

Interfacial microstructure of $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joint brazed using Au–Ni–V filler alloy

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Received: 12 June 2009 / Accepted: 16 December 2009 / Published online: 29 December 2009
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Abstract By using Au58.74Ni36.50V4.76 at.% filler alloy, a reliable $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joint was brazed at 1,423 K for 60 min in vacuum. The microstructure of the joint was investigated and analyzed by scanning electron microscope with energy dispersive spectroscopy, transmission electron microscopy, and X-ray diffraction. The results indicate that the joint consists of three main phases: a continuous VN reaction layer between filler alloy and Si_3N_4 ceramic; an Au[Ni] solid solution as the matrix of the joint; and Ni[Si,V] solid solution particles distributed homogeneously in the Au[Ni] solid solution. The mechanism of formation of the interfacial structure is discussed.

Introduction

Silicon nitride ceramic (Si_3N_4) with high strength and hardness, as well as good thermal and oxidation resistances, has been widely applied in the fields of the aerospace, automobile, turbine blades and so on. However, Si_3N_4 is difficult to manufacture because of its strong covalent bond between Si and N [1–3]. In order to produce large-size and complex-shape ceramic components, many investigations have been focused on the joining of ceramics. Over the last two decades, various techniques have been developed to join ceramics to themselves or to metals. The joining techniques include active brazing, diffusion bonding, partial transient liquid phase bonding, and glass adhesive bonding [4–7]. For joining Si_3N_4 , the active metal brazing has been considered to be one of the most effective

joining methods due to its simplicity, low costs, high-joint strength, good repetitiveness as well as perfect adaptability of joint size and shape [8].

In the case of active brazing, the filler alloy Ag–Cu–Ti has been developed and used widely. The bending strength of the joint brazed with Ag–Cu–Ti filler alloy can reach 550 MPa [9]. However, the operating temperature of the joint using Ag–Cu–Ti filler alloy is lower than 773 K because the melting point of the Ag–Cu–Ti alloy is 1053 K [10]. Ceramics such as Si_3N_4 are designed for higher temperature applications and the joints are expected to survive in corrosive environments at high temperatures under stress [11]. Therefore, the selection of a high temperature active brazing metal involves two tasks: (a) selection of a refractory metal and (b) identification of a reactive component which can react with ceramic and form a continuous reaction layer between filler alloy and substrate [12]. Several researches have been aimed to explore active brazing filler alloys for applications at high temperatures or in oxidized conditions during last 10 years. Xiong and coworkers [13] studied the joining of $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ using CuNiTiB filler alloy. The maximum bending strength of 338.8 MPa was achieved, and the relationship between the joint strength and reaction layer was explained clearly by the established interfacial reaction model. In addition, the 57.74Au–42.26Ni (Nioro) alloy and the active brazing alloy 57.74Au–36.5Ni–1Mo–4.76V (Nioro ABA) have been used to braze Si_3N_4 ceramic and applied for patent [14, 15]. This study revealed that the addition of V can improve the wettability of filler alloy on Si_3N_4 ceramic and obtain a final contact angle of about 45°. In particular, the joint brazed by Nioro ABA can be utilized at high temperature and in oxidized condition [16]. In the present study, Si_3N_4 ceramic was brazed by using the Au58.74Ni36.50V4.76 filler alloy. The study focused on

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the morphology and microstructure of the brazing joint because the bonding strength of the joint strongly depends on the interfacial microstructure. The interfacial microstructures were studied using transmission electron microscopy (TEM) to understand the bonding mechanism and the phase formation in the joint.

Experimental procedure

The Si_3N_4 ceramic used in this study was synthesized by hot-pressed sintering and was supplied by Shanghai Institute of Ceramics. It has a density of 3.2 g/cm^3 , a fracture toughness of $6 \text{ MPa m}^{1/2}$, and a bending strength of more than 780 MPa at room temperature. Si_3N_4 ceramic specimens with a size of $3 \times 4 \times 17 \text{ (mm)}$ were cut by diamond discs for brazing. The bonding surface ($3 \times 4 \text{ mm}$) was ground by SiC abrasive paper and then polished with diamond grinding paste of $1 \text{ }\mu\text{m}$. Foils of pure Au, Ni, and V with a thickness of $20 \text{ }\mu\text{m}$ were used to form the Au58.74Ni36.50V4.76 at.% filler alloy by measuring the weight of the three kinds of metal foils.

