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Thermal cyclic test of alumina/kovar joint brazed by Ni–Ti active filler

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Abstract

Active brazing was used to join high purity alumina ceramic and Kovar alloy with nickel and titanium foils. A sandwich structure was observed in the solder, an α-Ti solid solution belt at mid part and two Ti2Ni intermetallics belts at sides. Thermal cyclic tests were undertaken for the brazed joints at temperature ranging from 200 to 600 °C. Shear strength of joints were tested before and after thermal cycles. The results showed that shear strength increased dramatically after 40 thermal cycles. The determination and calculation of residual stress in joints indicated that thermal cycles reduced residual stress in joints observably due to similar effects as annealing, and resulting in improved strength.

Keywords: D. Alumina; Active brazing; Thermal cycles; Kovar; Nickel; Titanium

1. Introduction

In many applications, ceramic parts and metal parts often need to be joined together to combine their characteristics. This technique is broadly applied in many fields, such as mechanical engineering, atomic energy industry, aerospace facility, electronic device, and so forth. The techniques for joining ceramics are well documented [1–3], the most common include mechanical attachment, adhesives and brazing. Mechanical attachment and adhesives are suitable for relatively low-temperature applications; however, for high-temperature applications where strength and corrosion resistance is required, brazing and in particular active metal brazing, is appropriate [4]. Active brazing is a simple and effective method for bonding oxide ceramics such as alumina, because the addition of active element in filler metals can effectively improve the wettability of ceramics [5]. The process mechanism that enables the active braze alloy to wet the ceramic is a chemical reaction between the active element (Ti or V etc.) in the braze alloy with the ceramic. The exact reaction products, however, are not so well understood. In all cases reported, the reaction products with Titanium are many and varied, with many complex reactions taking place in the same series of experiments. Commercial brazing alloys are generally systems as AgCu, AgCuTi, AgCuSnTi, AgCuInTi, Ti, etc. The eutectic composition of the system AgCu (mp. 780 °C) is often preferred because it is relatively ductile and therefore able to limit the stresses arising between two materials with different thermal expansion coefficients [6]. Whereas, because of the noble metal component, these materials' operating temperatures are comparatively low. Ni–Ti alloy solder can be used at higher temperature (lowest mp 955 °C) than those cited above. However, it has not been widely applied nowadays due to its bad ductility, which is important for relieving stress in brazing joint. It is also difficult for machining or band rolling, especially for Ni–Ti alloy with high titanium content.

Ceramic/metal joining parts are often running in thermal shock situation. There are great discrepancies of properties between ceramics and metal, especially the thermal expansion coefficient. Therefore, high or low stresses always exist in brazed joint, which cause damage to joint's mechanical properties in different extent. This damage is usually aggravated by thermal shock or temperature cycling. To obtain good thermal

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shock resistance of ceramic/metal joints, the thermal expansion coefficients of ceramic and metal should be quite similar. Furthermore, some methods can be taken to decrease the joint stress, such as inserting one or several thin layers of ductile metals to release the stress [7]. However, thermal shock or thermal cyclic test reported on ceramic/metal brazing are very limited.

In this work, a method similar to PTLP (Partial Transient Liquid Phase) [8] bonding was used to join high purity alumina and 4J33-Kovar alloy. [9] Nickel foils and titanium foils were used as the filler. After brazing, the specimens were subjected to thermal cycles, and the joint shear strength was measured. The effect of thermal cycles on joint strength was discussed, by studying the thermal cycle process, thermal expansion coefficients of the alumina and 4J33-Kovar alloy and other factors.

2. Experimental procedure

High purity (>99.9%) alumina ceramic and 4J33-Kovar alloy were selected to join together. Tables 1 and 2 list the properties of alumina ceramic and composition of 4J33-Kovar alloy, respectively. Two types of brazing specimen assembly were designed, column for shear strength test and lamina for residual stress test. Kovar cylinders with ϕ 6 mm diameter and 6 mm height were brazed to alumina disks with ϕ 15 mm diameter and 4 mm height. The residual stress specimens are square pieces with sandwich structure. Solder foils were inserted between ceramic sheet (17 mm×6 mm×0.6 mm) and Kovar sheet (17 mm×6 mm×0.5 mm). For both the strength specimens and stress specimens, 15 μm thick nickel foils and 0.3 mm thick titanium foils were stacked as A/B/A structure to serve as filler. Fig. 1 shows the schematic drawings of specimen assembly.

