Interfacial structure and mechanical property of Al_2O_3 and Invar brazed joint

Zhao Lei, Hou Jinbao and Li Xiaohong
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Abstract *This paper introduces a brazing process between Al_2O_3 ceramic and Invar alloy. Al_2O_3 can be brazed with Invar effectively. The interfacial structure of Al_2O_3/Invar joint can be expressed as: Invar/ Ag(s,s) + Cu(s,s) + Fe_2Ti(zone I)/ Ag(s,s) + Cu(s,s) + Fe_2Ti + NiTi + Cu_3Ti(zone II)/ Ag(s,s) + Cu(s,s) + Cu_2Ti + Al(s,s) + TiC + TiO(zone III)/ Al_2O_3. The maximum shear strength of* 139 MPa *was measured for as-brazed Al_2O_3/Invar joint brazed at* 850 ℃ *for* 25 min *or* 900 ℃ *for* 15 min.

Key words engineering ceramics, ferrous metals and alloys, brazing

0 Introduction

As an important measure, joining of Al_2O_3 ceramic to metal offers a way to extend the use of Al_2O_3 ceramic into wider applications. Significant research and development efforts have been forced on developing reliable bonding techniques of Al_2O_3, such as diffusion bonding[1-2] and active brazing[3-7]. It has been observed that bonding using the filler alloy containing active elements like titanium can join ceramic to metal effectively, whether in diffusion bonding or active brazing. Abhijit Kar et al.[8] pointed out that active braze alloy 97(Ag28Cu)3Ti can successfully braze sintered Al_2O_3 to 304SS at 1 000 ℃, with the interfacial products like TiO, Cu_3Ti_3O and FeTi formed in the junction. M. I. Barrena et al.[9] observed that diffusion bonding between Al_2O_3 and Ti6Al4V can be achieved using Ag-Cu eutectic alloy, under the formation of diffusion layer composed of different intermetallic phases of the Ti-Cu system, Cu_3TiO_4 and Cu_2Ti_4O of the interface near Al_2O_3 base material. In addition, adhesive bonding, as a simple and effective type of bonding technology, has been widely applied in the bonding of metal to ceramic[10-11] in aerospace, automobile, construction, microelectronics and other industries[12-13]. Adhesive bonding can be effectively used on solid with high surface energy, but is hard on that with lower surface energy. It is emphasized that metal, metal oxide and ceramic have high surface energy but polymer and organic materials have low surface energy[14]. For successful bonding between dissimilar materials, it is promising to combine the above two kinds of bonding techniques. Therefore, a new bonding process namely epoxy resin assisted brazing (ERAB) was introduced and applied for bonding of Al_2O_3 ceramic to Invar. In the first period of ERAB process, active elements like Ti can be bonded at the surface of ceramic by adhesive glue, and following with the interdiffusion and interaction of interfacial components at brazing temperature.

1 Experimental procedures

The commercially available Al_2O_3 ceramic and Invar alloy (Fe-36Ni) were used in this study, and the specimens of Al_2O_3 and Invar were machined into 5 mm × 5 mm × 2 mm and 5 mm × 5 mm × 3 mm, respectively. The commercial Ag-Cu eutectic foil (thickness 100 μm) was used for brazing alloy and pure copper foil (thickness 100 μm) for buffer layer. The surfaces to be joined were ground by 500 grit silicon carbide papers for Al_2O_3 and 200 grit for Invar. All the materials were ultrasonically cleaned in acetone and dried in air prior to ERAB process.

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Commercial epoxy resin and TiH_2 powders were mixed in the volume ratio of 1∶1 to be active cement, which was applied to coat on the surface of Al_2O_3. The particle size of TiH_2 powder is 70 μm.

