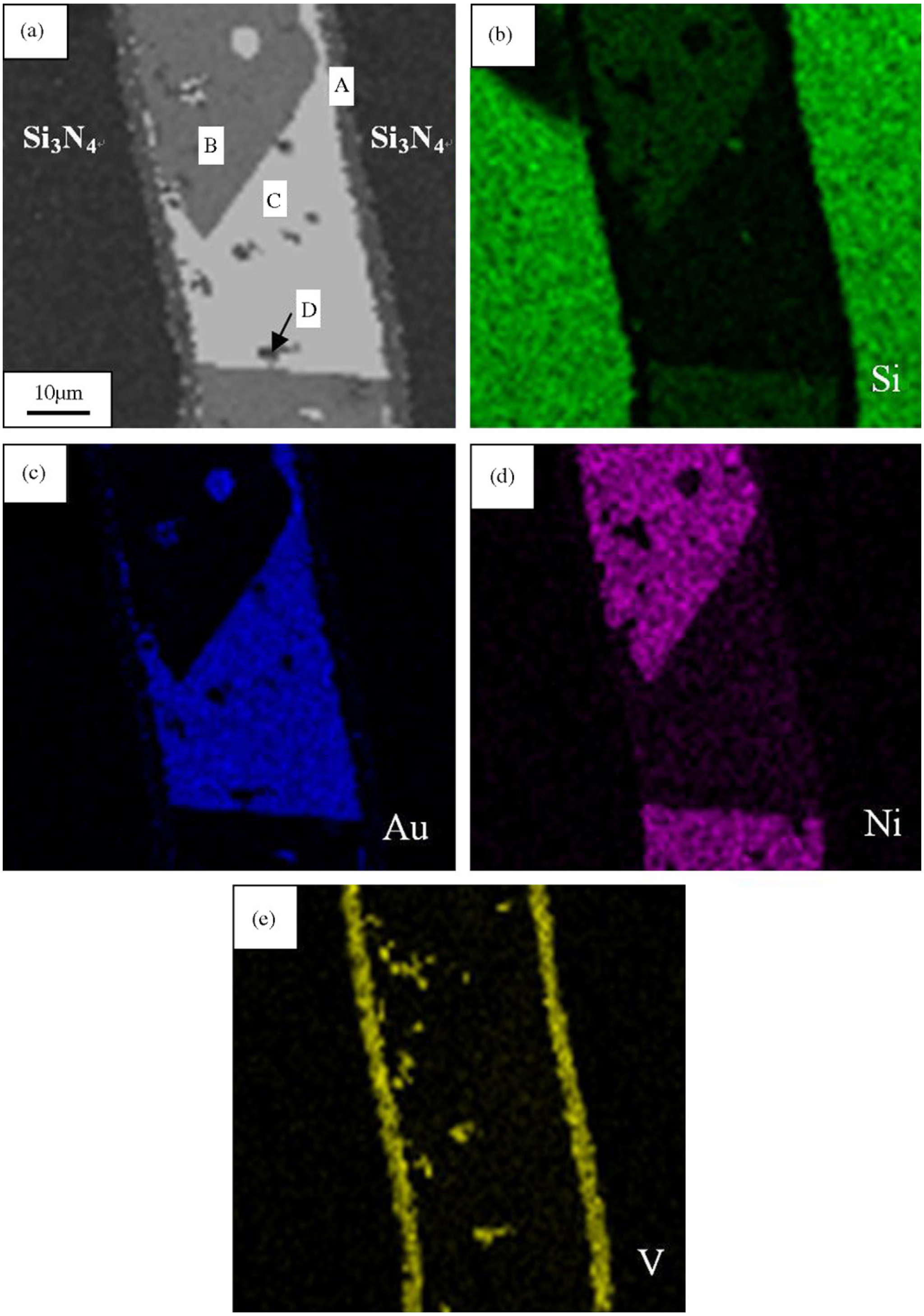

Fig. 4. Microstructure and elemental distribution of the joint brazed at 1423 K for 60 min using the filler alloy of Au55.5Ni34.5V10.0: (a) morphology; (b), (c), (d) and (e) distribution of Si, Au, Ni and V, respectively.