Prior to brazing, the Si_3N_4 ceramic specimens and metal foils were degreased and cleaned with acetone in an ultrasonic bath for 30 min. The filler foils were placed between two Si_3N_4 specimens and fixed by cyanacrylate adhesives, as shown in Fig. 1. Then the assembly was put into a graphite jig and placed into a vacuum furnace ($1.33 \times 10^{-3} \text{ Pa}$). In order to keep the filler alloy contacting closely with the Si_3N_4 ceramic, a pressure of $1.63 \times 10^3 \text{ Pa}$ was exerted on the brazing specimen. The brazing specimen was first heated to 573 K at a rate of 20 K/min and kept at the temperature for 20 min to volatilize the organic glue, and then heated to a brazing temperature of $1,423 \text{ K}$ at a 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 rate of 5 K/min . At last, the temperature decreased from 573 K to room temperature in the furnace without power.

The microstructure and composition of the joint were examined using scanning electron microscope (SEM) with an energy dispersive spectroscopy (EDS) unit. The crystal structures and phases in the joint zones were determined by X-ray diffraction (XRD). The specimen for XRD analysis

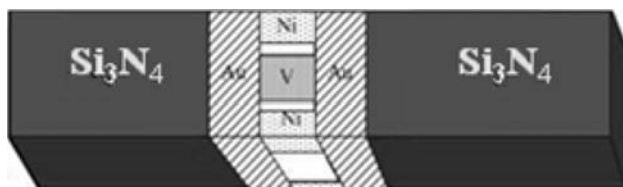


Fig. 1 Schematic of the placement of filler metals

was cut parallel to the joint surface and then ground to expose the filler alloy at the surface of the specimen. The morphology and crystal structure of the phase in the interfacial reaction layer were analyzed by a transmission electron microscopy (TEM). TEM specimen with the thickness of $0.2 \text{ }\mu\text{m}$ was made by focused ion beam (FIB) technique. Flexural tests at room temperature and elevated temperatures (873 , 973 , and $1,073 \text{ K}$) were carried out under 3-point-bend loading condition using a displacement rate of 0.5 mm/min . The long-term oxidation resistance of the joints was investigated by annealing the specimens in air. The specimens were first heated to annealing temperature (773 , 973 , and $1,073 \text{ K}$) at a rate of 50 K/min . After holding the specimens at annealing temperature for 100 h in air, the specimens were cooled at a rate of 10 K/min . And then the 3-point bending strength of specimens was measured at room temperature. At least three specimens were tested for each experimental condition.

Results

Figure 2 shows SEM image of the $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joint brazed at $1,423 \text{ K}$ for 60 min using Au58.74Ni36.50V4.76 filler alloy. It can be seen that the joint consists of three main phases: a continuous interfacial reaction layer with a thickness of $1\text{--}2 \text{ }\mu\text{m}$ between the filler alloy and Si_3N_4 ceramic; an Au-rich solid solution phase as the matrix of the central joint; and Ni-rich solid solution particles distributed in the Au-rich solid solution matrix homogeneously. Figure 3 shows the XRD result of the joint, in which the Si_3N_4 , Au-base solid solution, Ni-base solid solution, and VN compound are detected by XRD. The peaks of Si_3N_4 in Fig. 3 are caused from the substrate material.

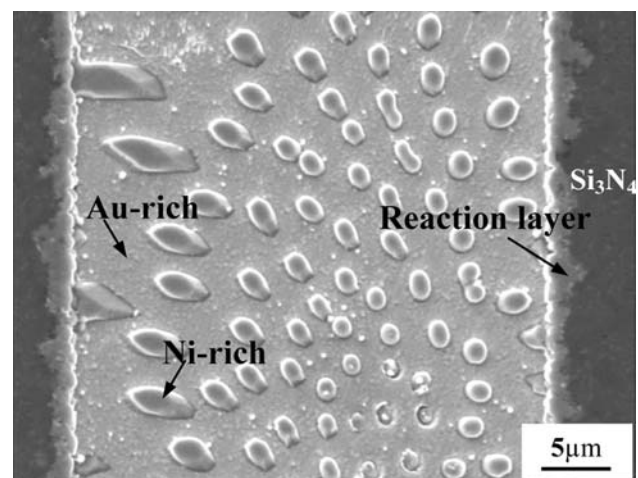


Fig. 2 SEM image of the $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joint brazed at $1,423 \text{ K}$ for 60 min using Au58.74Ni36.50V4.76 filler alloy