The bonding process consists of two steps, the first is coating of active cement at the brazing surface of Al_2O_3 ceramic, and the following is placing the coated Al_2O_3 and Invar plate into a vacuum hot press furnace using Ag-Cu eutectic foil and pure copper foil as filler metals in the assembly of coated Al_2O_3/Ag-Cu/Cu/Invar. Brazing experiments were carried out from 800 ℃ to 950 ℃ at a pressure of 2 MPa.

During the ERAB process, the temperature of furnace was raised to 700 ℃ at a heating rate of 20 ℃/min, and was subsequently raised to the set points for brazing (800 ℃, 850 ℃, 900 ℃ and 950 ℃) at 5 ℃/min, holding for 15 min at brazing temperature and followed with cooling at a rate of 10 ℃/min down to 500 ℃. Finally the joint cooled with the furnace to room temperature in vacuum. To analyze the impact of holding time on brazed joint, the brazing experiment for various holding times (5 min, 15 min, 25 min, 35 min) were carried out at 850 ℃.

Mechanical properties of the joints were evaluated by shearing test on a strength testing machine (Instron model 1186) using a fixture (see Fig. 1) at a crosshead speed of 1 mm/min. Three samples were tested for each process parameter and the arithmetical mean value was regarded as the average strength of joints. To characterize the microstructure of joint , the brazed couples were sectioned perpendicular to the joint and polished by standard metallographic procedure prior to inspection. The cross-sections of brazed joints were examined by means of scanning electron microscopy (SEM, Model S-570). The compositions of reaction phases and concentration profiles of various elements across the bonded zones were determined by X-ray diffraction (XRD, Model JDX-3530M) and energy dispersive X-ray spectrometer (EDS, model JXA-8600).

