



Cu + TiB₂ composite filler for brazing Al₂O₃ and Ti–6Al–4V alloy

Minxuan Yang^a, Tiesong Lin^{a,b}, Peng He^{a,*}

^a State Key Laboratory of Advanced Welding Production Technology, Harbin Institute of Technology, Harbin 150001, China

^b Department of Electronics Packaging Technology, School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

ARTICLE INFO

Article history:

Received 18 July 2011

Accepted 1 September 2011

Available online 4 October 2011

Keywords:

Ceramics

Metals and alloys

Microstructure

Mechanical properties

ABSTRACT

Al₂O₃ and Ti–6Al–4V alloy were brazed using Cu + TiB₂ composite filler, which manufactured by mechanical milling of Cu and TiB₂ powders. Typical interface microstructure of joint was Al₂O₃/Ti₄(Cu,Al)₂O/Ti₂Cu + Ti₃Al + Ti₂(Cu,Al)/Ti₂(Cu,Al) + AlCu₂Ti/Ti₂Cu + AlCu₂Ti + Ti₃Al + Ti₂(Cu,Al) + TiB/Ti(s.s) + Ti₂Cu/Ti–6Al–4V alloy. Based on temperature- and time-dependent compositional change, the formation of intermetallics in joint was basically divided into four stages: formation of interfacial Ti₄(Cu,Al)₂O in Al₂O₃ side, formation of Ti₂Cu, Ti₃Al, TiB, Ti₂Cu, and AlCu₂Ti in layers II and IV, formation of Ti₂(Cu,Al) and AlCu₂Ti in layer III, formation of Ti + Ti₂Cu hypereutectoid organization adjacent to Ti–6Al–4V alloy. TiB in situ synthesized in joint not only acted as low thermal expansion coefficient reinforcement to improve the mechanical properties at room temperature, but also as skeleton ceramic of joint to increase high temperature mechanical properties of Al₂O₃/Ti–6Al–4V alloy joint increasing. When the joint containing 30 vol.% TiB brazed at 930 °C and 10 min of holding time, the maximum room temperature shear strength of joint was 96.76 MPa, and the high temperature shear strength of joint was 115.16 MPa at 800 °C.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

In view of the superplasticity, low weight and high mechanical resistance of Ti–6Al–4V alloy, it is widely used for aeronautical application [1]. But it has poor wear resistance because of its low resistance to plastic shearing. Al₂O₃ is characterized with wear resistance, superior physical, chemical and mechanical properties, so joining of Al₂O₃ and Ti–6Al–4V alloy is especially meaningful, which can broaden the application of them [2].

So far brazing with active filler metals is a preferred method of joining, because active elements contained in filler metals can promote wettability of ceramic surfaces [3]. However, a significant difference in thermal and mechanical properties between ceramics and metals make it difficult to obtain ceramic–metal joints with adequate mechanical integrity. Therefore, it should be noted that residual stress arises during the brazing process as a result of the different thermal expansion coefficients between Al₂O₃ ($7.6 \times 10^{-6} \text{ K}^{-1}$) and Ti–6Al–4V alloy ($8.6 \times 10^{-6} \text{ K}^{-1}$). The disadvantage has been minimized using soft interlayer or adding low CTE materials into brazing filler metal till now [4–8]. Brochu et al. [9] have inserted a copper interlayer to absorb the residual stress produced during cooling of a Si₃N₄ brazed to an iron aluminide alloy. The maximum bending strength obtained was 160 MPa. Blugan et al. [10] have brazed silicon nitride ceramic composite to steel

using SiC-particle-reinforced commercially available active metal braze filler alloy (Incusil ABA). Using of Incusil ABA + 30 vol.% SiC resulted in a higher average flexural strength of 395 MPa at room temperature and lower residual thermal stresses.

In the present research, low CTE ceramic reinforcements were in situ synthesized in order to minimize the joint residual thermal stress. Furthermore, to have a successful joint between ceramic and metal, accurate investigation of the effects of TiB₂ content, brazing temperature and holding time on the microstructure and shear strength of Al₂O₃/Ti–6Al–4V alloy joint were taken into consideration, and the influence of TiB on high temperature properties of brazed joint was also investigated. The formation of the intermetallics in the joint was basically comprehensive analysis based on the temperature- and time-dependent compositional change.

2. Experimental procedures

The base materials used in the experiment were Al₂O₃ and Ti–6Al–4V alloy. Al₂O₃ was sawn by diamond discs into specimens with size of 5.0 mm × 5.0 mm × 3.0 mm for microstructure examination and 4.0 mm × 4.0 mm × 3.0 mm for shear testing. Ti–6Al–4V alloy was cut into the specimens with size of 10.0 mm × 8.0 mm × 1.2 mm by wire electro-discharge machining. The surfaces to be brazed were grounded by 800 grit SiC paper and then all specimens dipped into acetone and were cleaned with ultrasonic washer for 30 min.

Five series composite fillers with different mass fractions of TiB₂ powders (~5 μm in diameter, 95 wt.%) in Cu (~50 μm in diameter, 99.5 wt.%) powders were fabricated at room temperature under argon atmosphere by mechanical ball milling. The ball to powder weight ratio was 15:1, the rotation speed of value was 300 rpm and the milling time was 300 min. Fig. 1 shows the microstructure of four series Cu + TiB₂ as-milled powders. TiB₂ powders distribute uniformly in brazing filler metal. The size of powders in composite fillers decreases with the increasing of

* Corresponding author. Tel.: +86 451 86402787; fax: +86 451 86402787.
E-mail address: hithepeng@hit.edu.cn (P. He).

