JOURNAL OF MATERIALS SCIENCE **36** (2001) 2673 – 2678

Heat-resistant joints of Si_3N_4 ceramics with intermetallic compounds formed *in situ*

AIPING WU*, GUISHENG ZOU, JIALIE REN, WEIJIA REN, SHENG LI
Department of Mechanical Engineering , Tsinghua University, Beijing 100084, People's Republic of China
E-mail: wuaip@mail.tsinghua.edu.cn

The possibility of the improvement on the heat resistance of Si_3N_4 ceramic joints with intermetallic compounds formed *in situ* was investigated. The Si_3N_4 ceramics were joined with Ti/Ni/Ti multi-interlayers between 1000 and 1150°C. The effects of various parameters, which include the thickness of Ti and Ni foils, the pressure imposed during bonding, the bonding temperature and the holding time, on the microstructures and the strength (both at room temperature and at high temperature) of the joints were studied. The results indicated that the sound joints with higher strength both at room temperature and at elevated temperature could be acquired with intermetallic compounds formed *in-situ* under appropriate bonding parameters. The shear strength at 800°C could sustain about 88 MPa.
© *2001 Kluwer Academic Publishers*

1. Introduction

Silicon nitride is one of the most promising structural ceramics for high temperature applications. There is an increasing demand for joining this ceramic to metal or to itself to form complex structures and composite structures. Although direct brazing using an active filler metal and diffusion bonding using an active interlayer have been found to be capable of producing strong and reliable joints, these joints are difficult to use at elevated temperature. They generally can be used up to 400–500°C, due to the interlayer metal's poor heat resistance. To increase the heat resistant properties of the ceramic joints is one of the key research actions at present. These actions include brazing with heat resistant brazing filler metal [1–4], joining with glass ceramic by reaction sintering [5–9], joining with transient liquid phase bonding (TLPB) [10, 11], and so on. In these methods, the heat-resistant brazing filler metals are generally precious metal-based alloys, like Pd-, Pt-, Au-based alloys, or the brazing should be conducted at relatively high temperature, at which ceramics might be damaged. The utilization of the precious metals would impede their applications. The higher joining temperature would be inferior to the ceramics properties, while additional protecting should be necessary (for example, premetallizing [3]). The joining with glass ceramics is not suitable for bonding ceramics and metals. When bonding ceramics by the TLPB method, the heat resistant joint can be formed in theory at relatively lower bonding temperature, but long time solid diffusion is needed to increase the melting point of the interlayer metal. In addition, most interlayers still use precious metal deposition film [10]. These investigations have indicated that there is no promising joining method for heat resistant ceramic joints.

Intermetallic compounds possess the properties both of metal and ceramics, and are consequently receiving more attention, especially in elevated temperature fields. It could be presumed that the heat resistance of the ceramic joint could be improved if intermetallic compounds were used in joining ceramics. It could be supposed that the interlayer metals, consisting of two or more type metals, could form a transient liquid phase at a convenient temperature and this liquid phase could react with ceramics to form a sound joint at relatively lower pressure, and these two metals could react with each other to form intermetallic compounds *in-situ*. As a result, the sound high temperature strength ceramic joints might be formed at lower joining temperatures, pressure and shorter diffusion time. The difficulties to form heat resistant ceramic joints mentioned above would then be overcome.

According to the Ni—Ti phase diagram [12] (Fig. 1), Ni and Ti can form a eutectic at about 943°C. The joining temperature with transient liquid phase of Ni and Ti could be lower and they could react to form NiTi, Ni_3Ti and $NiTi_2$ intermetallic compounds. In addition, Ti is one of the active elements most often used to join ceramic materials. It could be predicted that the heat resistant ceramic joints might be obtained by TLP bonding with Ti/Ni/Ti multi-interlayers at lower joining temperatures and lower bonding pressure, producing microstructures containing intermetallic compounds.

This paper reports on an investigation of the effects of joining parameters, including Ti, Ni interlayer thickness, the pressure imposed during bonding, the bonding

*Author to whom all correspondence should be addressed.

