J Mater Sci (2011) 46:5830–5837
DOI 10.1007/s10853-011-5539-z

Effect of holding time on microstructure and mechanical properties of Si_3N_4/Si_3N_4 joints brazed with Au58.7Ni36.5V4.8 filler alloy

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Received: 10 January 2011 / Accepted: 5 April 2011 / Published online: 14 April 2011

Abstract Si_3N_4 ceramics were brazed using Au–Ni–V metal foils at 1423 K for different holding times. Effect of holding time on microstructure and mechanical properties of the joints was investigated. The results indicate that a reaction layer of VN exists at the interface between Si_3N_4 ceramic and filler alloy. With increasing holding time from 0 to 90 min, thickness of the VN reaction layer increases from 0.4 to 2.8 μm, obeying a linear relation. Mechanism of the interfacial reaction was discussed by calculating the formation of free energy of VN. No specific orientation relationship exists between VN reaction layer and Si_3N_4 ceramic. In addition, Ni_3Si intermetallic compound appears in the joint when the holding time increases to 90 min, resulting in the deterioration of the joint strength.

Introduction

Silicon nitride (Si_3N_4) is considered to be a promising structural material due to its excellent oxidation resistance and outstanding mechanical properties at high temperatures. Like most engineering ceramics, it is difficult to produce Si_3N_4 components with complex-shaped because of its brittleness in nature [1–3]. Therefore, it is necessary to join small and simple ceramic pieces to form large-size or complex-shaped ceramic components. Among the joining methods, active metal brazing is considered to be the potential technique of meeting ceramic joining requirements for industrial applications, due to its simplicity, low costs, high joint strength, good repetitiveness as well as perfect adaptability of joint size and shape.

Over the last two decades, copper and silver-based brazing alloys have been applied in brazing Si_3N_4 ceramic. Using Ag–Cu–Ti brazing alloy, which shows good wettability to Si_3N_4 ceramic, a reliable joint can be obtained, but the operating temperature of this joint is lower than 773 K [4]. In this case, the application of the joint is restricted at high temperature. However, Si_3N_4 ceramic is usually designed for higher temperature applications, and the joints are expected to survive in oxidizing environment and at high temperatures. Therefore, it is important to develop a new filler alloy with higher melting point and oxidation resistance to improve the thermal and oxidation resistance of the Si_3N_4/Si_3N_4 joint. The selection of such an active brazing alloy for high temperature service usually involves two important items. First, a refractory metal should be selected as the matrix of brazing alloy. According to the references [5–9], Au–Ni alloy was selected in this investigation since the Au–Ni alloy can form solid solution at 1228 K and has excellent resistance to oxidation at elevated temperatures [10]. Second, an active component should be added into brazing alloy. Ti, V, Zr, Cr, and Hf are generally chosen as the active elements during brazing. Among them, V is a refractory metal with high melting point and excellent oxidation resistance. What is more important is that elements of Ti, Zr, and Hf have a strong affinity with Ni. By contrast, the affinity between V and Ni is lower, so the interfacial reaction between V and Si_3N_4 ceramic will not be disturbed by Ni [11–15]. Our previous study has reported [14] that the room temperature three-point bending strength of Si_3N_4/Si_3N_4 joint brazed at

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1423 K for 60 min using Au58.7Ni36.5V4.8 filler alloy is 249 MPa, and the strength of the joint at 973 K is 80% of that at room temperature. Therefore, the high temperature active brazing alloy can be achieved by adding V into the Au–Ni alloy. In this study, Si_3N_4 ceramic was brazed using Au58.7Ni36.5V4.8 (at.%) filler alloy at 1423 K for different holding times. Effect of holding time on microstructure and mechanical properties of the Si_3N_4/Si_3N_4 joints was investigated. Besides, the formation mechanism of the reaction layer was studied in detail.

Materials and experimental procedures

Si_3N_4 ceramic was sintered by hot-pressing (Institute of Ceramics, Shanghai, China) in the experiment. A small amount of MgO, Al_2O_3, and Y_2O_3 were used as sintering additives. The pre-prepared process of Si_3N_4 samples was reported early in the literature [13]. The filler metals for brazing Si_3N_4 ceramic are pure Au, Ni, and V metal foils with thickness of 20 μm for each. Au58.7Ni36.5V4.8 (at.%) filler metal can be obtained by measuring the weight of the three kinds of metal foils.