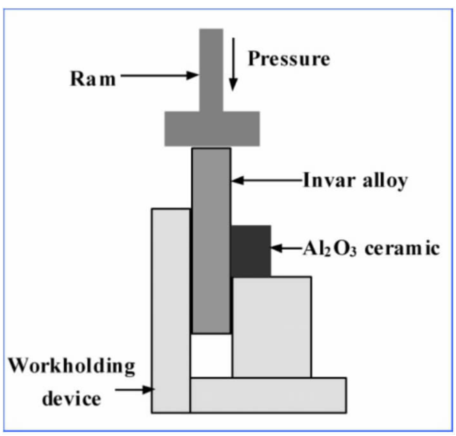


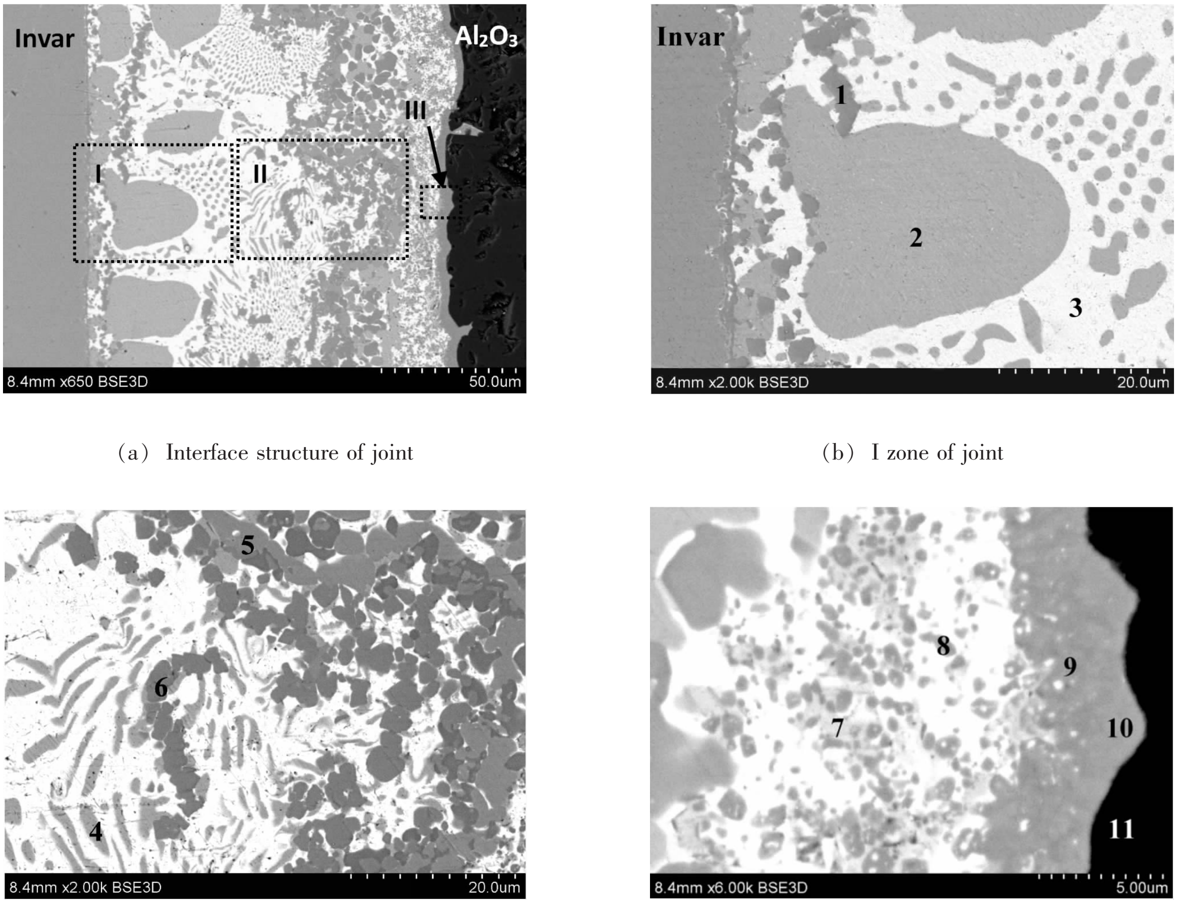
Fig. 1 Shear strength assembly of the specimen

2 Results and discussion

It was found that of Al_2O_3 was brazed with Invar by the ERAB process under the designed experimental conditions. The sound junction consists of three zones, as shown in Fig. 2, which was brazed at 850 ℃ for 15 min. For the sake of convenience, the three zones are marked as I, II and III in image.

To see this junction clearly, it is necessary to show the microstructures of Ag-Cu + Cu/Invar interface (zone I), center part of junction (zone II) and Al_2O_3/Ag-Cu interface (zone III) in Fig. 2b, Fig. 2c and Fig. 2d. Table 1 gives the average chemical compositions of each phase for determining interfacial reaction products in the junction.

It can be seen from Table 1 that there are many Fe and Ti in the black block phases (marked as 1 or 6 in Fig. 2), and the atom ratios of Fe to Ti are near 2∶1, which is same to that of Fe_2Ti. On basis of the results of reference [15], it can be inferred that these black block phases are Fe_2Ti. The gray block or strip phases (marked as 2, 4 or 7 in Fig. 2) mainly compose of Cu, so they are Cu-based solid solution (namely Cu(s, s)) according to phase diagram. It is same that the white zones (marked as 3 in Fig. 2b) are Ag-based solid solution (namely Ag(s, s)). In the zone II and III, the deep gray blocks (marked as 5 in Fig. 2c) consist of many Ti, Ni and Cu, which can be inferred that these deep gray blocks are intermetallic compounds between these three elements. In the small deep gray blocks (marked as 8 in Fig. 2d), the atomic ratio of Ti to Cu is near 3∶4, which is inferred as Cu_4Ti_3. It also can be inferred that this deep gray layer near Al_2O_3 (marked as 9 in Fig. 2d) is TiCu as its atomic ratio of Ti to Cu is near 1∶1. The white gray layers



(a) Interface structure of joint

(b) I zone of joint

(c) II zone of joint

(d) III zone of joint

Fig. 2 Microstructures of joint Al_2O_3/Invar brazed at 850 ℃ for 15 min through ERAB