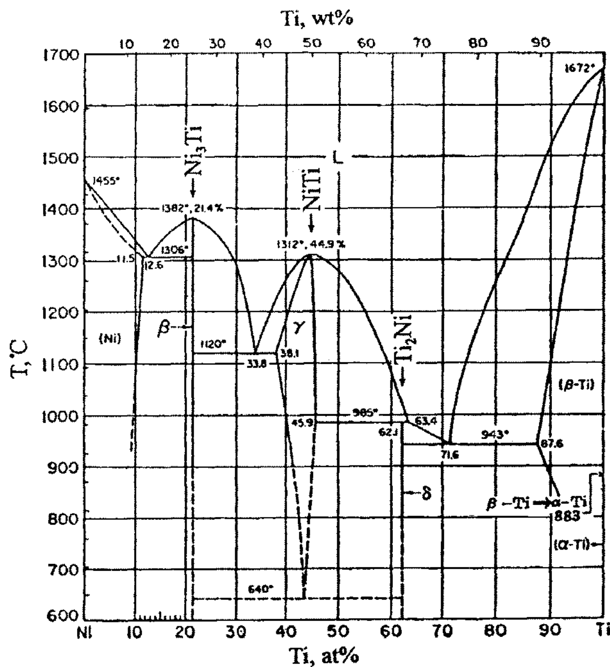


Figure 1 The phase diagram of Ni-Ti alloy [12].

temperature and the holding time, on the microstructures and strength (at room and elevated temperatures) of the joints. The possibility of the improvement on the heat resistance of Si_3N_4 ceramic joints with intermetallic compounds formed *in-situ* is discussed.

2. Experimental procedure

2.1. Materials

Joined ceramic material was hot press sintering silicon nitride, with 4-points bending strengths in the range 600–800 MPa. The size of the blocks to be joined was 10 mm × 5 mm × 4 mm. The surfaces to be joined were polished with 5 μm diamond paste. Following polishing, the samples were ultrasonic cleaned in acetone, alcohol and then dried. The interlayer metal Ti was 10–40 μm thick, 99.5wt% pure commercial titanium and Ni foil was 50–1000 μm thick, 97.5wt% pure nickel. Before joining, the surfaces of the Ni and Ti were cleaned mechanically to remove the oxide film and the impurities on the surfaces.

2.2. Bonding

The ceramic blocks and the interlayer metals were assembled as Si_3N_4/Ti/Ni/Ti/Si_3N_4 sandwich type with a setup built especially. Bonding was performed in a vacuum (6.7×10^{-3} Pa) furnace with a pressure of 0–7.5 MPa. Bonding temperature ranged from 1000°C to 1150°C with a heating rate of 20°C per second. At the bonding temperature, the holding time varied from 0 min to 180 min. After then, the samples were cooled in the furnace.

2.3. Shear testing

The joints were tested at room and high temperature using state shear loading with a displacement rate of 1 mm/min. When testing the high temperature shear strength, the heating rate was 15°C/min and the holding time at the temperature before shearing was 10 minute.

2.4. Microstructure and micro chemical characterization

The microstructures of the joints were inspected with a JSM-6301F scanning electron microscope (SEM) and energy disperse spectroscopy (EDS) to identify the microstructures. The fracture surfaces after mechanical testing were examined using the SEM to identify the fracture origins and with thin-film x-ray diffraction analysis with incidence angle of 0.3° to identify the reaction products between ceramic and the interlayer metal.

3. Results and discussions

3.1. The microstructures evolution during bonding

The microstructures of the joints bonded at various temperatures with 20 μm Ti and 400 μm Ni multi-interlayers, holding 60 minutes, pressing 2.5 MPa were examined with the SEM and the results are shown as Fig. 2. The compositions of the bonding products were identified with EDS. The microstructures of the joints bonded at 1000°C and 1050°C were composed of Si_3N_4/reaction layer/NiTi + Ni_3Ti/Ni_3Ti/Ni, while those of the joints bonded at 1100°C and 1150°C were composed of Si_3N_4/reaction layer/Ni_3Ti/Ni. The X-ray diffraction analysis on the fracture surface indicated that the reaction product closest to the Si_3N_4 ceramic was TiN, Ti_5Si_3, Ti_5Si_4, Ni_3Si were also found. In order to investigate the liquid phase formation and the microstructural evolution of the joint bonded with Ti/Ni/Ti multi-interlayers, the microstructures of the joints bonded at 1050°C for various holding time were examined by SEM and EDS. The results were shown as Table I.