After the ceramics and filler alloys were prepared and fixed by cyanacrylate adhesives as the literature [14], the specimen assembly was put into a vacuum furnace, and a uniaxial pressure of 1.63 kPa perpendicular to the bonding interfaces was applied to the specimen to keep them tightly in close contact. The vacuum in the furnace was kept in the range of 1.0×10^{-3} Pa to 3.0×10^{-3} Pa.

During the brazing process, the specimen was first heated to 573 K at a rate of 30 K/min in the vacuum furnace, and held for 20 min to make the organic glue volatilize and ensure the brazing surfaces against contamination, then heated to the brazing temperature of 1423 K at a rate of 10 K/min. The specimen was cooled down to 573 K at a rate of 5 K/min after holding the specimen at 1423 K for 0, 30, 60, and 90 min, respectively. Finally, the specimen was cooled in furnace without power.

The strength of the butt joint was measured by three-point bending test with a cross-head speed of 0.5 mm/min. At least three specimens were tested for each experimental condition. A scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) was employed for the analysis of microstructure of the joints. The morphology and crystal structure of phases in the joint were analyzed by transmission electron microscopy (TEM) at 200 kV to elucidate the bonding mechanism of the joint. Specimens for TEM investigation with thickness of 200 nm were prepared by focused ion beam (FIB) milling on a Hitachi FB-2000 S machine. Ion milling was performed using a beam of 30 kV Ga^+ ions.

Results and discussion

Effect of holding time on microstructure of the brazed joints

Figure 1 shows the microstructure of the joints brazed using Au58.7Ni36.5V4.8 filler alloy at 1423 K for different holding times. The composition of positions A, B, C, D, and E labeled in Fig. 1 was measured by EDS to identify these phases in the joint, as shown in Table 1. According to the previous results [13], the joints mainly consist of Au[Ni] solid solution (A) as the matrix of the joint, Ni-rich phases (B, D, and E) distributed in the Au[Ni] solid solution, and VN reaction layer (C) between Si_3N_4 ceramic and filler alloy.

From Fig. 1a and b, it can be seen that the average thickness of the discontinuous reaction layer between the Si_3N_4 ceramic and filler alloy is about 0.4 μm and the Ni-rich phases distribute in the Au[Ni] solid solution homogenously when the holding time is 0 min. Based on the EDS results (Table 1), the Ni-rich phase is proved to be Ni[Si, V] solid solution (B). With increasing the holding time, VN reaction layer becomes compact and continuous. The average thickness of VN reaction layer reaches 1.7 μm when the holding time is 60 min. Meanwhile, size of the Ni[Si, V] solid solution (D) increases, and the interspaces between the Ni[Si, V] solid solution phases increase, as shown in Fig. 1c–f. With increasing the holding time to 90 min, the average thickness of VN reaction layer increases to 2.8 μm, and Ni[Si, V] solid solution transforms to bulk phase in the joint, as shown in Fig. 1g and h, which is identified to be Ni_3Si intermetallic compound (E).

In order to determine the morphology and formation mechanism of interfacial reaction layer, the joints were analyzed by TEM. Figure 2 shows the bright field images and electron diffraction patterns of the joint brazed at 1423 K for 60 min. The area labeled “a” is Si_3N_4 substrate, the area “b” is Au[Ni] solid solution, and the phase “c” is Ni[Si, V] solid solution. The reaction layer between Si_3N_4 ceramic and filler alloy is face-centered cubic VN with grain size of 1–2 μm (label “d”), in which some black phases can be found. According to the analysis of electron diffraction pattern, the black phase located within VN grain is Au-bases solid solution. It can be concluded that VN grains were nucleated at the Si_3N_4 ceramic/filler alloy interface and grew in the molten filler metal quickly, and then connected with each other. During the process, some of the Au–Ni liquid phase was trapped in the VN grain.