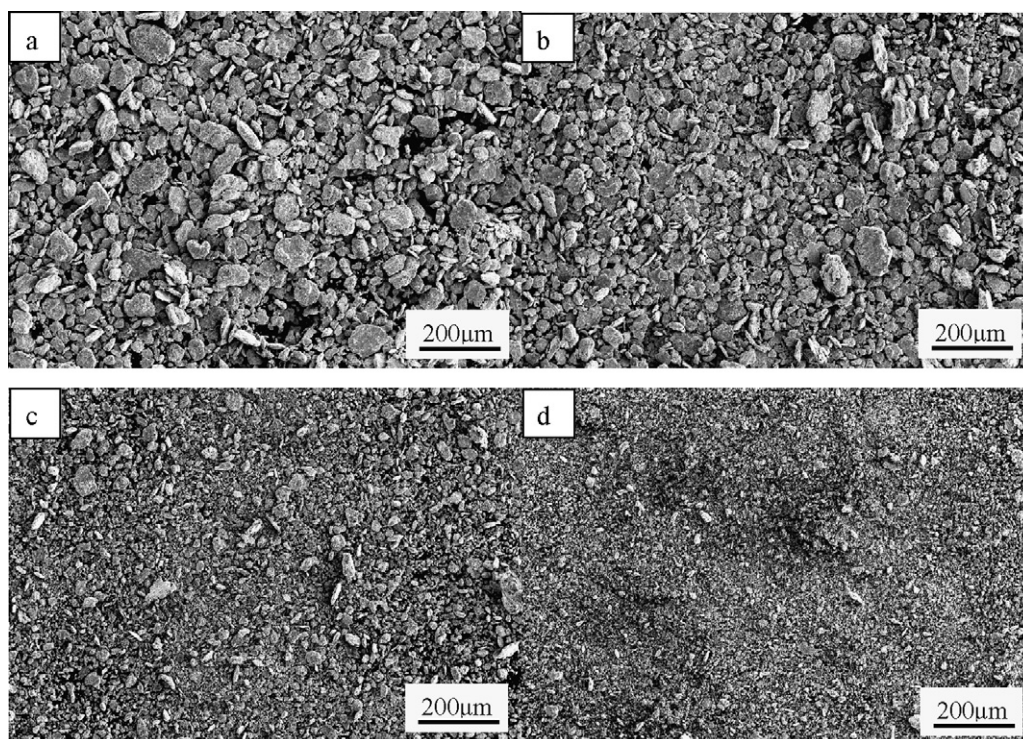


Fig. 1. Cu + TiB₂ composite fillers with different TiB₂ content corresponding to different volume fraction of TiB (a) 10 vol.%, (b) 20 vol.%, (c) 30 vol.%, and (d) 50 vol.%.

TiB₂ content. It can be attributed to the high hardness 34 GPa of TiB₂. The composite filler was mixed with binder into paste, and then the mixed paste was applied between Al₂O₃ and Ti-6Al-4V alloy by coating on the surface of Ti-6Al-4V alloy (~100–200 μm). After that the assembly was brazed at 930 °C for 10 min in a vacuum furnace with the vacuum of 3.0×10^{-4} Pa. During brazing, the assembly was first heated to 450 °C at a rate of 20 °C/min, and held for 10 min to volatilize the binder and ensure that the brazing surfaces were clean. Then the temperature was continuously increased to 930 °C at a rate of 10 °C/min and held for 10 min. At last, the assembly was cooled down to 400 °C at 5 °C/min and then cooled in the furnace without power.

The polished cross-sections of brazed joints were examined to characterize the interfacial microstructure by S-3400 scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) equipped with SEM. The JDX-3530M X-ray diffraction (XRD) was used to identify the metallographic phases of each reaction layer, which paralleled to Al₂O₃/Ti-6Al-4V alloy joint by layered stripping. The XRD testing with Cu K α radiation was operated at a voltage of 40 kV and angle incidence of 20–100°. Joints shear strength at room and high temperature (400–600 °C) were both examined using Instron-1186 universal testing machine with a displacement rate of 0.5 mm/min. At least five specimens were tested for each experimental condition.

3. Results and discussion

3.1. Typical microstructure of Al₂O₃/Ti-6Al-4V alloy joints

Fig. 2 shows the interfacial microstructure of Al₂O₃/Ti-6Al-4V alloy joint brazed at 930 °C/10 min (brazing temperature is 930 °C, holding time is 10 min). 30 vol.% TiB in situ synthesized in the joint. It indicates the successful joining of Al₂O₃ and Ti-6Al-4V alloy using the Cu + TiB₂ composite filler that the integral microstructure of the Al₂O₃/Ti-6Al-4V alloy joint as shown in Fig. 2(a). A variety of products are generated by reaction between composite filler and base materials during the brazing process. The layer-like interfacial microstructure of joint can be divided into five areas (marked by Areas I, II, III, IV and V). The magnification microstructure at interfacial area is observed in Fig. 2(b). A continuous light reaction layer (marked by Area I, ~0.5–1 μm) forms adjacent to Al₂O₃. Light gray phase B, Gray phase C1 and dark phase D make up Area II. Area III consists of dark gray phase C4 and just a little white phase E. Gray phase C2, white phase E, whisker-like black phase F

and dark phase D constitute Area IV. The hypereutectoid organization Ti + Ti₂Cu comprise a continuous reaction layer denoted Area V next to Ti-6Al-4V alloy, with a thickness of about 50 μm. The compositions of A–F phases measured by EDS are listed in Table 1. The joint interfacial products are confirmed by the results of XRD as shown in Fig. 3. Combining with the results of EDS and XRD, phase A is determined to be Ti₄(Cu,Al)₂O. As shown in Fig. 3(a), some Al₂O₃ remain in the first layer in order to detect Area I. The composition analysis results confirm similar elemental contents of gray phase in Area II (19.99 at.% Al + 65.75 at.% Ti + 14.26 at.% Cu), in Area III (8.93 at.% Al + 69.91 at.% Ti + 21.16 at.% Cu) and in Area IV (11.97 at.% Al + 65.85 at.% Ti + 22.19 at.% Cu), which are all demonstrated to be Ti₂(Cu,Al). Because Al atoms dissolve into brazing layer from Al₂O₃ and Ti-6Al-4V alloy, and then interdiffuse in Cu or Ti atoms [11]. The light gray phase B and dark phase D are Ti₂Cu and Ti₃Al. In Fig. 3(a)–(d), the XRD studies show obvious diffraction peaks associated with Ti₂Cu and Ti₃Al. The white phase E is AlCu₂Ti and whisker-like black phase F is TiB, which are detected in XRD results as shown in Fig. 3(d).