According to the phase diagram of Ti-Ni (Fig. 1), it should be possible that when Ti film and Ni foil are held together between 985°C and 1120°C, intermetallic phases could form. This process might consist of three stages. Within the first stage, liquid phase forms and extends until Ti disappears. The compositions of the liquid changes as Ni atoms diffuse into the liquid until the composition reaches that of the liquidus at the corresponding holding temperature. Within the second stage, TiNi compound precipitates as Ni atoms diffuse further

TABLE I The constitutions of the joints bonded at 1050°C for various holding time

Holding time (min)	Compositions of the microstructures
0	Si_3N_4/$NiTi_2$/NiTi/Ni_3Ti/Ni*
3	Si_3N_4/ NiTi/Ni_3Ti/Ni*
30	Si_3N_4/reaction layer/NiTi/Ni_3Ti/Ni
60	Si_3N_4/reaction layer/NiTi + Ni_3Ti/Ni_3Ti/Ni
120	Si_3N_4/reaction layer/NiTi + Ni_3Ti/Ni_3Ti/Ni
180	Si_3N_4/reaction layer /Ni_3Ti/Ni

*No obvious reaction layer.

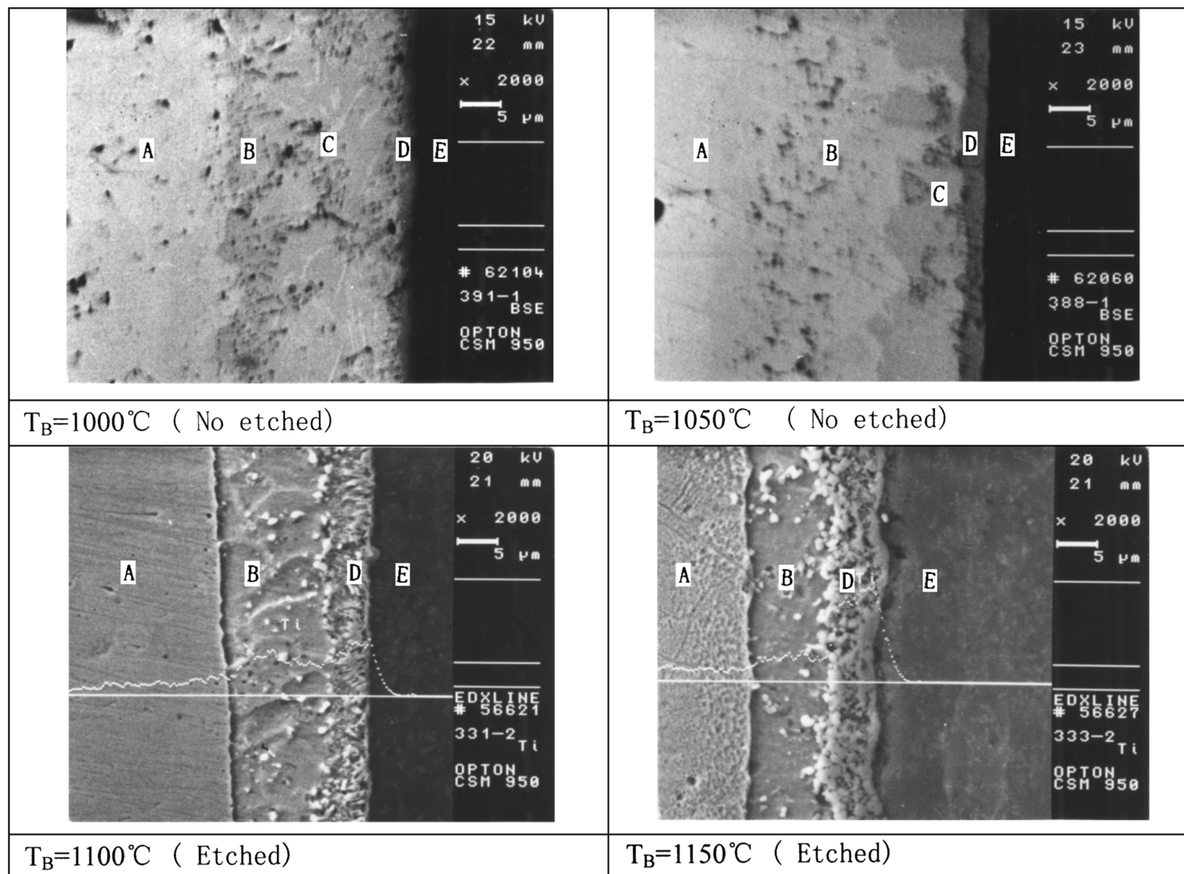


Figure 2 Microstructures of the joints bonded at different temperature A: Ni; B: Ni_3Ti; C: NiTi; D: reaction layer; E: Si_3N_4 ($\delta_{Ti} = 20\,\mu$m, $\delta_{Ni} = 400\,\mu$m, $t_B = 60$ min, $P_B = 2.5$ MPa).

into the liquid until the liquid phase disappears and the unique TiNi intermetallic compounds form. Within the last stage, Ni atoms diffuse into NiTi and react with it to form Ni_3Ti until NiTi almost changes into Ni_3Ti. The durations of the three stages should be dependent on the holding temperature. The higher holding temperature, the shorter each duration, due to the higher rates of diffusion. The results of the Fig. 2 indicated that NiTi changes completely into Ni_3Ti when holding 60 minutes at 1100°C, while NiTi still exists when holding 60 minutes at 1000°C and 1050°C.