After carefully grinding and cleaning, all these materials were assembled into two kinds of specimens as shown in Fig. 1. All samples were brazed at 995 °C for 30 min in a vacuum furnace under 300–400 g/cm^2 loads to enhance interfacial reactions. After brazing, specimens were subjected to 200–600–200 °C thermal cyclic tests, as shown in Fig. 2. Thermal cyclic tests were undertaken in a vacuum furnace to simulate their practical service conditions. Oxidation of solder can also be avoided while heating and cooling are repeated in vacuum. Joint shear strength was measured in a testing clamp by the method shown in Fig. 3. The tests were undertaken through a universal testing machine with crosshead speed of 0.5 mm/min. The residual stresses of the lamina specimens were measured by X-ray method and the measurements were taken at the mid point on alumina surface before and after thermal cycles. Some specimens were annealed in vacuum at 400 or 600 °C and the residual stress in the same point was measured before and after annealing. Besides, both alumina ceramic and 4J33-Kovar alloy's thermal expansion curves were also recorded at 30–900 °C range for residual stress analysis and calculation. One brazed joint was split and polished for microstructure observation by SEM.

Table 1
Properties of alumina ceramic

Density (g cm^{-3})	Porosity (%)	Young's modulus (GPa)	Bending strength (MPa)

Table 2
Composition of 4J33-Kovar alloy (wt.%)

C	Mn	Si	Ni	Co	Fe
⩽0.05	⩽0.50	⩽0.30	32.1∼33.6	14.0∼15.2	Remnant

3. Results and discussion

3.1. Microstructure of solder

Fig. 4 shows the SEM micrograph of the solder by using 5% HF to slightly etch the joint vertical cutting/

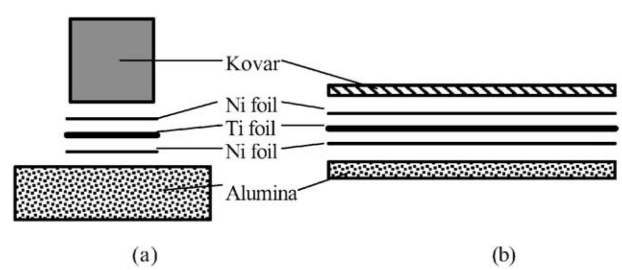

Fig. 1. Schematic drawings of (a) strength specimen and (b) stress specimen.

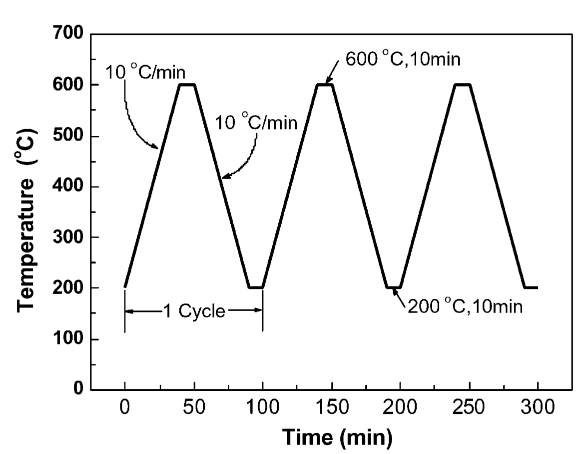

Fig. 2. Thermal cyclic testing program.

polishing surface. It can be shown that the thickness of solder layer is about 180 μm, smaller than that of the sum of Ti and Ni foils. It is attributed to alloying and some alloy flowing out of the brazing seam at high temperature. The dark color phase is α-Ti solid solution and the light color blocks are Ti2Ni intermetallics because the latter is much more resistant to erosion than the former. A sandwich structure is shown in the solder image, an α-Ti solid solution belt (actually mixed with tiny flakes of Ti2Ni) at mid part and two Ti2Ni intermetallics belts at sides. It has been shown that Ti2Ni intermetallic acts an important role in alumina active brazing with Ni–Ti filler [10] However, the higher hardness and brittleness of Ti2Ni phase are adverse to release stress in brazed joint, which is an important reason why Ni–Ti has not widely applied as active brazing filler. Because superfluous Ti was supplied in comparison with Ni, a ~ 100 μm width α-Ti solid solution belt was formed while Ni had exhausted. This Ti layer was expected to release joint stress for its good plasticity, as other brazing interlayer did.