Figure 2b shows the morphology and selected area diffraction patterns of Si_3N_4 substrate and VN reaction layer, indicating that there is no specific crystal orientation relationship between VN and Si_3N_4 substrate. Bright field image (Fig. 2c) of the Ni[Si,V] solid solution identifies that there are dislocations in the Ni[Si,V] solid solution, which

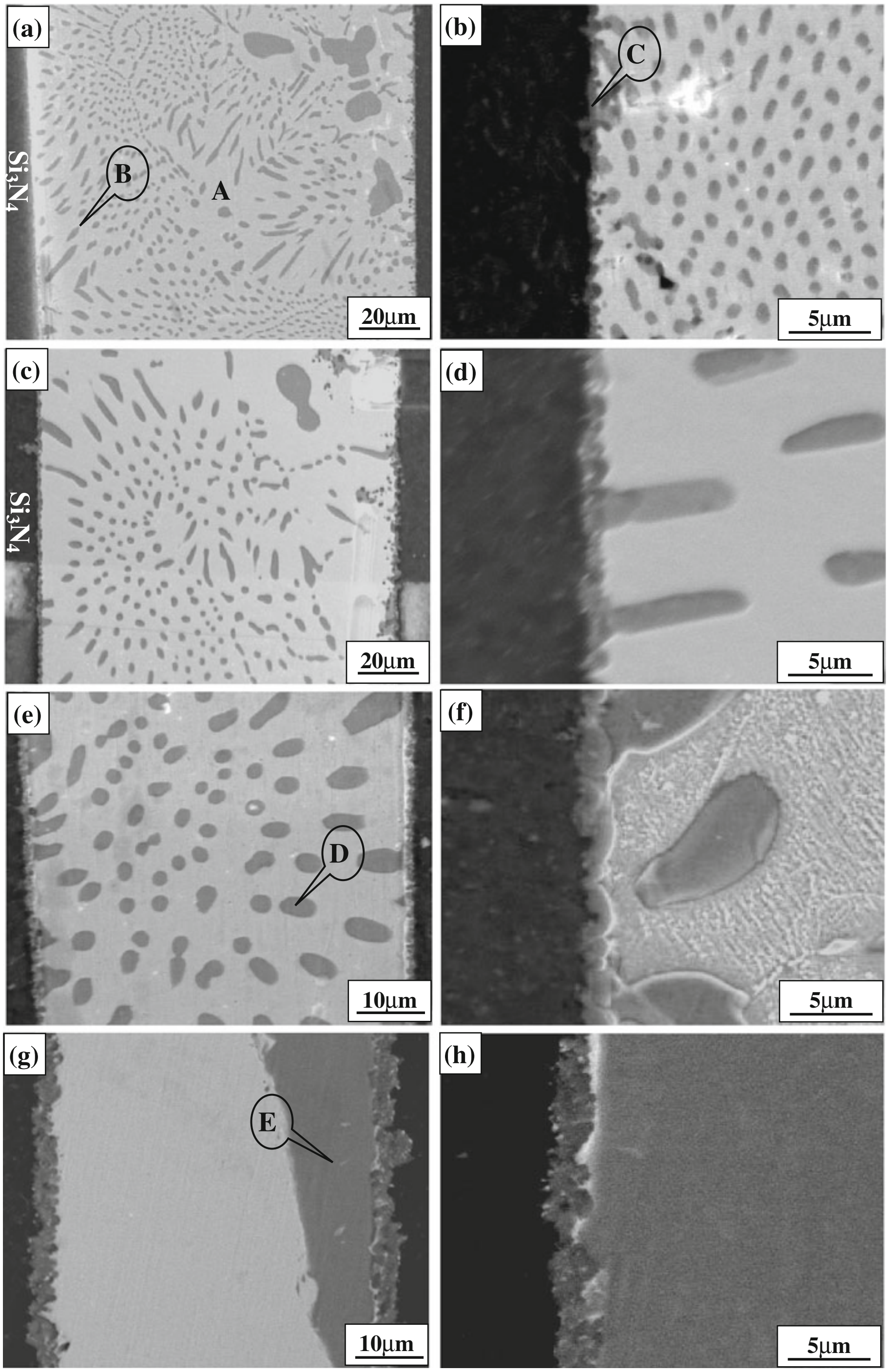

Fig. 1 SEM micrographs of the joints brazed at 1423 K for different holding times: **a**, **b** 0 min; **c**, **d** 30 min; **e**, **f** 60 min; and **g**, **h** 90 min

are considered to be formed by the local plastic deformation in the filler alloy when the residual stress is larger enough during the cooling from brazing temperature because of the large difference of the coefficient of thermal expansion (CTE) between Si$_3$N$_4$ ceramic and filler alloy.