When the holding temperature was between 1120°C and 1380°C, the process of the liquid phase formation and the microstructure evolution of the thin Ti and thick Ni multiplayer metals would be relatively simple. Firstly, the liquid forms and extends until the solid Ti film disappears. The compositions of the liquid changes as Ni atoms diffuse into it until the content of Ni reaches the liquidus composition at the corresponding holding temperature. Ni_3Ti intermetallic compound precipitates from the liquid as Ni atoms diffuse further into it until the liquid disappears and all changes into Ni_3Ti. When bonding within this temperature range, there was no occurrence of NiTi compound during bonding and Ni_3Ti was the unique intermetallic compound in the joint.

It can be seen from the results of Table I that when bonding at 1050°C, the intermetallic compounds in the interlayer metal changed from $NiTi_2 + NiTi + Ni_3Ti$ through $NiTi + Ni_3Ti$ into Ni_3Ti. The time of existence of the transient liquid was less than 3 min (if there was liquid phase existing, $NiTi_2$ would occur in the microstructures of the joints cooled) and within this duration the reaction between ceramics and the interlayer metals was very weak and the reaction layer was not detectable. The further reaction would continue through solid diffusion and the reaction layer became thicker with increasing holding time.

3.2. The strength of the joints at room temperature

3.2.1. The effect of the holding time

The strength of the joints bonded at 1050°C and pressing 2.5 MPa changed with holding time as shown in Fig. 3. The strength was higher when the holding time was between 60 minutes and 120 minutes. The highest shear strength was 140 MPa. Both shorter and longer holding time was inferior to the strength. Testing of the corresponding microstructures indicated that when the holding time was in this range, the microstructures of the joints were identical, which were made of Si_3N_4/reaction layer/NiTi (or $+Ni_3Ti$)/Ni_3Ti/Ni. However, the reaction layer between ceramics and the interlayer metal was not detectable or very thin when the holding time less than 60 minutes, while the NiTi in the interlayer metal had changed into Ni_3Ti on the whole and the Ti-Si compounds in the reaction layer became distinctly thicker if the holding time was longer than 120 minutes.