Eventually, the typical interface structure of joint brazed at 930 °C for 10 min is determined to be Al₂O₃/Ti₄(Cu,Al)₂O/Ti₂Cu + Ti₃Al + Ti₂(Cu,Al)/Ti₂(Cu,Al) + AlCu₂Ti/Ti₂Cu + AlCu₂Ti + Ti₃Al + Ti₂(Cu,Al) + TiB/Ti(s.s) + Ti₂Cu/Ti-6Al-4V alloy.

3.2. Effect of different TiB₂ content on Al₂O₃/Ti-6Al-4V alloy joints microstructure

In addition to the joint containing 30 vol.% described above, Fig. 4 shows the microstructure of joint with four compositions of TiB₂ versus in situ synthesizing 0, 10, 20 and 50 vol.% TiB. For the brazing filler without TiB₂, the joint microstructure is mainly composed of Ti₂Cu and Ti + Ti₂Cu hypereutectoid organization. A distinct cracking appears near the interface between Al₂O₃ and brazing layer as shown in Fig. 4(a). Fig. 4 indicates that the volume fraction of TiB increase with the addition increasing of TiB₂. During brazing process, TiB in situ synthesized by the reaction of

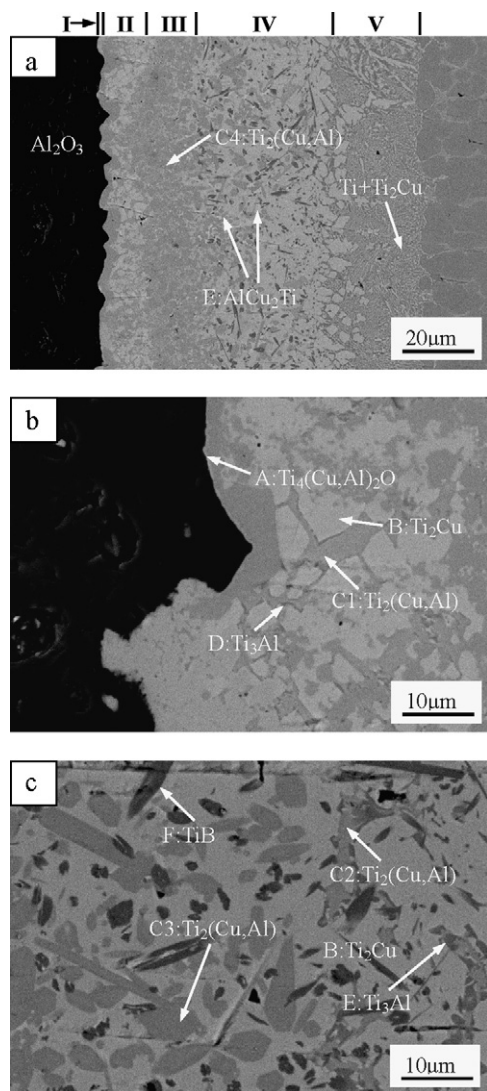


Fig. 2. The microstructure of $\text{Al}_2\text{O}_3/\text{Ti-6Al-4V}$ alloy joint using $\text{Cu} + \text{TiB}_2$ (in situ synthesizing 30 vol.% TiB) composite filler brazed at 930°C for 10 min (a) integral joint, (b) in Al_2O_3 side, and (c) in Area IV.

$\text{TiB}_2 + \text{Ti} \rightarrow \text{TiB}$, together with the interaction of Cu-Ti (-10 kJ/mol) and B-Ti (-42 kJ/mol), thus Ti dissolution in the melt increases by TiB_2 . For the joint containing 10 vol.% TiB , AlCu_2Ti and $\text{Ti}_2(\text{Cu,Al})$ form Area II in the center of joint. For joint with 20 vol.% and 30 vol.% TiB , the content of AlCu_2Ti decreases, and that of $\text{Ti}_2(\text{Cu,Al})$ increases as shown in Fig. 2. $\text{Ti}_2(\text{Cu,Al})$ is refined, which composed Area III compacts and moves to Al_2O_3 side. For the joint with 50 vol.% TiB , AlCu_2Ti intermetallics disappear. The content of $\text{Ti}_2(\text{Cu,Al})$ increases continuously while the size decreases, and they assemble in Al_2O_3 side. Hence, the increase in the addition of TiB_2 in

brazing filler leads to form increasingly Ti-rich intermetallics due to the increasing of Ti atoms dissolution. From the location and shape of $\text{Ti}_2(\text{Cu,Al})$ and Ti_3Al it may be concluded that they precipitate at the cooling [12]. Furthermore, the intermetallics formed during brazing temperature are also observed, mainly in the large block forms near Al_2O_3 and Ti-6Al-4V alloy side.