In order to investigate the effect of V content in the filler alloy on the microstructure of the joint, additional brazing experiments were carried out by using the Au55.5Ni34.5V10.0 filler alloy to braze Si_3N_4 at the same brazing conditions. Fig. 4(a) shows the microstructure of the Si_3N_4/Si_3N_4 joint brazed at 1423 K for 60 min using the Au55.5Ni34.5V10.0 filler alloy. It indicates that the reaction layer becomes thicker because of the increasing of the V content from 4.8 at.% to 10 at.%. Fig. 4(b)–(e) shows the elemental distribution of Si, Au, Ni, and V, respectively. A small amount of V was found in the center of the seam, as shown in Fig. 4(d), which corresponds to particle D in Fig. 4(a). EDS result of particle D indicates that this phase contains N and V, as shown in Table 2. By comparing with the XRD result shown in Fig. 2, it is confirmed that particle D is VN. Fig. 4 also shows that there is a new phase with a large size in the center of the seam marked by label B in Fig. 4(a). Fig. 4(b) and (d) shows that

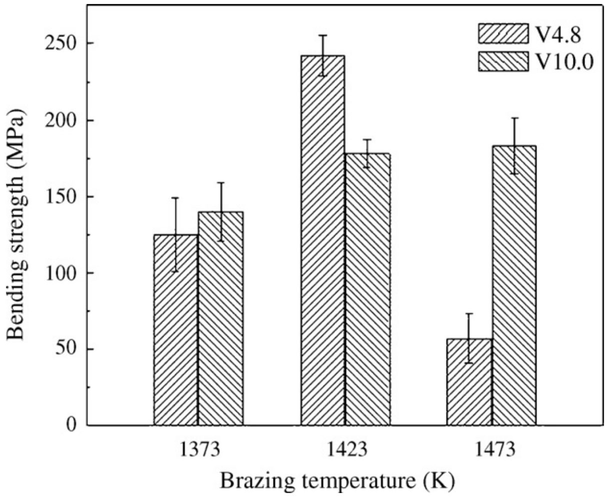

Fig. 5. Effects of brazing temperature and V content in the filler alloy on bending strength of the joint.

this new phase contains mainly Ni and Si. The composition of the new phase is Ni74.3Si25.7, as shown in Table 2. It is known from Ni–Si binary diagram that when the content of Si reaches 25 at.%, Si will react with Ni, forming intermetallic compound Ni_3Si.[11] By comparing with the XRD result shown in Fig. 2, this new phase is confirmed to be Ni_3Si.

With the increasing of V content, the reaction between V and Si_3N_4 becomes more active, resulting in the thickness of VN reaction layer increasing as well as Si in the Ni[Si,V] solid solution. When the Si content in the Ni[Si,V] solid solution reaches 25 at.%, following reaction will take place[12]:

$$Si + 3Ni = Ni_3Si \tag{1}$$

Datta et al.[13] and Zhou and Bakker[14] reported that the activation energy for restoration process of the Ni_3Si phase at 700 K is about 163 kJ/mol. Their results also suggest that crystallite size of the ordered Ni_3Si is about 135 nm at the formation tem-