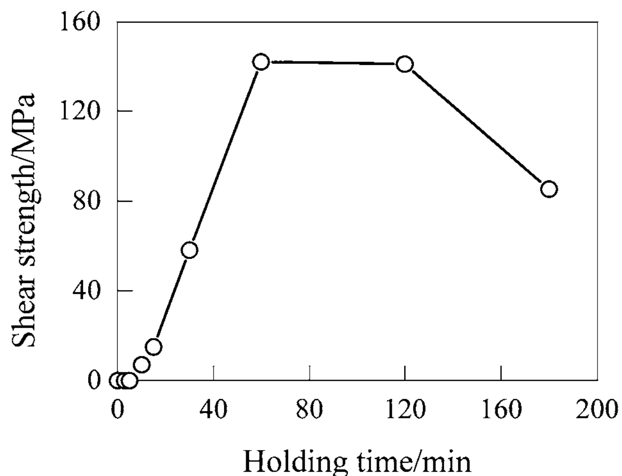


Figure 3 Effect of the holding time on the joint's shear strength at room temperature ($\delta_{Ti} = 20\ \mu m$, $\delta_{Ni} = 400\ \mu m$, $T_B = 1050°C$, $P_B = 2.5$ MPa).

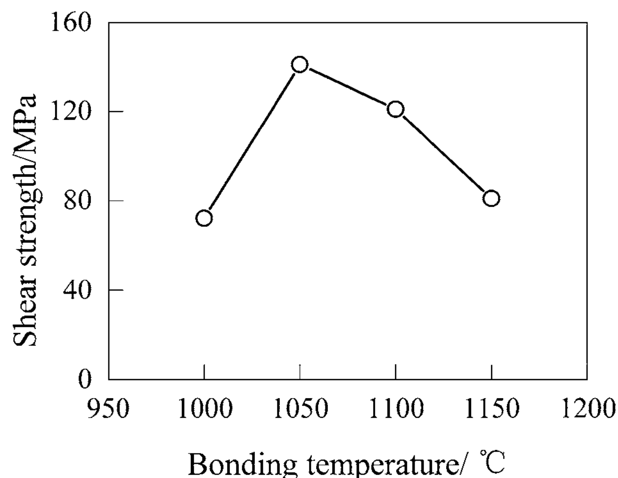


Figure 4 Effect of the bonding temperature on the joint's shear strength at room temperature ($\delta_{Ti} = 20\ \mu m$, $\delta_{Ni} = 400\ \mu m$, $t_B = 60$ min, $P_B = 2.5$ MPa).

Comparing with NiTi, Ni_3Ti is a Daltanide type intermetallic compound, which consists of covalent bond and ionic bond, and presents more brittleness. Moreover, Ti-Si compounds in the reaction layer close to Ni_3Ti were also brittle. When the holding time was longer, the interlayer between the ceramics and surplus Ni consisted of brittle compounds. Consequently, the shear strength of the joint was lower. Fractographic testing indicated that the fracture emerged along the interface of the ceramics and the reaction layer when the holding time was shorter, while the fracture occurred in the ceramics and in the reaction layer if the holding time was longer. These results confirm that the reaction was insufficient when the holding time was shorter, while the reaction layer would be the weak link in the joint when the holding time was longer. As a result, when the ceramics was bonded with Ti/Ni/Ti multi-interlayer metals, the strength of the joint would be higher if NiTi existed in its microstructures, in addition to the formation of a sufficient reaction layer.