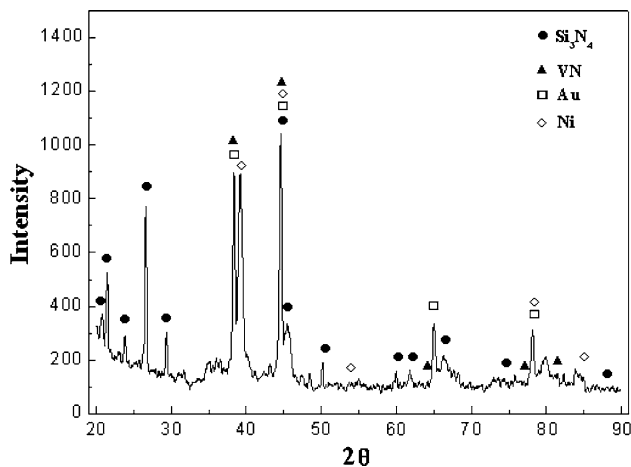


Fig. 3 XRD result of the $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ the joint brazed at 1,423 K for 60 min using Au58.74Ni36.50V4.76 filler alloy

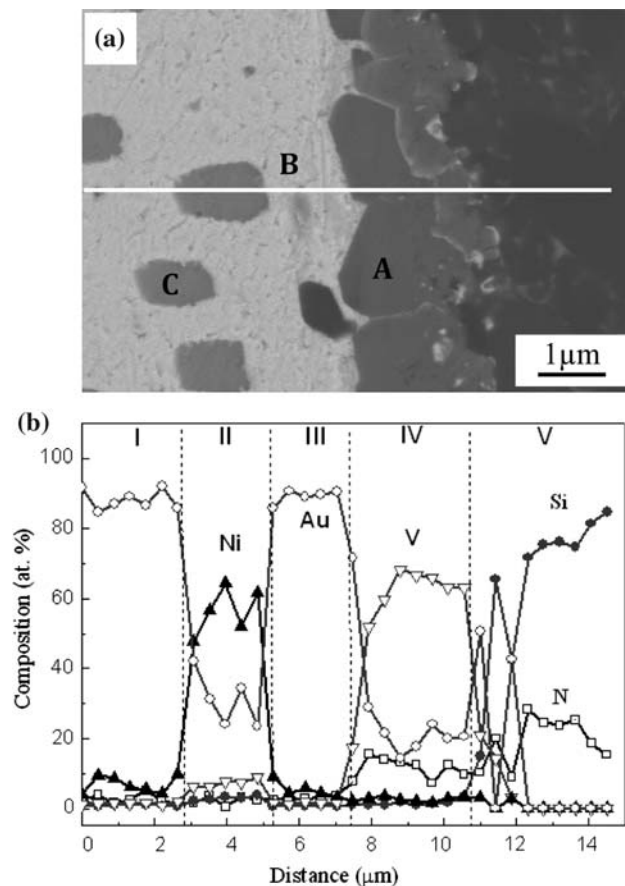


Fig. 4 BSE image of the joint (a) and elemental distribution of Au, Ni, V, Si, and N across the reaction layer along the white line (b)

Figure 4 shows the morphology of the joint imaged by backscattered electrons (BSE) and the elemental distribution results across the reaction layer. The elemental distribution of Au, Ni, V, N, and Si of the joint is measured along the white line in the Fig. 4a, and the results are

shown in Fig. 4b. The examination of Fig. 4a and b confirms that the matrix is Au-base (zones I and III), containing particles of a Ni-base solid solution (zone II) distributed in the joint homogeneously. Si and V are also observed in zone II. The reaction layer (zone IV) contains mainly V and N, and a small amount of Au. It is evident that the reaction layer is composed of a V–N compound, which is surrounded by Au-rich phase. Therefore, it can be concluded that V diffused towards the interface between the filler alloy and Si_3N_4 ceramic, and then reacted with Si_3N_4 to form the reaction layer. In order to identify the phases in the center of joint, compositions at special points (A, B, and C in the Fig. 4a) are measured. The result is shown in Table 1. It indicates that: (1) the reaction layer is a compound of V and N, which cannot be confirmed exactly because the content of N cannot be determined accurately by means of the EDS; (2) the matrix of the joint is an Au-base solution containing 15.61 at.% Ni; and (3) the phase marked by C is Ni-base solid solution containing about 8 at.% Si and V.