Figure 3 shows the morphology of the reaction layer of the joint brazed at 1423 K for 30 min. Diffraction pattern (Fig. 3b) confirms the reaction layer is VN. The size of the VN grain is about 1 μm, and the grains did not connect with each other. Figure 4 shows the reaction layer of the joint brazed at 1423 K for 90 min. The reaction layer is also VN, as confirmed in the Fig. 4b. It can be found from Fig. 4a that the VN grains increase in size and tend to grow towards the filler alloy.

According to above analysis and Au–Ni–Si, Si–V–N, and Ni-Si–V ternary phase diagrams [16], liquid phases

Table 1 Composition at the points A, B, C, D, and E shown in Fig. 1

Position	Composition (at.%)					
	Au	Ni	V	Si	N	Phase
A	80.4	19.6	–	–	–	Au[Ni]
B	1.8	82.1	8.6	7.5	–	Ni[Si, V]
C	–	–	68.7	–	31.3	VN
D	1.6	80.5	8.2	9.7	–	Ni[Si, V]
E	–	75.2	–	24.8	–	Ni_3Si

will appear between Au and Ni foils when the temperature increases above 1228 K. During the brazing process, after Au and Ni foils melted, vanadium was dissolved into the Au–Ni molten alloy gradually and aggregated at the Si_3N_4/filler alloy interface, and then reacted with Si_3N_4 ceramic. Wang et al. [17] reported that when V reacted with N, the reaction products of VN and $VN_{0.456}$ were both stable phases. When 1 mol of pure V, either solid or liquid, reacts with nitrogen gas, the standard Gibbs energy of VN and $VN_{0.456}$ is $\Delta G_f^0\ (VN) = -217.4 + 0.089T$ kJ/mol and $\Delta G_f^0(VN_{0.456}) = -127.98 + 0.043T$ kJ/mol, respectively. Based on the calculation of the standard Gibbs energies of the two phases at the temperature range of 273–1423 K, VN is more stable than $VN_{0.456}$.

Furthermore, the standard Gibbs energies of formation for Si_3N_4 [18] and VN [19], when one mole of N_2 participates in the reactions, are represented by the following formulas, respectively:

$$\begin{aligned} N_2(g) + \frac{3}{2}Si\ (s) &= \frac{1}{2}Si_3N_4(s) \\ \Delta G_f^0(Si_3N_4) &= -361.9 + 0.1575T\ (kJ/mol) \end{aligned} \tag{1}$$

$$\begin{aligned} N_2(g) + 2V\ (s) &= 2VN(s) \\ \Delta G_f^0(VN) &= -434.3 + 0.1688T\ (kJ/mol) \end{aligned} \tag{2}$$

The free energy of formation for VN and Si_3N_4 at different temperature can be calculated by Eqs. 1 and 2, and the graph of $\Delta G_f^0(VN)$ and $\Delta G_f^0\ (Si_3N_4)$ are shown in Fig. 5. The calculated data of $\Delta G_f^0(VN) - \Delta G_f^0(Si_3N_4)$ are also shown in Fig. 5. The graph indicates that VN is more stable than Si_3N_4 at 1423 K during brazing. An accurate calculation for the reaction during brazing cannot be realized here due to the lack of data for the thermodynamic quantities of mixing V in the Au–Ni liquid solution. Nevertheless, it can be verified by above TEM results that V can react with Si_3N_4 to form VN compound. Therefore, the following reaction can take place spontaneously during the brazing process:

$$4\ V\ (l) + Si_3N_4(s) = 4\ VN\ (s) + 3\ Si\ (l) \tag{3}$$

With increasing the holding time, VN grains grew in size, and connected with each other, leading to the formation of VN reaction layer. Figure 6 shows the curve of the effect of holding time on the average thickness of VN reaction layer. It can be seen from the curve that the thickness of reaction layer increases as a linear relation with increasing holding time. It testifies that the growth rate of the VN reaction layer is controlled by the reaction between V and Si_3N_4, but not by the diffusion of V and N in the reaction layer.