Table 1 Chemical compositions of Al_2O_3/Invar joint brazed at 850 ℃ for 15 min (at. %)

Points	O	Al	Ag	Ti	Fe	Ni	Cu	Possible phases
1	4.31	0.26	0.51	30.05	58.39	5.07	1.41	Fe_2Ti
2	0.00	0.37	1.33	1.43	1.75	1.95	93.17	Cu(s,s)
3	5.84	0.26	78.33	5.80	3.58	2.50	3.67	Ag(s,s)
4	0.80	0.54	1.81	0.67	1.15	1.34	93.70	Cu(s,s)
5	2.14	0.51	1.03	28.19	3.08	19.49	45.56	NiTi, Cu_3Ti, Cu(s,s)
6	2.93	0.00	0.23	28.89	59.39	6.55	2.01	Fe_2Ti
7	3.51	0.99	2.31	3.81	0.87	1.08	87.43	Cu(s,s)
8	6.12	0.52	6.02	35.50	3.77	5.28	42.79	Cu_4Ti_3
9	6.82	3.16	0.33	44.69	0.73	0.62	43.65	CuTi
10	14.68	7.32	0.55	39.21	0.84	0.36	37.03	TiO, Cu_2Ti
11	42.88	28.49	0.23	21.58	0.45	0.67	5.69	Al_2O_3, Al, TiO

(marked as 10 in Fig. 2d) compose of many Ti, Cu, O and little Al, which inferred that the layer may contain intermetallic compounds between Ti and Cu, and the oxides of titanium.

In order to identify the reaction products of the joint, the specimens brazed at 850 ℃ for 15 min were ground along the direction paralleling to the interface. After that, XRD patterns were performed on each zone of joint, the results of which are shown in Fig. 3. It can be seen from Fig. 3 that the reaction products in the interface of Ag-Cu + Cu/Invar (zone I) are mainly Fe_2Ti, Cu(s,s) and Ag (s,s). Because zone I is near Invar alloy, solid solution of Fe and Ni (namely (Fe,Ni)) can be detected easily in XRD pattern result of zone I. Also, Al_2O_3 can be detected easily in these XRD pattern results as a small quantity of fragments of Al_2O_3 ceramic at the fringe of specimen. In the same, it can be confirmed that the reaction products in the center of junction (zone II) are mainly NiTi, Fe_2Ti, Ag(s,s), Cu_3Ti and Cu(s,s), those in the interface of Ag-Cu/Al_2O_3 (zone III) are TiO, CuTi, Cu_2Ti, Cu_4Ti_3, Ag(s,s), Cu(s,s), Al(s,s) and Al_2O_3.