It is noticeable that $\text{Ti}_2(\text{Cu,Al})$ intermetallics, i.e. Area III formation in brazing joint occur when TiB_2 powders are added into the Cu powders. This substantial difference results from an important factor that affects $\text{Ti}_2(\text{Cu,Al})$ intermetallics formation, namely the presence of B atoms in the composite filler. The examination of the mixing enthalpies of Ti-B (-42 kJ/mol) clearly indicates that its formation in the liquid generate plenty of heat, as a result, the temperature of reaction zone is improved, thus a large amount of TiB distributes in the joint and that of Ti or Al atoms from Ti-6Al-4V alloy inwardly diffuse into brazing joint, eventually, joint microstructure with $\text{Cu} + \text{TiB}_2$ composite filler compared with pure Cu filler changes apparently. On the other hand, a significant decrease in Area II is detected. This decrease can be attributed to trapping of part of Ti atoms available in the liquid alloy by TiB_2 action during brazing process.

3.3. Effect of brazing temperature and holding time on $\text{Al}_2\text{O}_3/\text{Ti-6Al-4V}$ alloy joints microstructure

Two composition joints (10 and 30 vol.% TiB) are studied as shown in Figs. 5(a) and (c), 2(a) and 4(b). Joint shown in Fig. 5(a) and (c) are brazed at $970^\circ\text{C}/10 \text{ min}$, and that shown in Figs. 2(a) and 4(b) are brazed at $930^\circ\text{C}/10 \text{ min}$. Effect of brazing temperature on joint microstructure is investigated by Figs. 5(a) and (c), 2(a) and 4(b). The most visible change comes in Area III. For the joint with 10 vol.% TiB , the quantity of dissolved Ti and the generated quantum of $\text{Ti}_2(\text{Cu,Al})$ increases at 970°C of brazing temperature, compared with 930°C . However, for the joint containing 30 vol.% TiB , $\text{Ti}_2(\text{Cu,Al})$ content decreases at 970°C of brazing temperature owing to the addition increasing of TiB_2 . In agreement with the analysis presented in the previous Section 3.2, the strong temperature effect is a combination of two effects. One direct effect is related to the temperature. The other indirect effect may result from the increase in B atoms from TiB_2 powders. Both of the factors favor $\text{Ti}_2(\text{Cu,Al})$ intermetallics forming.

The effect of holding time is studied for the joint with 10 and 30 vol.% TiB , respectively as shown in Figs. 5(b) and (d), 2(a) and 4(b). The joint microstructure tends to be even and Ti_2Cu intermetallics distribute in the whole joint when the holding time is 30 min. For the joint with 10 vol.% TiB , Area III moves to Ti-6Al-4V alloy side and Area IV becomes narrow when the holding time is 30 min. For the joint with 30 vol.% TiB , however, Area III moves to Al_2O_3 side, and Area IV broadens. The reaction between B atoms and Ti atoms is an important factor, which leads to the evolution of considerable heat with the increasing of B atoms. Therefore, the change of Area IV results from the long holding time and the released heat as TiB forming.

Table 1

EDS compositional analysis results of the $\text{Al}_2\text{O}_3/\text{Ti-6Al-4V}$ joint ($T=930^\circ$, $t=10 \text{ min}$).

Element (at.%)	O	Al	Ti	Cu	B	Possible phase
A	15.99	8.68	55.40	19.93	–	$\text{Ti}_4(\text{Cu,Al})_2\text{O}$
B	–	7.29	60.73	31.97	–	Ti_2Cu
C1	–	20.65	64.07	15.28	–	$\text{Ti}_2(\text{Cu,Al})$
C2	–	11.14	67.72	21.14	–	$\text{Ti}_2(\text{Cu,Al})$
C3	–	11.35	67.45	21.19	–	$\text{Ti}_2(\text{Cu,Al})$
C4	–	8.93	69.91	21.16	–	$\text{Ti}_2(\text{Cu,Al})$
D	–	22.31	70.06	7.63	–	Ti_3Al
E	–	22.65	24.48	52.87	–	AlCu_2Ti
F	–	3.79	43.56	6.78	45.87	TiB