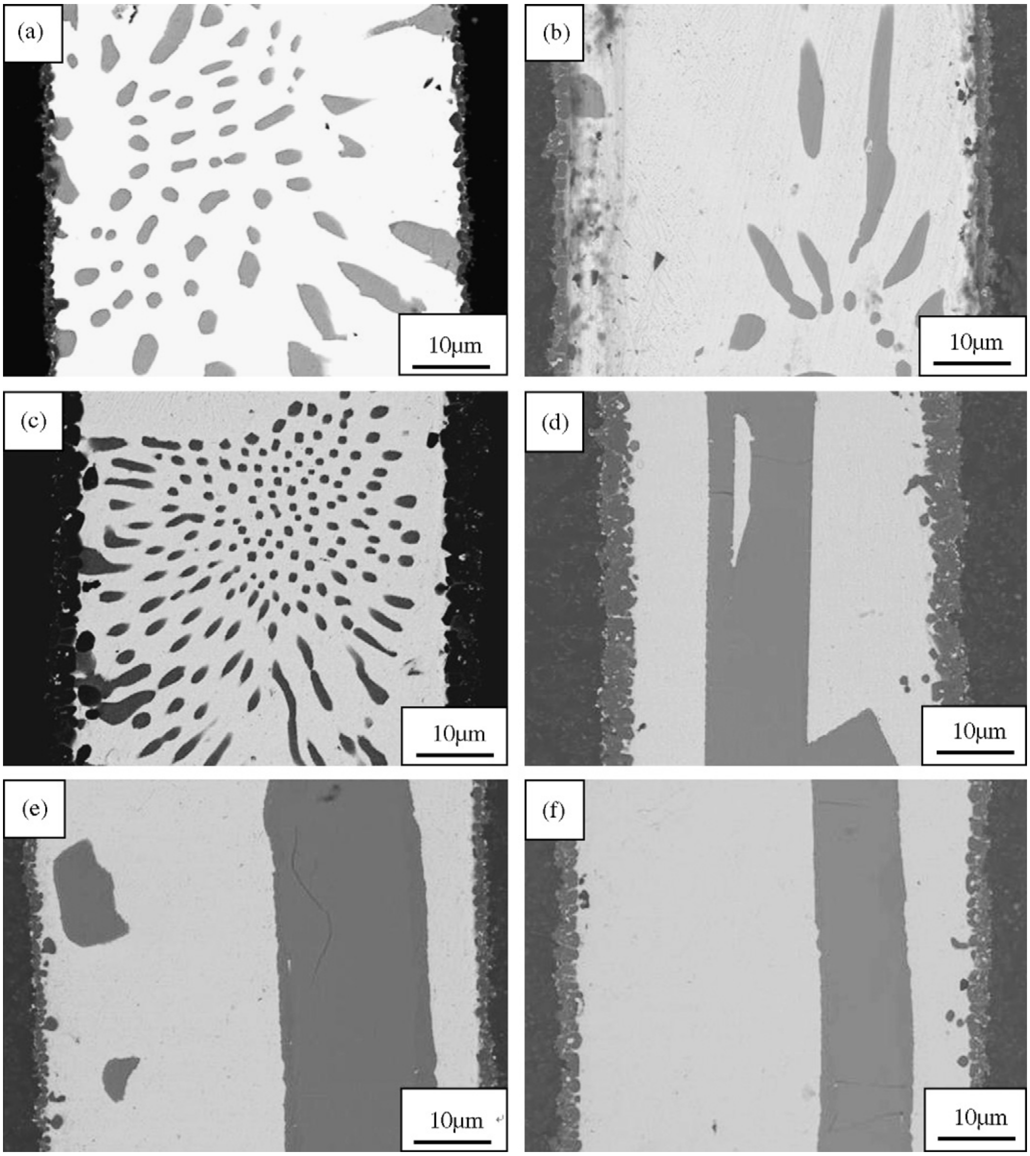

Fig. 6. Microstructures of the Si_3N_4/Si_3N_4 joints brazed at different temperatures using the filler alloys containing 4.8 at.% and 10 at.% V: (a) 1373 K, 4.8 at.% V; (b) 1373 K, 10 at.% V; (c) 1423 K, 4.8 at.% V; (d) 1423 K, 10 at.% V; (e) 1473 K, 4.8 at.% V; (f) 1473 K, 10 at.% V.

perature (723 K), which reveal that the grain growth is very fast for this phase and it is probably stable only in the bulk state (above 100 nm). In our experiment, the brazing temperature is 1423 K, so the growth of the Ni_3Si phase is very fast, leading to the formation of the large size Ni_3Si phase in the seam.

Fig. 5 shows the effects of brazing temperature and V content in the filler alloy on bending strength of joints. When the V content is 4.8 at.%, bending strength of the joint is improved with increasing brazing temperature from 1373 K to 1423 K, and then decreases when the brazing temperature reaches 1473 K. However, the bending strength of the joint is improved slightly with increasing brazing temperature when the V content is 10 at.%. A maximum bending strength of 242 MPa is obtained at the brazing temperature of 1423 K when the filler alloy containing 4.8 at.% V was used. At the brazing temperature of 1473 K, bending strength of the joint with higher V content (10 at.%) is much higher than that with lower V content (4.8 at.%).