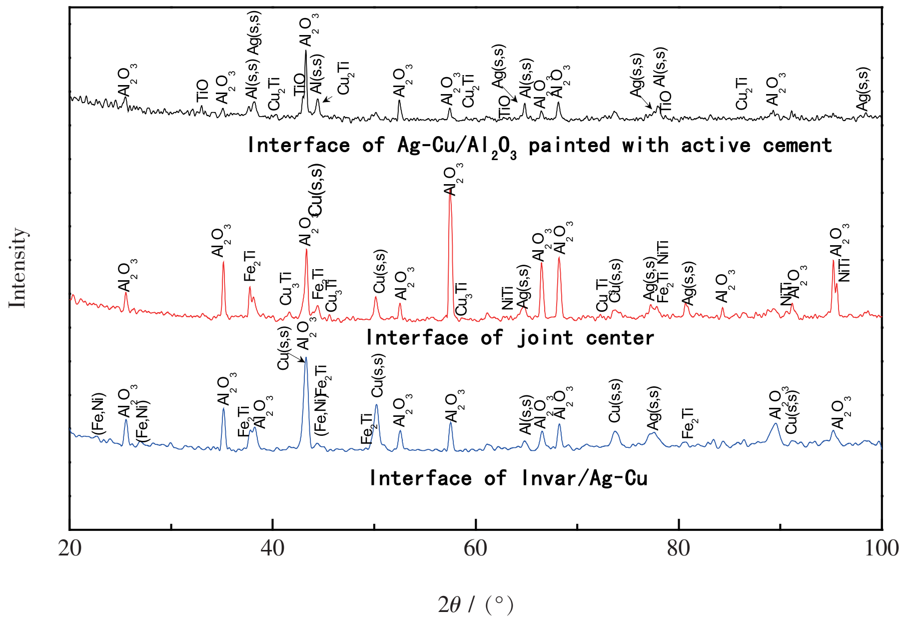


Fig. 3 XRD for interlayers of Al_2O_3/Invar joint brazed at 850 ℃ for 15 min

Based on the discussion mentioned above, it can be inferred that interaction occurred between active cement, brazing alloy and base materials during the bonding process. The free energy changes for each possible reaction calculated by software HSC Chemistry 5.0 or cited are shown as follows.

$$2Fe + Ti = Fe_2Ti \quad (1)$$

$$\Delta G_1(850\ ℃) = -70.500\ kJ \cdot mol^{-1}$$

$$Ni + Ti = NiTi \quad (2)$$

$$\Delta G_2(850\ ℃) = -56.842\ kJ \cdot mol^{-1}$$

$$Al_2O_3 + 3Ti = 3TiO + 2Al \quad (3)$$

$$\Delta G_3(850\ ℃) = -1\,016.714\ kJ \cdot mol^{-1}$$

On basis of the results of reference [16], the free energy of following reactions are as follows.

$$2Ti + Cu = Ti_2Cu \quad (4)$$

$$\Delta G_4(850\ ℃) = -6.866\ kJ \cdot mol^{-1}$$

$$Ti + Cu = TiCu \quad (5)$$

$$\Delta G_5(850\ ℃) = -7.532\ kJ \cdot mol^{-1}$$

$$3Ti + 4Cu = Ti_3Cu_4 \quad (6)$$

$$\Delta G_6(850\ ℃) = -7.190\ kJ \cdot mol^{-1}$$

Ti comes from the decomposition reaction of TiH_2 powders as equation (7).

$$TiH_2 = Ti + H_2 \quad (7)$$

The decomposition critical temperature of equation (7) is $T_7 = 775$ ℃. And the free energy of reaction (1) – (6) at 775 ℃ are as follows:

$$\Delta G_1(775\ ℃) = -72.539\ kJ \cdot mol^{-1}$$

$$\Delta G_2(775\ ℃) = -57.776\ kJ \cdot mol^{-1}$$

$$\Delta G_3(775\ ℃) = -72.539\ kJ \cdot mol^{-1}$$

$$\Delta G_4(775\ ℃) = -7.218\ kJ \cdot mol^{-1}$$

$$\Delta G_5(775\ ℃) = -7.777\ kJ \cdot mol^{-1}$$

$$\Delta G_6(775\ ℃) = -7.361\ kJ \cdot mol^{-1}.$$

It can be inferred that the above reactions maybe occurred when temperature reaches 775 ℃.

In addition, the solid decomposition remains of active cement are Ti and C in vacuum furnace. In view of theoretical analysis, TiC can be formed under the reaction as equation (8).