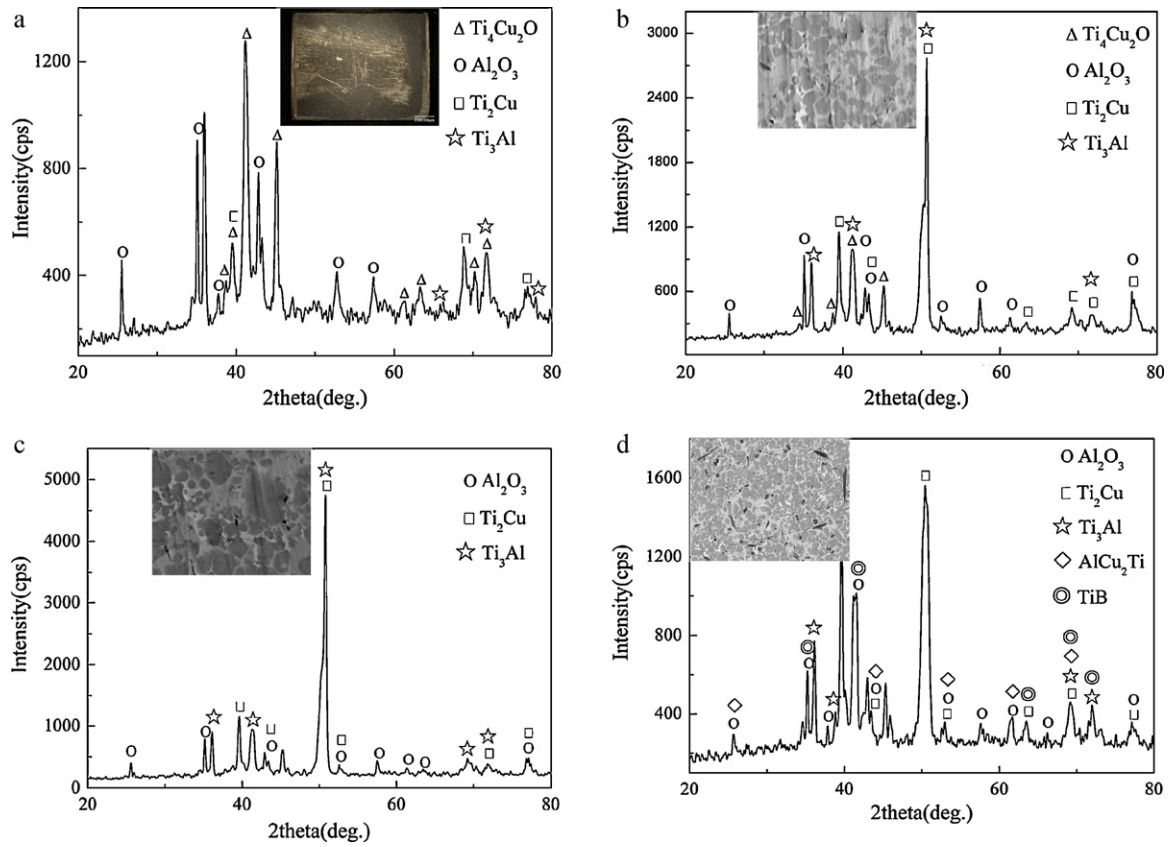


Fig. 3. XRD results of every area after stripping layer by layer (a) mixing layer of Areas I and II, (b) Area II, (c) Area III, and (d) Area IV.

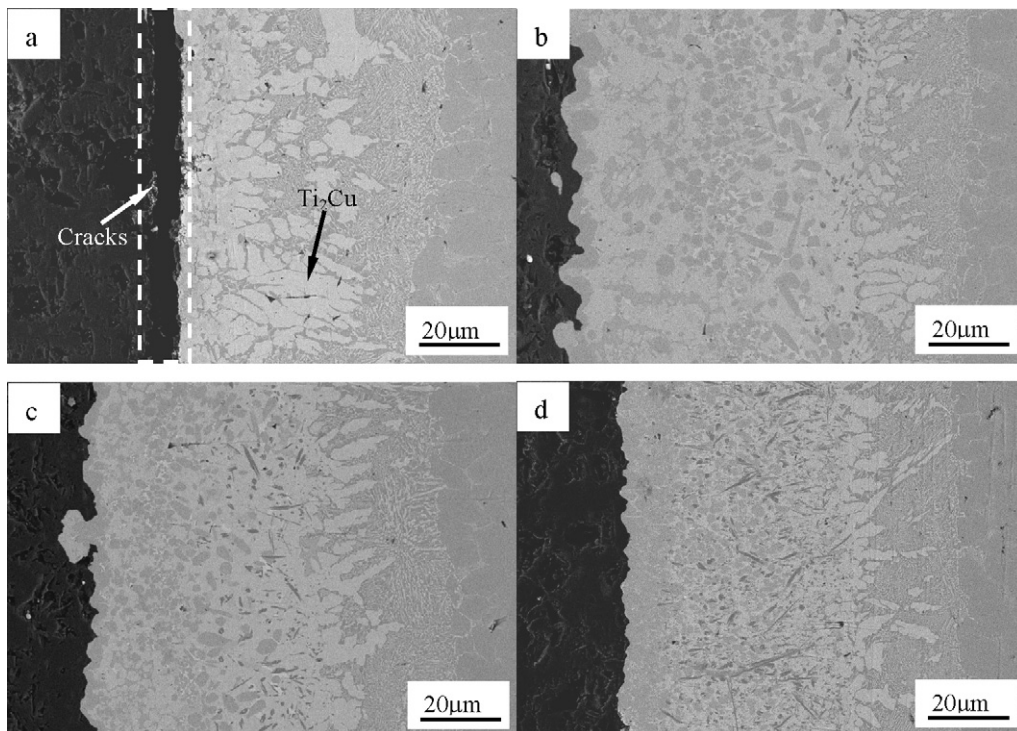


Fig. 4. Microstructure of $\text{Al}_2\text{O}_3/\text{Ti-6Al-4V}$ alloy joints containing different volume fraction of TiB (a) 0 vol.%, (b) 10 vol.%, (c) 20 vol.%, and (d) 50 vol.%.