Figure 5 is a bright field TEM image, showing the morphology of the interface reaction layer of the joint. The black phase is the Au[Ni] solid solution, which is confirmed by the diffraction pattern shown in Fig. 5b. Figure 5c and d indicates that the reaction layer between the Si_3N_4 ceramic and filler alloy is a FCC lattice VN with grain size of 1–2 μm . According to the analysis of TEM, no specific orientation relationship exists between VN and Si_3N_4 .

The mechanical properties of the joint were evaluated by 3-point bending test. Figure 6 shows the bending strength of the joint (each value is the average from three specimens). The oxidation resistance of the joints was evaluated by bending strength testing at room temperature after annealing treatment of the joints in air for 100 h at 773, 973, and 1,073 K, respectively. From the results shown in Fig. 6a it can be seen that bending strength of the joint annealed at 773 K is close to the bending strength of the joint without annealing treatment. It is also found that the bending strength of the joint annealed at 1,073 K decreased sharply due to the oxidation of the filler alloy at the annealing temperature. Figure 6b shows the bending strength of the joint at elevated temperatures. It is found

Table 1 Composition at the points A, B, and C shown in Fig. 4a

Point	Composition (at.%)				
	Au	Ni	V	Si	N
A	0.91	0	68.12	1.02	29.95
B	84.39	15.61	0	0	0
C	2.29	81.13	8.73	7.85	0

Fig. 5 TEM results of the reaction layer of the joint: **a** the morphology of the interface reaction layer, **b** electron diffraction pattern of the phase rich in Au, **c** and **d** electron diffraction pattern of VN

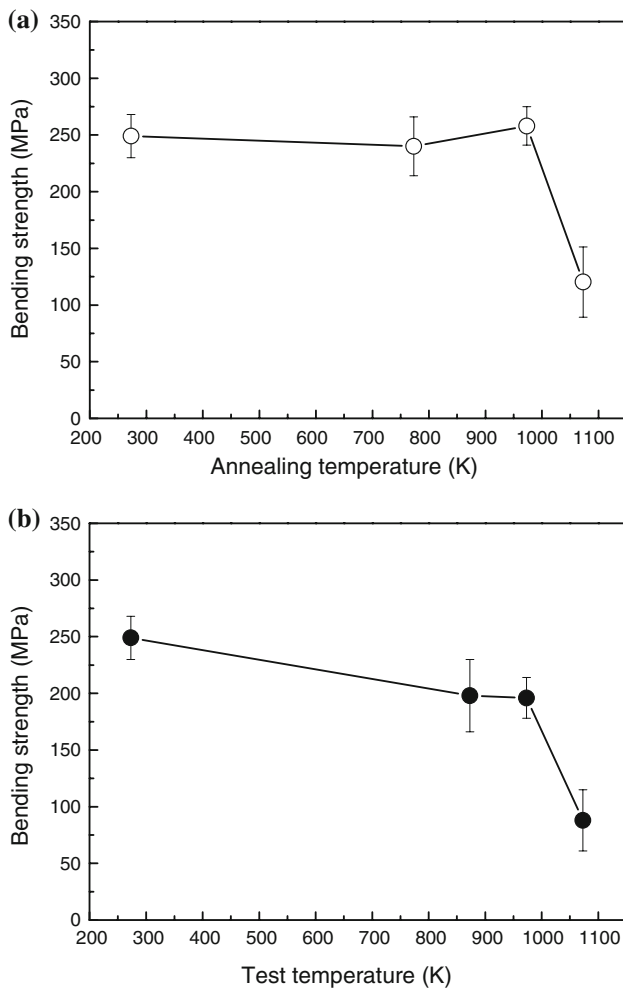
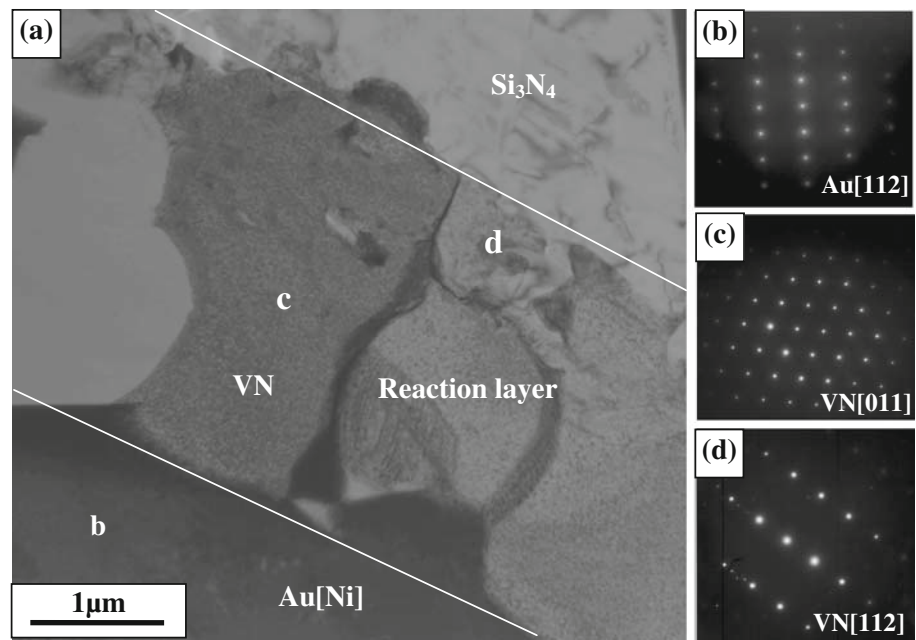