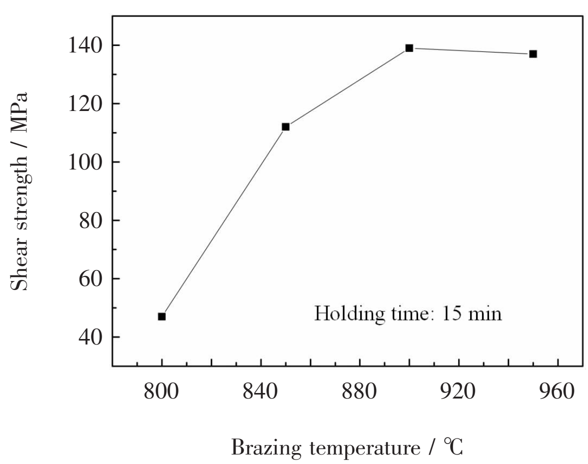
$$Ti + C = TiC \quad (8)$$

$$\Delta G_8(850\ ℃) = -172.003\ kJ \cdot mol^{-1}$$

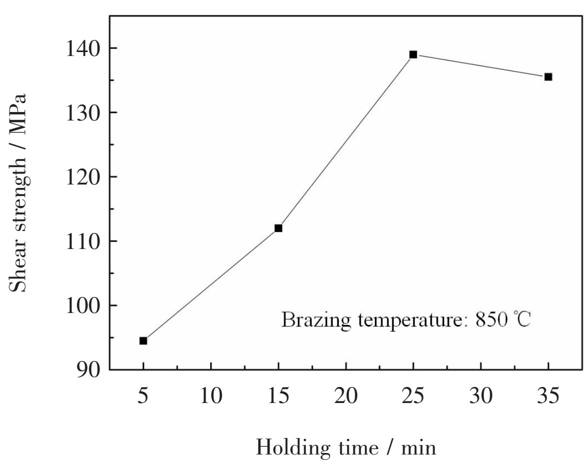
And its free energy changes of equation (8) is –172.828 $kJ \cdot mol^{-1}$ at 775 ℃ through calculation. The results indicated the formation of TiC at the region of original epoxy resin when temperature reaches 775 ℃. In fact, there is no TiC observed in the interface of specimens for its small amount.

From what discussed above, it can be concluded that there are 8 compounds and 3 solid solutions generated in the ERAB process, and the interfacial structure of Al_2O_3/Invar joint bonded by ERAB at 850 ℃ for 15 min can be described as Invar/Ag(s,s) + Cu(s,s) + Fe_2Ti(zone I)/Ag(s,s) + Cu(s,s) + Fe_2Ti + NiTi + Cu_3Ti(zone II)/Ag(s,s) + Cu(s,s) + CuTi + Cu_2Ti + Cu_4Ti_3 + Al(s,s) + TiC + TiO(zone III)/Al_2O_3.

The shearing strengths of Al_2O_3/Invar joints bonded by ERAB at various brazing temperatures and holding times are depicted, as shown in Fig. 4. It can be known from Fig. 4 that when brazing temperature is lower or hold-



(a) Joint brazed at various brazing temperatures



(b) Joint brazed at various holding times

Fig. 4 Shear strengths of joint Al_2O_3/Invar

ing time is short, shear strengths of joints are not satisfactory. Increasing of brazing temperature or holding time caused the maximum shear strength value of joint. Based on Fig. 4, the maximum shear strength of Al_2O_3/Invar joint is 139 MPa obtained at 900 ℃ for 15 min or 850 ℃ for 25 min.

3 Conclusions

Al_2O_3 ceramic and Invar alloy can be successfully bonded through ERAB using self-made active cement, Ag-Cu eutectic braze alloy and pure copper foil as buffer layer. Interaction occurred in the active cement coated Al_2O_3/Invar junction with the interfacial structure of Invar/Ag(s,s) + Cu(s,s) + Fe_2Ti (zone I)/Ag(s,s) + Cu(s,s) + Fe_2Ti + NiTi + Cu_3Ti (zone II)/Ag(s,s) + Cu(s,s) + CuTi + Cu_2Ti + Cu_4Ti_3 + Al(s,s) + TiC + TiO (zone III)/Al_2O_3. The maximum shear strength of 139 MPa for Al_2O_3/Invar joint was brazed at 900 ℃ for 15 min or 850 ℃ for 25 min, equally.

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