3.2. Joint strength after thermal cycles

Fig. 5 shows the shear strength of joints after several 200–600 °C thermal cycles. It is commonly considered that thermal cycles will reduce ceramic/metal joint strength. Joint stress will vary ceaselessly during thermal cycles, which may cause tiny cracks in the joint to spread. In some cases, thermal cycles could severely damage the ceramic/metal joint. While, the experiment results did not correspond to the analysis. As shown in Fig. 5, when the thermal cycle number is between 10 and 40, the joint strength rises rapidly with the cycle number increasing and when it exceeds 40, the trend nearly stops. It is an interesting phenomenon that strength of ceramic/metal joint increases after thermal cycles, for metal and ceramic are so different in properties. It also has been reported that the residual strength after thermal shock for a ceramic-metal laminate by active brazing increase dramatically [11] The coordination of the alumina and 4J33-Kovar alloy's thermal expansion coefficients is mostly responsible for the phenomenon as well as the thermal cycle process. Since composition or microstructure cannot be changed at so low temperature of 600 °C, residual stress relief in the joint probably acts the main role.

3.3. Residual stress in joint

4J33-Kovar alloy is a kind of magnetic material, which has a Curie point at about 450 °C. Therefore its thermal expansion coefficient has a saltation at about 450 °C. Unlike Kovar alloy, the curve of thermal expansion coefficient of alumina is relatively smooth.

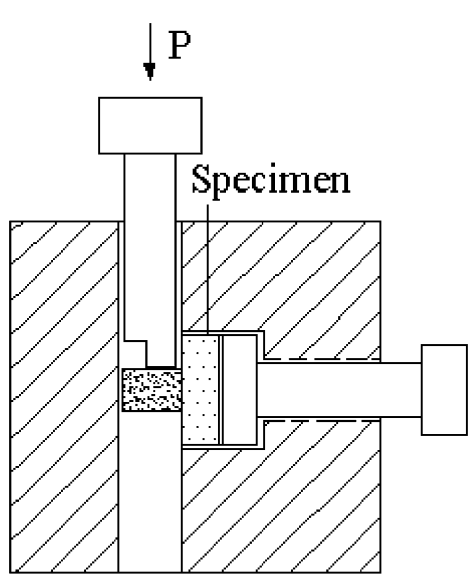

Fig. 3. Apparatus for joints shear strength testing.

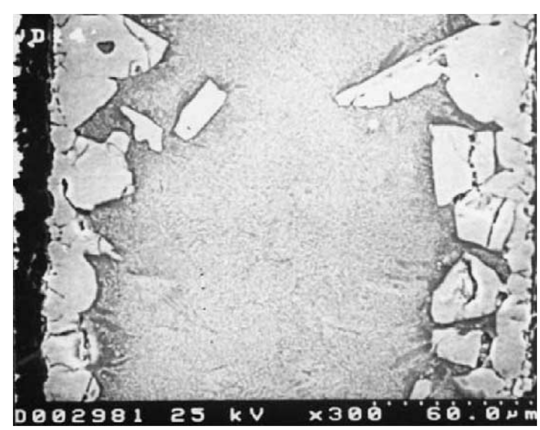

Fig. 4. SEM graph of the solder.