Fig. 6 Bending strength of the joints: **a** effect of annealing temperature in air on room temperature bending strength of the joint, **b** bending strength of the joint at various temperatures

that the bending strength of the joint decreases slightly with increasing temperature up to 973 K but decreases sharply when the temperature increases to 1,073 K. The fracture surface of the annealed joints is shown in the Fig. 7. From Fig. 7a–c, it can be seen that the fracture of brazing joint was typical fracture mold which formed mostly in the Si₃N₄. The crack initiated at the edge of the filler/Si₃N₄ interface and propagated in the ceramic substrate parallel to the bonding interface. It indicates that the reaction layer can form a reliable bonding interface and possess long-term oxidation resistance below 973 K. However, the joint annealed at 1,073 K was obviously oxidized, as shown in Fig. 7d. Figure 8 shows the surface fracture of the joints which were tested at high temperature. The results indicate that the joint obtained at 1,073 K has a lower strength due to the softening of the metals in the joint at this temperature.

Discussion

The present work focused on the interfacial reaction between Si₃N₄ and the high temperature Au–Ni–V brazing alloy. Based on the experimental results, the sequence of phase formation in the joint can be deduced. According to the reference [15], the melting point of the Au–Ni–V alloy is about 1,233 K. Therefore, during heating, the Au, Ni, and V foils soften and contact each other closely with increasing temperature. When the temperature reaches 1,228 K, liquid phase appears between the Au and Ni foils, and then the amount of the liquid phase increases with increasing temperature. Meanwhile, V is dissolved into the

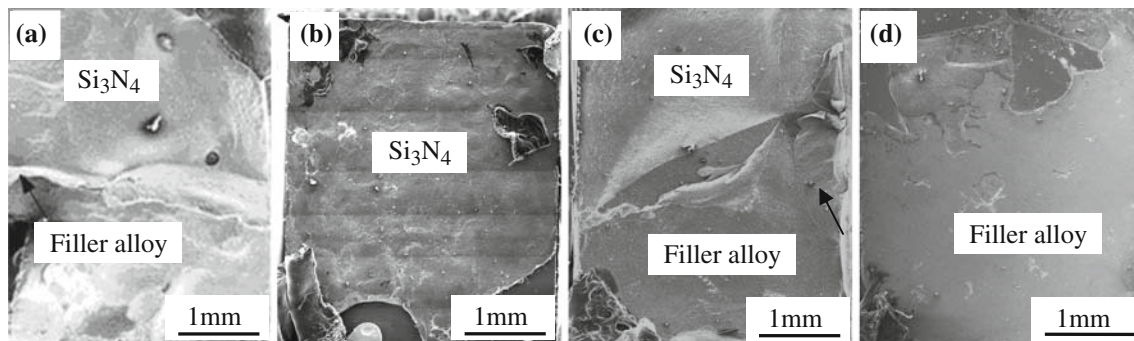


Fig. 7 Fracture surface of bending test joints annealed at different temperatures in air for 100 h: **a** room temperature, **b** 773 K, **c** 973 K, and **d** 1,073 K