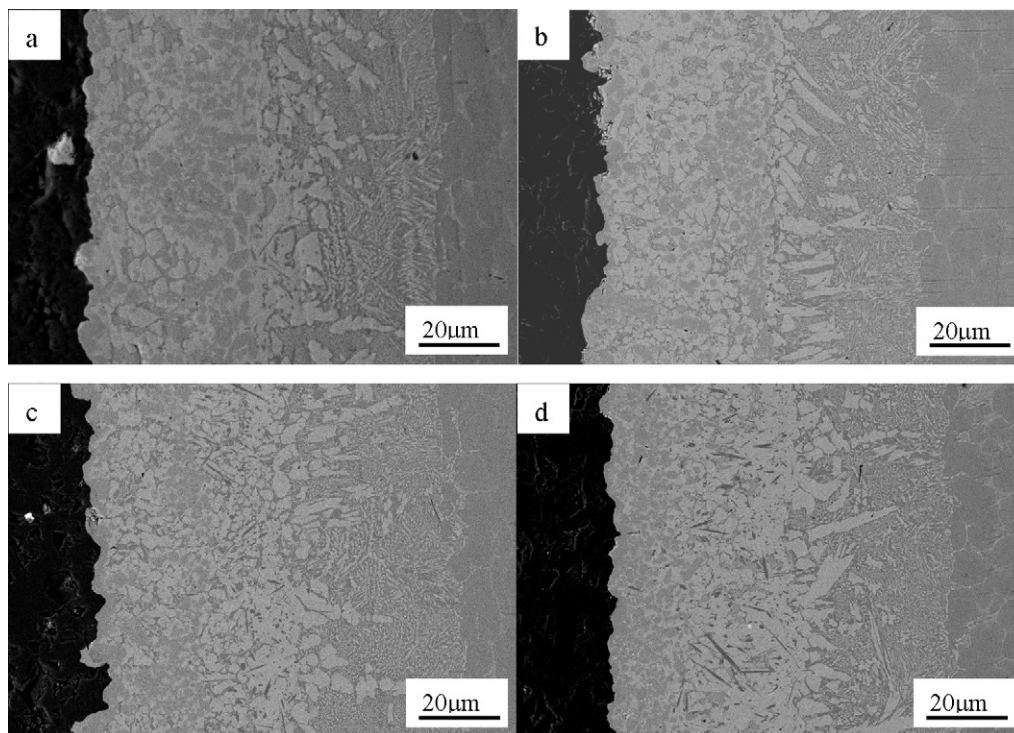


Fig. 5. Microstructure of $\text{Al}_2\text{O}_3/\text{Ti-6Al-4V}$ alloy joints containing 10 vol.% TiB brazed (a) at 970°C for 10 min, (b) at 930°C for 30 min, and containing 30 vol.% TiB brazed (c) at 970°C for 10 min, (d) at 930°C for 30 min.

3.4. Formation mechanism and microstructural evolution of $\text{Al}_2\text{O}_3/\text{Ti-6Al-4V}$ alloy joints

The formed phases are largely Ti–Cu based compounds in $\text{Al}_2\text{O}_3/\text{Ti-6Al-4V}$ alloy joint brazed at $930^\circ\text{C}/10$ min as shown in Fig. 2. Some of Ti–Cu based compounds are stable not only at room temperature but also at 930°C of brazing temperature. It is expected that the formation of the phases is closely related with an isothermal solidification and a subsequent solid-state interdiffusion between the base metals and molten liquid during the isothermal holding at brazing temperature [13]. The others are not stable at 930°C and form during cooling. The microstructure evolution during brazing process can also be estimated by the microstructure and compositions of each joint at room temperature, although the cooling rate after the isothermal holding is not rapid enough to eliminate a compositional change.

Figs. 4 and 5 show that the atomic interdiffusion occurs through the amount and distribution of formed phases varying in joint. Based on the compositional variation and the morphologies of formed phase as shown in Fig. 2, the microstructure evolution of joint brazed at $930^\circ\text{C}/10$ min is divided into four stages: (1) formation of interfacial $\text{Ti}_4(\text{Cu,Al})_2\text{O}$ in Al_2O_3 side (labeled layer I), (2) formation of Ti_2Cu and Ti_3Al in Al_2O_3 side, together with TiB, Ti_2Cu , and AlCu_2Ti in Ti-6Al-4V alloy side, (3) formation of $\text{Ti}_2(\text{Cu,Al})$ and AlCu_2Ti intermetallics, (4) formation of Ti + Ti_2Cu hypereutectoid organization adjacent to Ti-6Al-4V alloy (labeled layer V).

Stage (1): according to Cu–Ti phase diagram, the system has a eutectic temperature of 875°C . When the temperature is elevated to the eutectic temperature of Cu–Ti system, Cu atoms from Cu + TiB_2 composite filler start to react with Ti atoms from Ti-6Al-4V alloy. Liquid Cu–Ti eutectic then forms at the interface between brazing filler and Ti-6Al-4V alloy. Cu, B atoms from brazing filler and Ti, Al from Ti-6Al-4V alloy begin to dissolve into the appeared liquid until the brazing filler entirely melts as temperature rises. Cu atoms diffuse towards Al_2O_3 side and Ti-6Al-4V

alloy side, respectively. Ti and Al atoms dissolved from Ti-6Al-4V alloy diffuse towards liquid brazing filler. The reaction among Ti, Cu, Al and O atoms occurs on the Al_2O_3 surface by sufficient Ti atoms aggregating at the Al_2O_3 /brazing alloy interface under the action of concentration gradient, and the attraction of O atoms on the Ti atoms as well. $\text{Ti}_4(\text{Cu,Al})_2\text{O}$ compounds form immediately to Al_2O_3 . Moreover, at Ti-6Al-4V alloy side, the inwardly diffused Ti atoms are isothermally solidified into the Ti solid solution layer by reacting with the Cu atoms outwardly diffused from the molten liquid.

Stage (2): Ti_2Cu phases form not only in Ti-6Al-4V alloy interfacial area, but also in Al_2O_3 interfacial area (light gray phases in Areas II and IV). Ti-6Al-4V alloy dissolves actively at the initial stage of brazing. The reactions between Cu from brazing filler and Ti, Al from Ti-6Al-4V alloy proceed. Ti_2Cu phases start to nucleate in $\text{Ti}_4(\text{Cu,Al})_2\text{O}$ or βTi site and grow into the joint. With the diffusion of Al atoms, Ti_3Al phases precipitate in interdendritic region. TiB phases in situ synthesize and distribute in Ti_2Cu formed at Ti-6Al-4V alloy side. This is because B atoms diffuse towards Ti-6Al-4V alloy due to the strong interaction between B and Ti (-42 kJ/mol). As its melting point of 2980°C (much higher than the brazing temperature), TiB_2 powders, which contact with the liquid system, will react with Ti atoms as well [14]. With the reaction of $\text{Ti} + \text{TiB}_2 \rightarrow \text{TiB}$, TiB forms with a needle-like shape because TiB has an anisotropic growth behavior [15], as shown in Fig. 2(c). Areas II and IV are thereby evolved by the isothermal solidification of the molten liquid at stage (2). But there are some liquid existed in the grain boundary of Ti_2Cu , and others are ejected into the center of $\text{Al}_2\text{O}_3/\text{Ti-6Al-4V}$ alloy joint by Ti_2Cu .