Fig. 6 shows the microstructure of the joint brazed at different temperatures using the filler alloys containing 4.8 at.% and 10 at.% V, respectively. It can be seen that the thickness of the VN reaction layer increases slightly with increasing brazing temperature, leading to an improvement in the bonding strength of the joint, as shown in Fig. 5. The slight difference on the strength of the joints at 1423 K for 4.8 at.% V and 10 at.% V is because of appearance of the large size Ni_3Si phase in the seam, as shown in Fig. 5(c) and (d). According to the analysis of fractured surfaces of the joints by SEM with EDS, the fracture of the joint were mostly formed in the Si_3N_4, which initiated at the edge of the filler/Si_3N_4 interface and propagated in the ceramic substrate parallel to the bonding interface. This result indicates that the reaction layer can form a reliable bonding interface, but the joint bonding strength can be decreased by the residual stress in the joint. It is well known that the residual stress forms in the joint during cooling process from brazing temperature to room temperature due to the difference of the coefficients of thermal expansion between ceramic and filler alloy. It can be reduced at a certain extent by plastic deformation of the filler alloy. The Vickers microhardness testing result shows that the hardness of the Ni_3Si phase is about 2 times higher than that of the Ni[Si,V] solid solution. Therefore, the seam containing Ni[Si,V] solid solution particles has a higher capability for releasing the residue stress in the seam compared with that containing the Ni_3Si phase. This may be one of the important reasons for the change of bending strength of the joint with brazing temperature and V content. The sharp decrease of the joint bending strength at 1473 K for 4.8 at.% V is caused by the quick spread of V4.8 filler alloy between ceramics at high temperature, which result in a lot of filler alloy flowing away from the surface of Si_3N_4 ceramics during the brazing process.

Based on the experimental results and analysis above, Fig. 7 schematically shows the procedure of the phase formation in the joint. With increasing temperature during heating in the brazing process, the foils of filler alloy became softer and contact each other under the pressure of 1.63×10^3 Pa. When the temperature reached the initial melting point of Au–Ni alloy, liquid phase appeared between Au and Ni foils. With further increasing temperature, the content of liquid phase increased and V melted into the Au–Ni molten alloy gradually. Before the temperature reached brazing temperature, all the foils had become liquid phase and V atoms melted in the filler alloy had diffused to