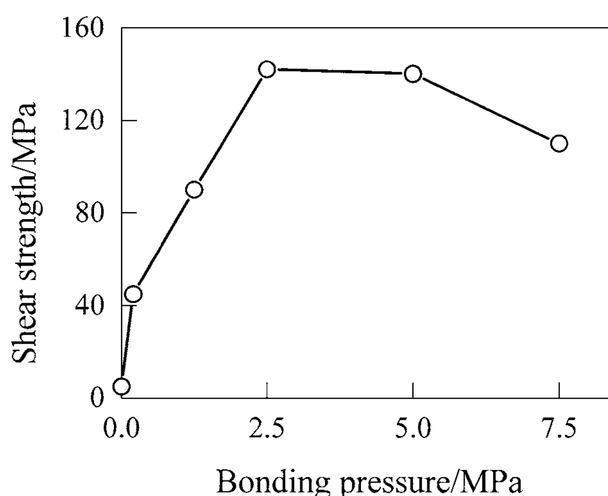


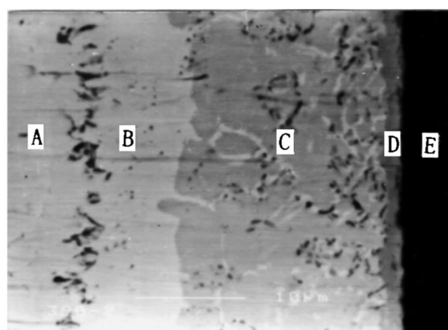
Figure 5 Effect of the bonding pressure on the joint's shear strength at room temperature ($\delta_{Ti} = 20\ \mu m$, $\delta_{Ni} = 400\ \mu m$, $T_B = 1050°C$, $t_B = 60$ min).

3.2.2. The effect of the bonding temperature

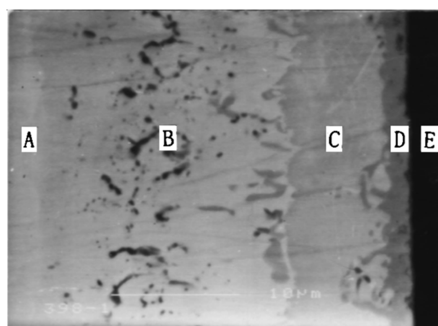
The shear strength at room temperature of the joints bonded at various temperature with a holding time of 60 minutes and pressure of 2.5 MPa is shown as Fig. 4. At the same holding time, the lower and the higher bonding temperatures were inferior to the room temperature strength of the joints. When bonding at 1000°C, the shear fracture propagated along the interface of the ceramics and the reaction layer due to the lack of the reaction, although the microstructures were composed of NiTi and Ni_3Ti. While the fracture took place in the ceramics or in the reaction layer when the joint was bonded at 1150°C, as the joint bonded for longer holding time, on which occasion, NiTi in the interlayer metal all changed into Ni_3Ti. The microstructures in the joint bonded at higher temperature were inferior in shear strength. The bonding temperature at which there was NiTi in the interlayer metal and sufficient reaction layer formation led to higher shear strength.

3.2.3. The effect of pressing during bonding

Fig. 5 shows the shear strength of the joints bonded at 1050°C with 60 minutes holding time changed as the pressure varied. Both higher and lower pressures were not beneficial to the strength. Because the duration of the existence of transient liquid was very short and its wettability to the ceramics at this temperature was low, the solid diffusion was needed to produce further interface reaction. Pressing during bonding could facilitate the liquid to wet the ceramics and promote the solid diffusion to form sufficient reaction layer. As a pressure less than 2.5 MPa, it was difficult to form strong joints. On the contrary, if the pressure was excessive, the transient liquid would be squeezed out of the joint thereby reducing the formation of NiTi or making the active element (Ti) deficient in full reaction layer. As the result, the strength would be reduced. Fig. 6 shows the microstructures of the joints with pressing 1.25 MPa and 5.0 MPa. It can be seen that the reaction layer was thin while the NiTi layer was thick when the pressure was 1.25 MPa.

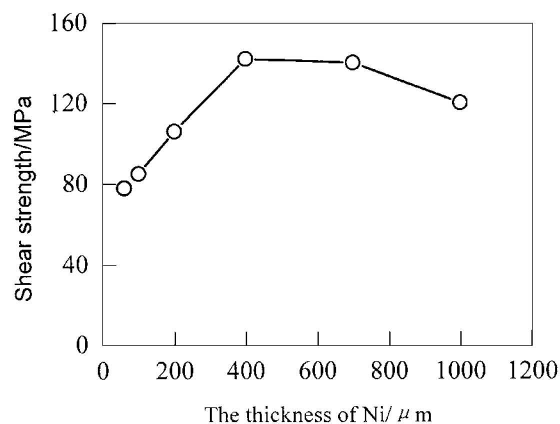


(a)