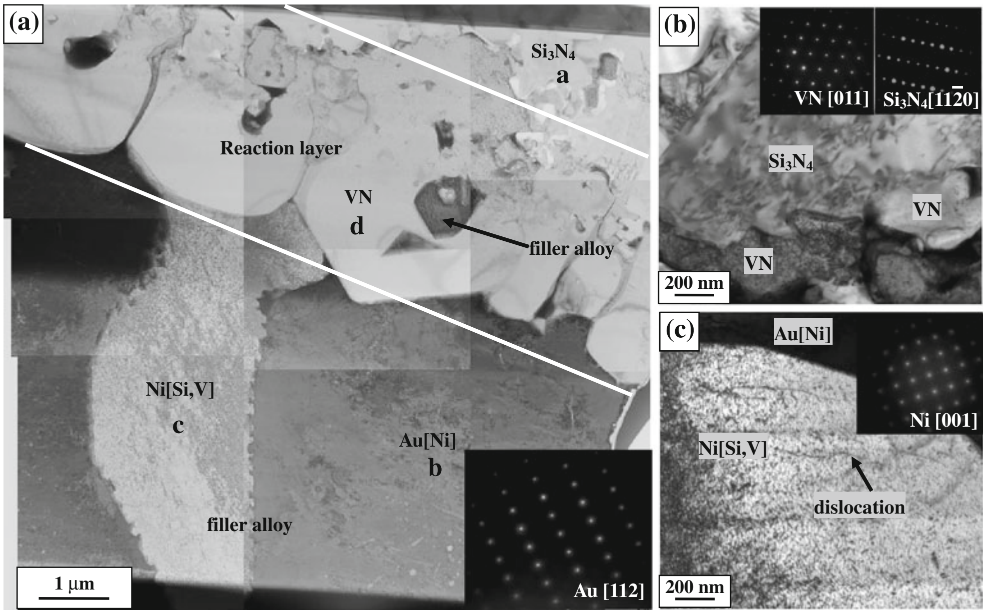

Fig. 2 TEM results of the joint brazed at 1423 K for 60 min: **a** the morphology of the joint, **b** the interface of VN and Si_3N_4 ceramic, and **c** Ni[Si,V] solid solution in the joint

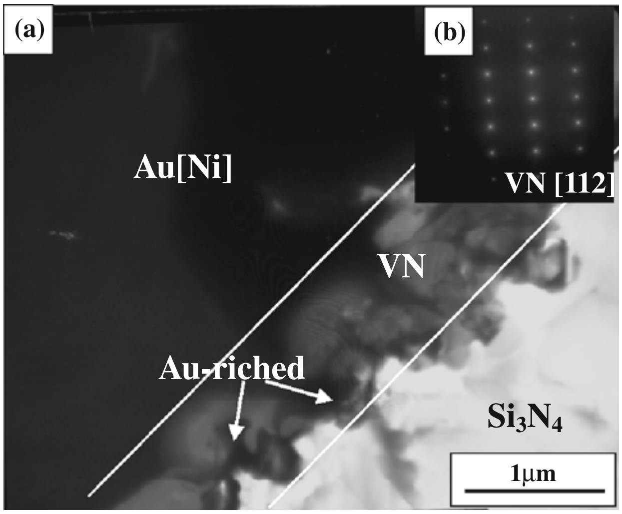

Fig. 3 TEM image of the joint brazed at 1423 K for 30 min: **a** morphology of the VN reaction layer between Si_3N_4 ceramic and filler alloy and **b** diffraction pattern of the VN

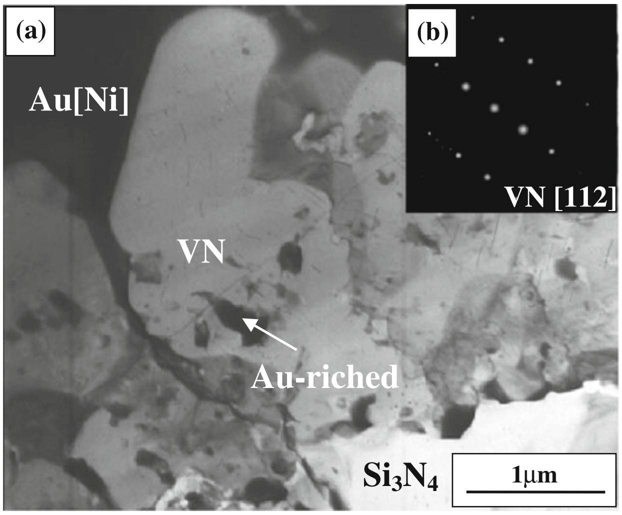

Fig. 4 TEM image of the joint brazed at 1423 K for 90 min: **a** morphology of the VN reaction layer between Si_3N_4 ceramic and filler alloy and **b** diffraction pattern of the VN