Stage (3): it is expected that $\text{Ti}_2(\text{Cu,Al})$ forms through the residual molten liquid in the grain boundary of Ti_2Cu because the diffusion of Al atoms dissolve in Cu atoms. Similar to the molten liquid in the vicinity of the previously formed Ti_2Cu phase, $\text{Ti}_2(\text{Cu,Al})$ intermetallics start to solidify isothermally, and then AlCu_2Ti solidify at this area as Ti atoms decrease in residual molten liquid.

The solute concentration of residual liquid rises because of the unbalanced inward diffusion of the Ti and Al atoms that lowers the solidification temperature. Simultaneously, the composition undercooling of this area increases gradually, and that will lead to nucleate and serve as nucleus of equiaxed grain during the heated process. It is the reason why $Ti_2(Cu,Al)$ and $AlCu_2Ti$ form from residual molten liquid. Namely Al atoms previously included in the Cu or Ti atoms dissolve out for limited solubility as temperature drops. For the joint with 10 vol.% TiB, $Ti_2(Cu,Al)$ content in Area III increases with the rise of brazing temperature or holding time as shown in Fig. 5(a) and (b) compared with that brazed at normal parameter as shown in Fig. 4(b) due to the increasing diffusion of Ti and Al atoms through the solid/liquid interface from Ti-6Al-4V alloy. $Ti_2(Cu,Al)$ content decreases, however, when the joint with 30 vol.% TiB is brazed at high brazing temperature or long holding time as shown in Fig. 5(c) and (d) compared with that brazed at normal parameter as shown in Fig. 2(a). Because some of Ti atoms react with TiB_2 , others form Ti_2Cu firstly in Areas II and IV, respectively. The high brazing temperature means the high growth rates on intermetallics. The key factor to the formation of $Ti_2(Cu,Al)$ and $AlCu_2Ti$ is the interdiffusion of Ti and Al atoms between residual molten liquid and Ti_2Cu solidified previously.

Stage (4): temperature decreases after the holding process, hypereutectoid $\alpha Ti + Ti_2Cu$ organizations precipitate by the eutectoid reaction: $(\beta Ti) \leftrightarrow (\alpha Ti) + Ti_2Cu$ during cooling process until the temperature drops to 790 °C. So far $Al_2O_3/Ti-6Al-4V$ alloy joint has already well formed.

3.5. Mechanical properties of $Al_2O_3/Ti-6Al-4V$ alloy joints

3.5.1. Room temperature properties

The joints keep their mechanical integrity although the difference in CTE among Al_2O_3 ($\alpha_{Al_2O_3} = 7.6 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$), brazing filler ($\alpha_{Cu} = 17 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) and Ti-6Al-4V ($\alpha_{Ti-6Al-4V} = 8.6 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$). The microstructure of joint shows that TiB content has an important effect on forming a stable reaction layer between Al_2O_3 and Ti-6Al-4V alloy in Figs. 2 and 4. Thus to be able to optimize the reactive brazing process it is necessary to understand the influence of TiB content on the mechanical performance of the joint due to the low CTE ($\alpha_{TiB} = 8 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) of TiB.

The shear strength of $Al_2O_3/Ti-6Al-4V$ alloy joints brazed at 930 °C/10 min with different volume fraction of TiB is shown in Fig. 6(a). The joints shear strength increases from 26.45 to 96.76 MPa with the TiB content from 0 to 30 vol.%. The notable increase in joint shear strength results from the adequate amount of TiB, which can reasonably match the CTE of the brazing alloy to that of Al_2O_3 for alleviating the residual thermal stress of the joint. On the other hand, the formation of multi-layer structure of ductile-rigid-ductile as shown in Fig. 7 due to the addition of TiB_2 , can reduce the strain energy most effectively and help to alleviate the joint residual stress [16,17]. TiB phases distribute in Ti_2Cu and make Area IV act as metal matrix composite liked structure [18,19]. Furthermore, in situ synthesized TiB can act as reinforcement of $Al_2O_3/Ti-6Al-4V$ alloy joints. But the joint shear strength drops from 96.76 MPa to 44.31 MPa till TiB content increased from 30 to 50 vol.%. It was believed that more TiB brought more reinforcements in joint and led to a brazing layer with a higher elastic modulus [20]. Then the joint thermal stress, generating during brazing process, cannot be relaxed effectively, and a high thermal residual stress will be kept in the joint. As a result, only with suitable TiB whiskers contents can the shear strength of joints be improved.

Fig. 6(b) shows the shear strength of $Al_2O_3/Ti-6Al-4V$ alloy joint with 30 vol.% TiB at 930 °C/10 min, 970 °C/10 min and 930 °C/30 min, respectively. The joint shear strength achieves the maximum value 96.76 MPa at 930 °C/10 min. For the joint brazed at 970 °C/10 min and 930 °C/30 min, the joint shear strength decreases