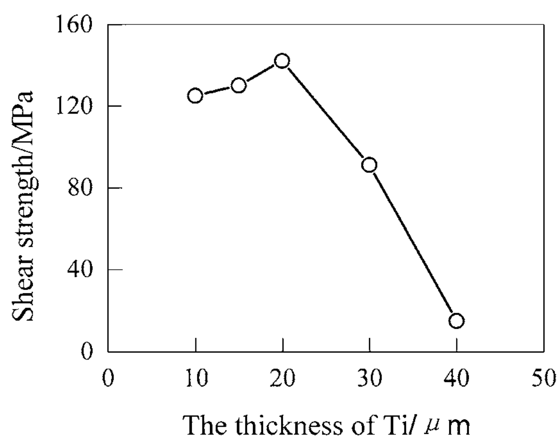


(b)

Figure 6 Effect of the bonding pressure on the microstructures of the joints: (a) $P_B = 1.25$ MPa (No etched); (b) $P_B = 5.0$ MPa (No etched) A: Ni; B: Ni_3Ti; C: NiTi; D: reaction layer; E: Si_3N_4; ($\delta_{Ti} = 20$ μm, $\delta_{Ni} = 400$ μm, $T_B = 1050$°C, $t_B = 60$ min).



(a)



(b)

Figure 7 Effect of the thickness of Ti and Ni on the joint's shear strength (a) ($\delta_{Ti} = 20$ μm, $T_B = 1050$°C, $t_B = 60$ min, $P_B = 2.5$ MPa) (b) ($\delta_{Ni} = 400$ μm, $T_B = 1050$°C, $t_B = 60$ min, $P_B = 2.5$ MPa).

3.2.4. The effect of the thickness of Ti film and Ni foil

When the Si_3N_4 ceramics was TLP bonded with Ti/Ni/Ti (Ti thin and Ni thick) multi-interlayers, the amount of the liquid phase and the thickness of NiTi and Ni_3Ti layers in the joints were dependent on the thickness of the Ti film. In addition, the active element participating in the reaction between the ceramic and the interlayer metal mostly came from the Ti film. When the ceramic was bonded between 985 and 1120°C, the active element Ti in the transient liquid not only reacted with the ceramic but also participated in the isothermally precipitation of NiTi due to the diffusion of Ni into the liquid. After the liquid all changed into NiTi, one part of the Ti atoms in it continued to react with the ceramic by solid diffusion and formed TiN and Ti-Si compounds, while the other participated in the forming of Ni_3Ti as the result of Ni atoms diffusion into NiTi. These comprehensive reactions could be expressed as $Si_3N_4 + NiTi + Ni \rightarrow TiN + Ti_xSi + Ni_3Ti$. The thickness of the Ti film influenced the width of the NiTi, the thickness of the reaction layer at certain holding time and the width of the surplus NiTi. The strength of the joints bonded at 1050°C for 60 minutes with a pressure 2.5 MPa changed with the thickness of the Ti film as shown in Fig. 7. When the Ti film was less than 20 μm, Ni_3Ti was the main intermetallic compound in the interlayer metal with some NiTi left. On this occasion, the strength of the joint was rather low. On the other hand, if the Ti film was too thick, the width of the NiTi and Ni_3Ti layers increased, which also limited the strength.

The thickness of the Ni foil mostly influenced the width of the surplus Ni in the interlayer metal. The existence of the soft Ni in the joint made of brittle Si_3N_4/reaction layer/Ni-Ti intermetallic compounds would mitigate the stress resulted from the mismatch of the thermal expansions and reduce the brittleness of the joint. This effect would be reduced if the surplus Ni was too thin, while the strength would be reduced if the surplus Ni too thick owing to its lower strength. As a result, there was a preferable range of the Ni foil thickness. The effect of the Ni foil thickness on the strength of the joints is shown in Fig. 7.