While the VN reaction layer formed between Si_3N_4 ceramic and filler alloy, Si atoms were produced by decomposition from Si_3N_4 and dissolved continuously into the molten brazing alloy, where Au and Ni atoms were distributed uniformly initially. Due to the strong affinity of Ni and Si, Si atoms in the molten brazing alloy will gather around the Ni atoms, forming Ni–Si clusters. In summary, during the holding period, V atoms reacted with Si_3N_4 continuously, resulting in the agglomeration of Ni and Si clusters in the molten alloy and the segregation of Ni- and Au-rich liquid phase. According to the Ni–Si phase diagram [20], Ni_3Si intermetallic compound will be formed when the atomic ratio of Si and Ni is more than 1:3 in filler alloy at 1423 K, so the bulk Ni_3Si compound occurs when the holding time is longer (90 min), as shown in Fig. 1g. If the composition ratio of Si and Ni is less than 1:3 in Ni-rich phase, Ni[Si,V] solid solution will form in the joint when the temperature decreases below the liquidus of Au–Ni alloy [21].

Effect of holding time on bending strength of the Si_3N_4/Si_3N_4 joints

Figure 7 shows the effect of the holding time on bending strength of the joints brazed with Au58.7Ni36.5V4.8 filler alloy at 1423 K. It can be seen that the bending strength increased first and then decreased with increasing the holding time continuously. The maximum bending strength reached 249 MPa when the joint was brazed at 1423 K for 60 min.

Figure 8 shows the fractographs of the joints brazed at 1423 K for different holding times. According to the fractographic analysis, it can be found from all the joints that the fracture occurs in the Si_3N_4 ceramic substrate and the fractured surface is smooth dome-shaped, which indicates that all the joints were fractured in the direction of the residual tensile stresses. This fractured mode demonstrates a strong interfacial bonding between Si_3N_4 ceramic and filler alloy. However, a high residual stress exists in the ceramic due to the mismatch in the CTE between Si_3N_4 ceramic and filler alloy [22]. During bend testing, crack initiates in the ceramic near the ceramic/filler alloy interface where the greatest residual tensile stress is concentrated in the joint, and then the crack propagates in the ceramic under external loads, as shown in Fig. 8.

Combined with the above analysis, the maximum bending strength can be contributed to two reasons. The first reason is that a suitable thickness of reaction layer at the Si_3N_4/filler alloy interface can reduce the thermal stress gradient between Si_3N_4 ceramic and filler alloy, leading to the increase of the joint strength [23]. In this study, the CTE of VN, Si_3N_4 ceramic and filler alloy are 9.52×10^{-6}/K, 2.75×10^{-6}/K, and 14×10^{-6}/K, respectively, indicating that the CTE value of VN is between that of Si_3N_4 ceramic and filler metal. Therefore, VN reaction layer can transmit load effectively and reduce the residual stress in the joint during the cooling process through decreasing the CTE gradient between the Si_3N_4 ceramic and filler alloy. The second reason is that the residual stresses can also be alleviated effectively by plastic deformation of the filler alloy during cooling [24]. According to the literature [25], the yield stresses of Au and Ni metals are lower than 120 MPa at room temperature, and the stresses will decrease with increasing the temperature. Au[Ni] and Ni[Si, V] solid

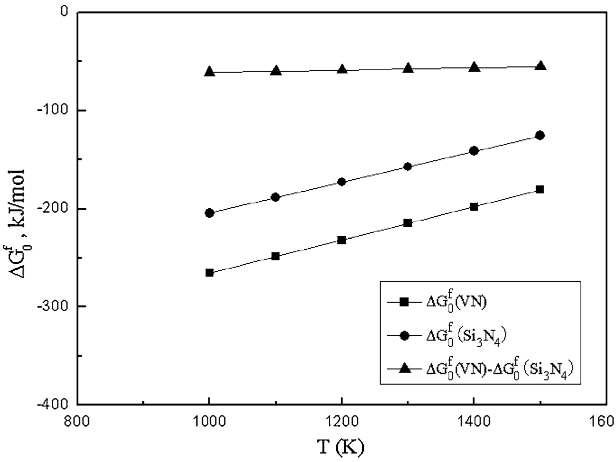

Fig. 5 The graph of the $\Delta G_f^0(VN)$, $\Delta G_f^0(Si_3N_4)$ and $\Delta G_f^0(VN)$-$\Delta G_f^0(Si_3N_4)$ at different temperatures