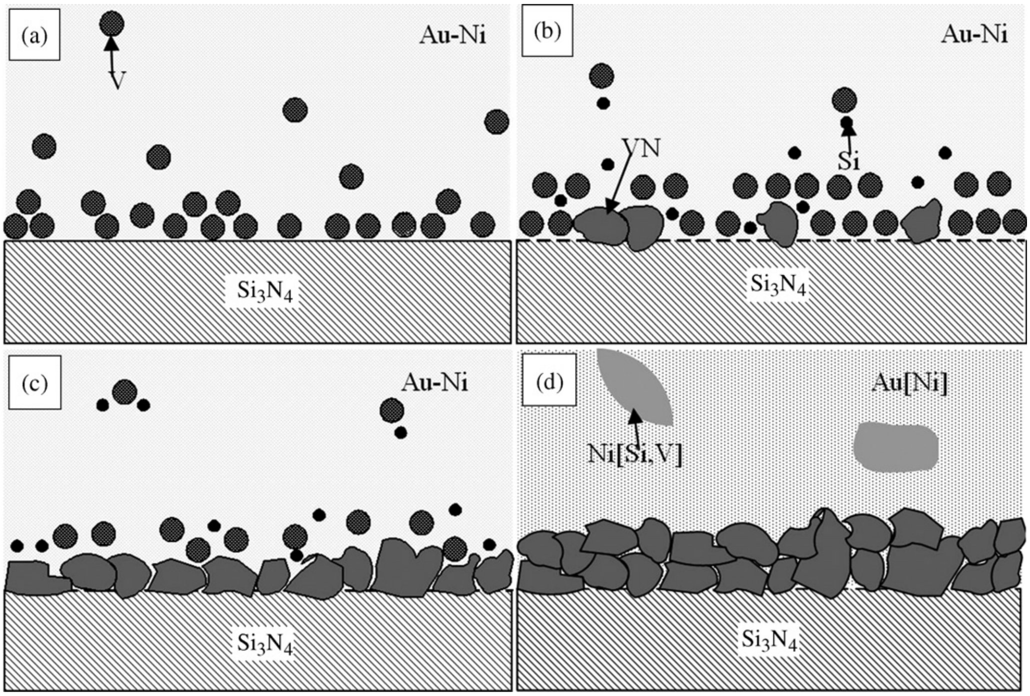

Fig. 7. Schematic drawing of the formation of the microstructure of Si_3N_4/Si_3N_4 joint: (a) enrichment of V atoms at the Si_3N_4/filler interface; (b) formation of VN phase and diffusion of Si atoms into the molten alloy; (c) formation of a continuous VN reaction layer at the Si_3N_4/filler interface; (d) formation of Ni-based and Au-based solid solutions in the center of the seam during cooling process. (▬) Au–Ni liquid phase; (◍) V atom; (●) Si atom; (⬟) VN phase; (⁙) Au[Ni] solid solution; (⬬) Ni[Si,V] solid solution.

Si_3N_4/filler interface. During the brazing holding time, the active metal V reacted with Si_3N_4 ceramic, resulting in the formation of VN reaction layer at the interface, as shown in Fig. 7(a). At the same time, Si atoms were affranchised by this reaction and diffused into the molten alloy because most of N atoms reacted with V, as shown in Fig. 7(b). With increasing holding time at the brazing temperature, the VN reaction layer increased in size and formed a continuous VN interlayer at the interface between filler alloy and Si_3N_4 ceramic. Finally, the VN layer reached a certain thickness (4–5 μm) and became compactly and continuously, as shown in Fig. 7(c). At the end of the brazing process, the joint was cooled at a rate of 5 K/min. When the temperature is below the liquidus of the Au–Ni alloy, two kinds of solid solutions, Au[Ni] and Ni[Si,V], were formed during the solidification process. The matrix of the solidified seam is Au[Ni] solid solution, and Ni[Si,V] solid solution distributed homogeneously in the Au[Ni] solid solution, as shown in Fig. 7(d).

In addition, with increasing brazing temperature or V content in the filler alloy, the reaction between V and Si_3N_4 became more serious, resulting in the increasing of the thickness of the VN reaction layer and the content of Si in the filler alloy. As the Si content in Ni[Si,V] solid solution reached 25 at.%, the intermetallic compound Ni_3Si was formed instead of Ni[Si,V] in the middle of the seam. In this case the Ni[Si,V] solid solution phase shown in Fig. 7(d) was replaced by the Ni_3Si intermetallic compound.

4. Conclusions

(1) A VN reaction layer was formed at the interface between Au–Ni–V filler alloy and Si_3N_4 ceramic, and thickness of the reaction layer increased with the increasing of brazing temperature and V content in the filler alloy.

(2) When Au58.7Ni36.5V4.8 filler metal was used, the center of the seam brazed at 1373 K and 1423 K is Au[Ni] solid solution containing Ni[Si,V] solid solution particles; while brazed at 1473 K, the center of the seam is Au[Ni] solid solution containing large size intermetallic compound Ni_3Si, which leads to a sharp decrease of bending strength of the joint.

(3) When Au55.5Ni34.5V10.0 was used as filler alloy, the center of the seam is Au[Ni] solid solution containing large size Ni_3Si phase, which results in a decrease of the joint bending strength compared with that using Au58.7Ni36.5V4.8 as filler alloy at the brazing temperature of 1423 K.

(4) The bending strength of the joint is 242 MPa when the joint was brazed at brazing temperature of 1423 K for holding time of 60 min using Au58.7Ni36.5V4.8 filler alloy.

Acknowledgements

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