3.3. The strength at high temperature

The shear strength of the joints bonded at two different conditions changed with testing temperature as shown in Fig. 8. When the joint was bonded at 1050°C for 60 minutes, its room temperature strength was higher, but the strength fell as the testing temperature raised and became steady until the temperature was between 500 and 800°C. The shear strength at 800°C still retained 61 MPa. On the other hand, the shear strength of the joint bonded for holding 180 minutes with 60 μm Ni foil, with microstructures composed of Si_3Ni_4/reaction layer/Ni_3Ti/trace Ni, rose as the testing temperature increased reaching a maximum of 130 MPa at 600°C, and

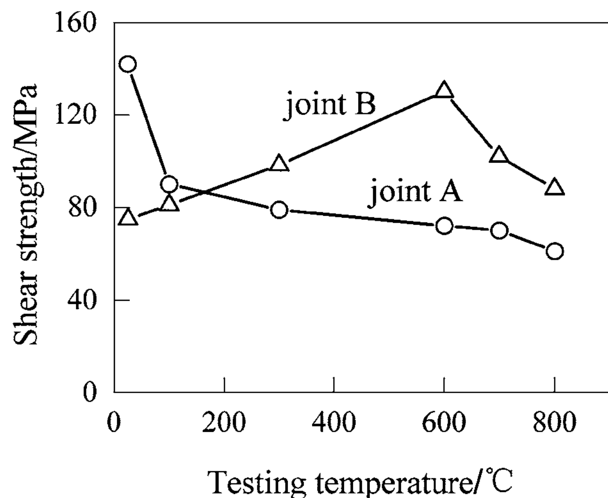


Figure 8 Shear strength of the joints at high testing temperature (joint A: $\delta_{Ti} = 20\ \mu$m, $\delta_{Ni} = 400\ \mu$m, $T_B = 1050°$C, $t_B = 60$ min, $P_B = 2.5$ MPa; joint B: $\delta_{Ti} = 20\ \mu$m, $\delta_{Ni} = 60\ \mu$m, $T_B = 1050°$C, $t_B = 180$ min, $P_B = 2.5$ MPa).

then falling again, but it could hold 88 MPa at 800°C. These results contributed to the performance of the intermetallic compounds and the stress relaxation as the temperature increased.

4. Conclusions

The Si_3N_4 ceramics could be bonded with Ti/Ni/Ti multi-interlayers (thin Ti and thick Ni) at 1000 to 1150°C. The high temperature strength is enhanced with the intermetallic compounds formed *in-situ* during TLP bonding. The joints with preferable room temperature strength and high temperature strength could be acquired under reasonable bonding parameters and suitable thickness of the interlayer metals. The shear strength at 800°C was 88 MPa.

Acknowledgments

The authors gratefully acknowledge the financial support provided by the Chinese Council of National Nature Science Foundation.

References

1. W. TILLMANN, E. LUGSCHEIDER, K. SCHLIMBACH, *et al.*, *Welding Journal* **76**(8) (1997) 300s.
2. W. TILLMANN, E. LUGSCHEIDER, K. SCHLIMBACH, *et al.*, *ibid.* **77**(3) (1998) 103s.
3. E. LUGSCHEIDER and W. TILLMANN, *Materials & Manufacturing Process* **8**(2) (1993) 219.
4. K. MIYAMA, M. ITO and T. NARITA, *Transactions of Japan Metal Society* **60**(5) (1996) 497 (in Japanes).
5. R. TORRECILLAS, M. A. SAINZ and J. S. MOYA, *Scripta Metallurgica et Materialia* **31**(8) (1994) 1031.
6. M. SINGH, *Ceramic Joining Technology. Advanced Materials & Processes* **10** (1998) 89.
7. P. A. WALLS and M. UEKI, *J. Amer. Ceram. Soc.* **78**(4) (1995) 999.
8. RONG-JUN XIE, LI-PING HUANG, YUAN CHEN, *et al.*, *J. Mater. Sci.* **34**(1999) 1783.
9. M. SALVO, M. FERRARIS, P. LEMOINE, *et al.*, *Journal of Nuclear Materials* **233–237** (1996) 949.
10. M. R. LOCATELLI, A. P. TOMSIA, K. NAKASHIMA, *et al.*, *Key Engineering Materials* **111–112** (1995) 157.
11. M. L. SCALZ, B. J. DALGLEISH, A. P. TOMSIA, *et al.*, *Journal of Materials Science* **29** (1994) 3200.
12. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloy (II)" (McGRAW-Hill Book Company, INC, New York, 1958) p. 807.

Received 19 May
and accepted 13 November 2000