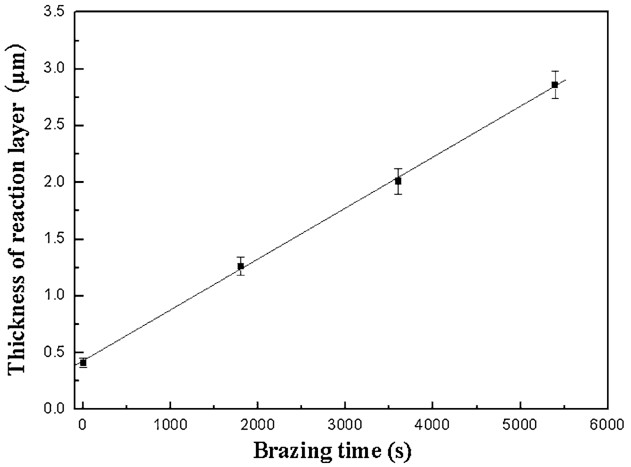

Fig. 6 Effect of the thickness of reaction layer on the holding time

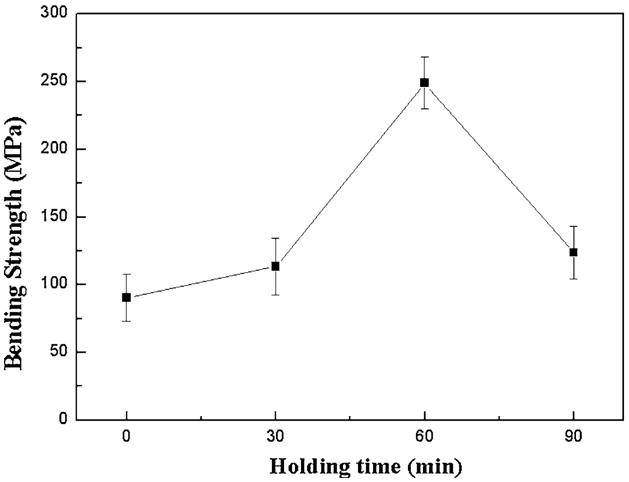

Fig. 7 Bending strength of the joints brazed at 1423 K for different holding times

solution can release the residual stress to a certain extent by plastic deformation during cooling, as indicated by the dislocations found in the filler alloy by TEM. However, the bulk intermetallic compound Ni_3Si is difficult to deform to release the residual stress since the yield stress of Ni_3Si is up to 800 MPa at 800 K [26]. According to the above results, when the holding time is 30 min, thickness of the reaction layer between the Si_3N_4 ceramic and filler alloy is only 1.3 μm, which is very thin, and the filler alloy mainly consists of Au [Ni] and Ni [Si, V] solid solution. Therefore, the bending strength of joint is only 107.6 MPa. With increasing holding time to 60 min, the thickness of reaction layer increased to 1.7 μm, and the filler alloy also consists of solid solution. The bending strength value of the joint can reach to 249 MPa. With increasing holding time to 90 min, thickness of the reaction layer reaches 2.8 μm. However, bulk Ni_3Si intermetallic compounds occur in the joint, leading to the deterioration of the joint strength (123.7 MPa). In order to obtain the joint with the highest mechanical properties, intermetallic compounds should be limited in the joints.

Conclusions

(1) Si_3N_4 ceramics were brazed using Au–Ni–V metal foils at 1423 K for different holding times. A reaction layer of VN exists between Si_3N_4 ceramic and filler alloy. No specific orientation relationship exists between VN and Si_3N_4. With increasing holding time from 0 to 90 min, the average thickness of VN reaction layer increases from 0.4 to 2.8 μm, which obeys the linear relation.