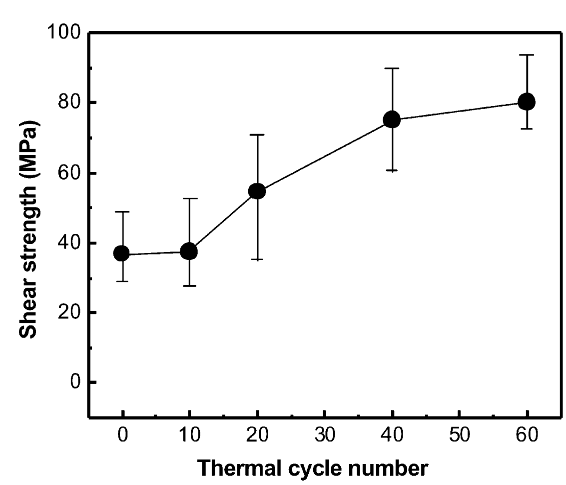

Fig. 5. Shear strength of the joints after thermal cycles.

Fig. 6 shows the measurement results for relative thermal expansion of Kovar and alumina from 30 to 900 °C. It can be shown that the expansion curve of Kovar can be divided into two parts by 450 °C. From 30 to 450 °C the thermal expansion of Kovar is approximately the same as that of alumina, while Kovar expends much more than alumina at temperatures over 450 °C. Therefore it can be concluded that on cooling from high temperature to room temperature, the stress in the Kovar/alumina joint is produced mostly between higher temperatures to 450 °C. In other words, thermal stress will always be introduced after cooling from a temperature over 450 °C.

In order to estimate the residual thermal stress in alumina section of the joint cooled from different start temperatures to 30 °C a simple equation was used as:

$$\sigma_c = \frac{\Delta\alpha \Delta T E_m E_c t_m}{(1-\nu)(t_m E_m + E_c t_c)} \quad (1)$$

where σ_c is the thermal stress in ceramic section, subscript c and m express ceramic and metal respectively, $\Delta\alpha$ is the difference of thermal expansion coefficients, ΔT is temperature difference, E is Young's modulus, t is thickness of ceramic or metal layer and ν is Poisson's ratio of ceramic. In this estimation the effect of solder was not considered. The estimation results were shown in Fig. 7 and the data $E_m = 180$ GPa, $\nu = 0.26$ were used. Although the t_c/t_m ratios are different, all estimation shows the same trend that when cooling from start temperatures lower than 500 °C, there is little stress introduced. This result is corresponding to above analysis.

Table 3 shows the annealing experiment and residual stress testing results by X-ray. It should be indicated that column-shaped samples were used to determine shear strength, but laminar samples were used to determine residual stress because residual stress could not be measured accurately with the strength specimens. Higher measurement accuracy can be achieved only for thin ceramic layer. Residual stress is about 250–280 MPa in ceramic section of laminar specimens after brazing, which indicates that ~750 °C is the initial stress-free temperature from Fig. 7. Considering the softening of Kovar and solder at high temperature, this estimation is reasonable. After annealing at 400 °C for 8 h, residual stress was reduced markedly and the shear strength increased by factor of two. The effects of 60 thermal cycles on strength and residual stress are similar to that of annealing at 400 °C for 8 h. It is fantastic that the shear strength has not increased after annealing at 600 °C for 8 h, and the residual stress after annealing is also higher than 400 °C annealing. There is larger thermal expansion difference at 600 °C, as shown in Fig. 6, hence stress will be introduced during cooling

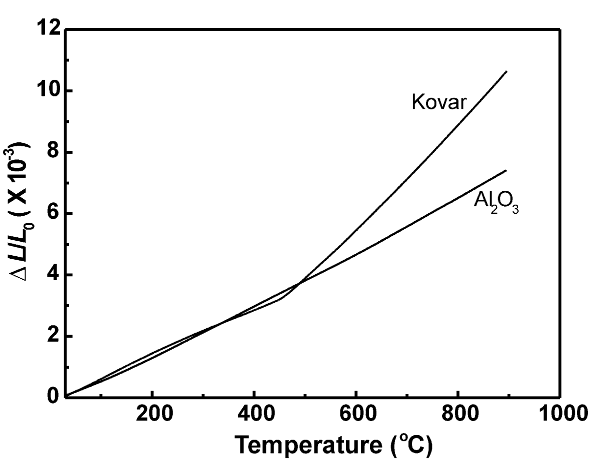

Fig. 6. Curves of relative expansion measurement.