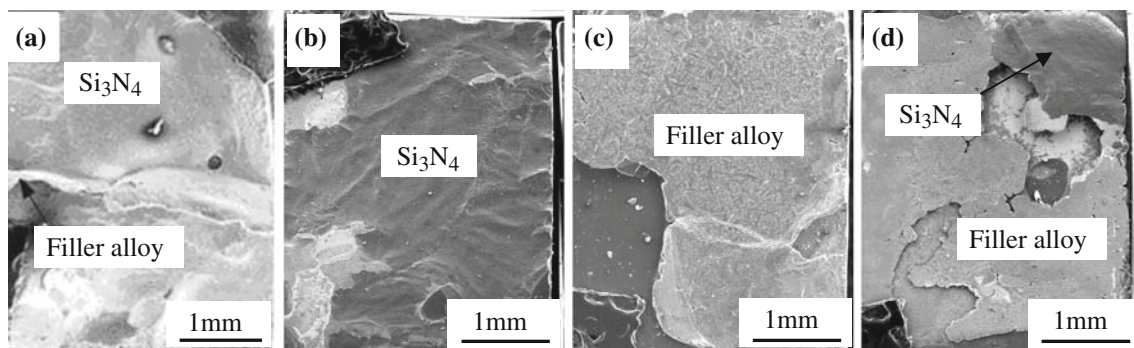
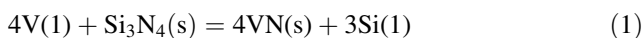


Fig. 8 Fracture surface of bending test joints tested at different temperatures: **a** room temperature, **b** 873 K, **c** 973 K, and **d** 1,073 K

Au–Ni melt gradually, and all the filler metals will become liquid before the temperature reaches the brazing temperature. The free V atoms in the liquid diffuse towards the interface between the filler alloy and Si_3N_4 ceramic. According to the references [17, 18] the standard Gibbs energy of formation of Si_3N_4 and VN per mole of N_2 at 1,423 K is, respectively, equal to -138 and -194 kJ. Because there is a lack of data for the thermodynamic quantities of mixing of V in the Au–Ni liquid solution, a detailed calculation for the reaction occurring during brazing cannot be made. However, the above data indicate that the reaction between V and Si_3N_4 to form VN is possible:



This reaction is favored by strong interactions developed between Si liberated by the reaction and the components of Au–Ni solution, especially with Ni [19]. With increasing the brazing temperature and time, the VN grains increase in amount, grow in size, and connect each other leading to a continuous VN reaction layer 1–2 μm thick formed at the interface between the filler alloy and Si_3N_4 ceramic. At the end of the brazing processes, the joint is cooled at a rate of 5 K/min. When the temperature is below the liquidus of the Au–Ni alloy, solidification of the melt begins with formation of Au[Ni] solid solution followed, at a lower

temperature, by the precipitation of Ni-base particles (the Au–Ni phase diagram presents a solid state miscibility gap below about 1,090 K). Due to comparatively stronger interactions with Ni, residual V and Si released by the reaction dissolve in Ni-base solid solution rather than in Au[Ni].

Conclusion

Si_3N_4 ceramic has been successfully brazed to itself using Au58.74Ni36.50V4.76 filler alloy at 1,423 K for 60 min. The following conclusions were drawn:

- (1) The $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joint consists of three phases: the reaction layer VN between the Si_3N_4 ceramic and filler alloy, the matrix of Au[Ni] solid solution, and Ni[Si,V] solid solution particles distributed homogeneously in the Au[Ni] matrix.
- (2) A continuous VN reaction layer with a thickness of 1–2 μm is formed at the interface between filler alloy and substrate ceramic. According to TEM characterization, no specific orientation relationship exists between VN and Si_3N_4 .
- (3) With increasing temperature from room temperature to 973 K, bending strength of the joint is slightly

decreased from 249 to 198 MPa, and then sharply decreased to 88 MPa at 1,073 K. Air annealing at 773 K for 100 h results in a little increase of the joint strength to 258 MPa, while, annealing at 1,073 K and above for 100 h leads to a serious decrease of the joint strength.

Acknowledgement This work was supported by the National Nature Science Foundation of China under the number of 50472012.

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