(2) The filler alloy in the joints consists of Au[Ni] solid solution and Ni-rich phases. When the holding time is not more than 60 min, the Ni-rich phase is Ni[Si, V] solid solution and distributed in the Au[Ni] matrix alloy homogeneously. When the holding time increases to 90 min, the Ni-rich phase is Ni_3Si.

(3) The bending strength of the joint increased first and then decreased with increasing holding time. The maximum bending strength of the joint reaches 249 MPa at the brazing condition of 1423 K for 60 min.

(4) The fracture of the joints brazed at 1423 K for different holding times occurs in Si_3N_4 ceramic substrate, and the fractured surface is smooth dome-shaped. This fractured mode demonstrates that strong interfacial bonding has been obtained, but the high residual stress exists in the joint.

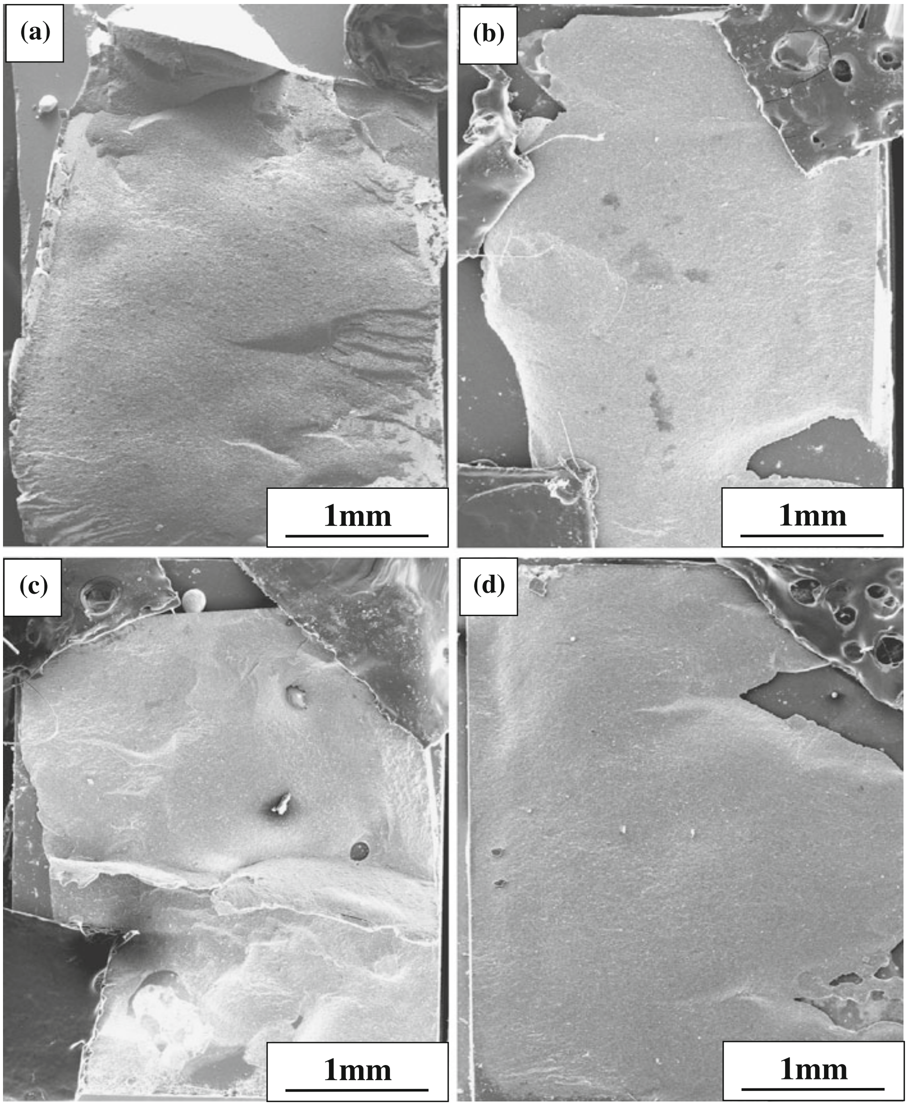

Fig. 8 Fracture surfaces of the joints brazed at 1423 K for different holding times: **a** 0 min, **b** 30 min, **c** 60 min, and **d** 90 min

Acknowledgements This study was supported by the National Nature Science Foundation of China under the number of 50975064 and 51021002.

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