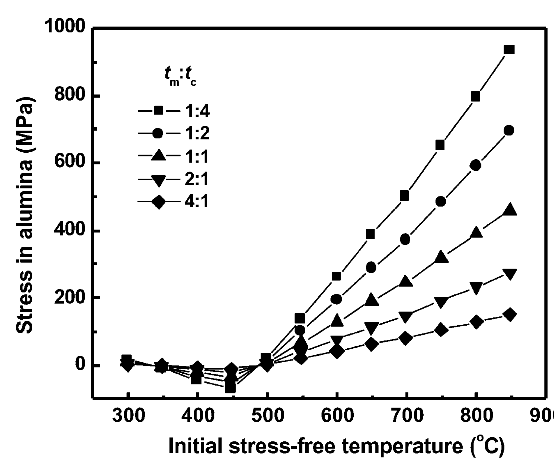

Fig. 7. Thermal stress estimation.

Table 3
Residual stress after annealing or thermal cycles

Treatments	Stress before treatment/MPa	Stress after treatment/MPa	Shear strength/MPa
400 °C 8 h annealing	274±03	162±04	~80
600 °C 8 h annealing	259±64	208±42	~31
60 thermal cycles	264±08	157±12	~80

process even if there is no stress at 600 °C. This result is consistent with Fig. 7.

4. Conclusions

Alumina ceramic and Kovar alloy were joined by active brazing with titanium and nickel foils as filler. This is a simple way to join ceramic and metal, especially for situations that noble metals such as Ag or Cu cannot be used. A sandwich structure was shown in the solder, which was composed of α-Ti solid solution belt at mid part and two Ti2Ni intermetallics belts at sides. Fantastic thermal cyclic behavior was observed in the joints, i.e. the shear strength increased remarkably after 200–600 °C thermal cycles. By means of thermal stress estimation and determination it can be shown that thermal cycles reduce residual stress evidently, whose influence is the same as annealing at 400 °C. This interesting effect of thermal cycle on strength can be attributed to the small thermal expansion difference between alumina and Kovar, the soft α-Ti belt acting as interlayer, especially the annealing effects from thermal cycles due to the gentle cooling program.

References

[1] R.E. Loehman, Advances in Joining Newer Structural Materials, Pergamon Press, New York, 1990.
[2] J.A. Fernie, W.B. Hanson, Ceramics Joining—Best Practice Guide, TWI, 1997.
[3] G. Elssner, G. Petzow, Metal/ceramic joining, ISIJ International 30 (1990) 1011–1032.
[4] M.G. Nicholas, Joining of Ceramics, Chapman and Hall, 1990.
[5] J.H. Chai, W.P. Weng, T.H. Chuang, Relationship between wettability and interfacial reaction for Sn10Ag4Ti on Al_2O_3 and SiC substrates, Ceram. Int. 24 (1998) 273–279.
[6] D. Sciti, A. Bellosi, L. Esposito, Bonding of zirconia to super alloy with the active brazing technique, J. Eur. Ceram. Soc. 21 (2001) 45–52.
[7] D.Y. Zhu, M.L. Ma, Z.H. Jin, Y.L. Wang, The effect of molybdenum net interlayer on thermal shock resistance of Al_2O_3/Nb brazed joint, J. Mater. Proc. Tech. 96 (1999) 19–21.
[8] M.R. Locatelli, B.J. Dalgleish, K. Nakashima, A.P. Tomsia, A.M. Glaeser, New approaches to joining ceramics for high-temperature applications, Ceram. Int. 23 (1997) 313–322.
[9] C.G. Zhang, G.J. Qiao, Z.H. Jin, Partial transient liquid phase bonding of Al_2O_3-Kovar with Ni–Ti filler, Rare Metal Mater. Eng. (in press).
[10] C.G. Zhang, G.J. Qiao, Z.H. Jin, Interface reaction mechanism of joining alumina with Ni–Ti active filler, Rare Metal Mater. Eng. (in press).
[11] D. Sherman, D. Schlumm, The mechanical behavior of ceramic-metal laminate under thermal shock, J. Mater. Res. 14 (1999) 3544–3551.