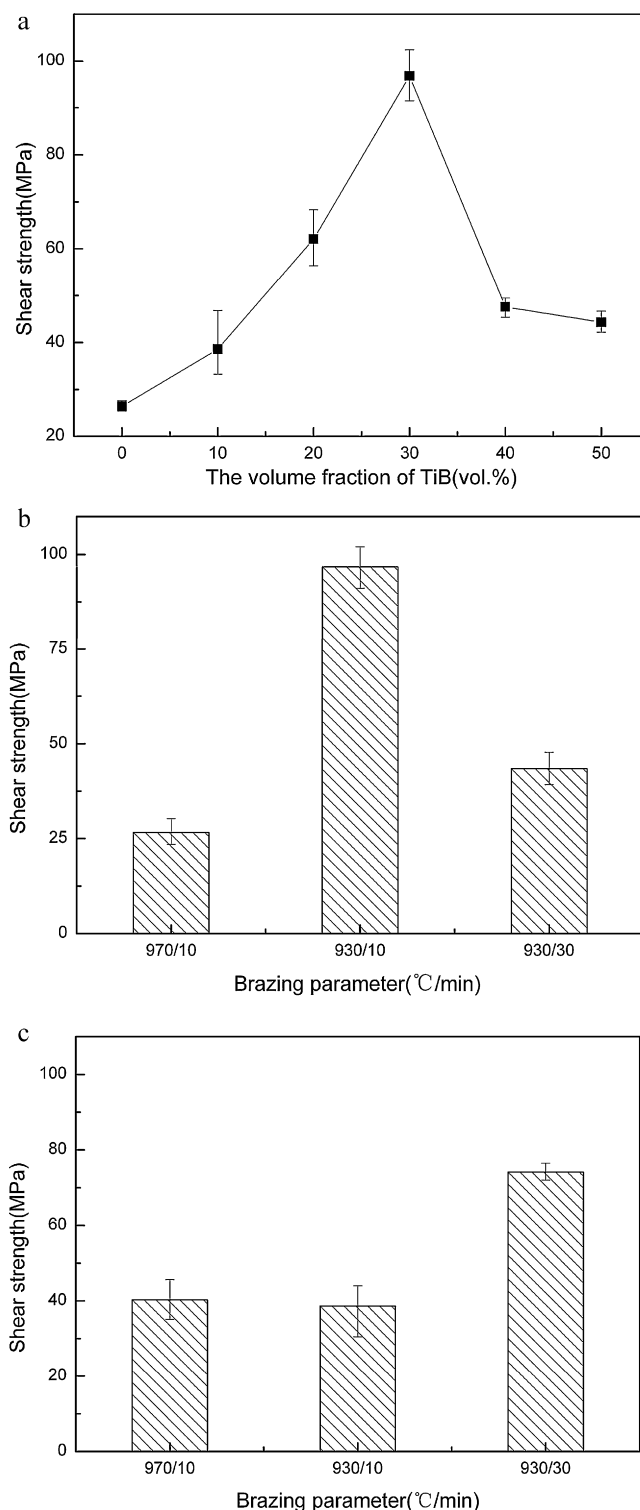


Fig. 6. Shear strength of $Al_2O_3/Ti-6Al-4V$ alloy joints with (a) different volume fraction of TiB at 930 °C for 10 min, (b) 30 vol.% TiB at different brazing parameter, and (c) 10 vol.% TiB at different brazing parameter.

to 26.63 MPa and 43.45 MPa, respectively. This decrease results from much more Ti and Al atoms diffusing into brazing layer from Ti-6Al-4V alloy, that leads to increasingly hard, brittle Ti_3Al phases form in joints under excessive temperature or long holding time. And the multi-layer structure of ductile-rigid-ductile disappears gradually in joints due to Ti_2Cu rapid growth rate. At the same time, $Ti_2(Cu,Al)$ content reduces, and Area III becomes thin, that is

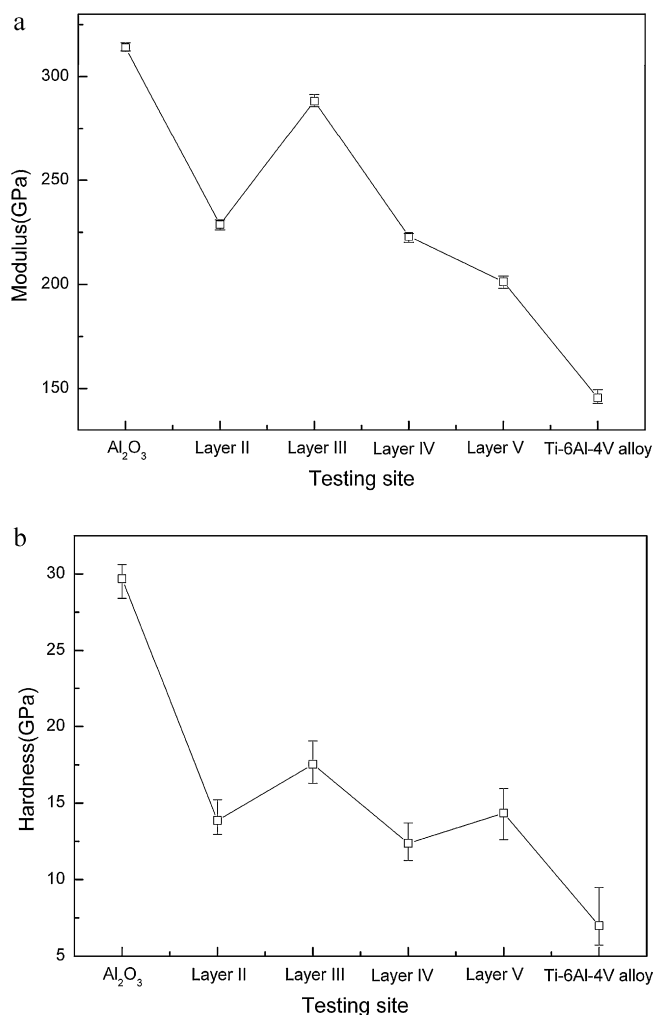


Fig. 7. (a) Elastic modulus and (b) hardness of each area on the Al₂O₃/Ti-6Al-4V alloy joint with 30 vol.% TiB at 930 °C for 10 min.

consistent with the interpretation of the stages (3) and (4). Eventually, the joint residual stress is not readily alleviated, and the joint shear strength decreases.

Fig. 6(c) shows the shear strength of Al₂O₃/Ti-6Al-4V alloy joints with 10 vol.% TiB brazed at 930 °C/10 min, 970 °C/10 min and 930 °C/30 min. It is noteworthy that the shear strength of joint with 10 vol.% TiB brazed at 930 °C/10 min is 38.63 MPa, which is lower than the results in 970 °C/10 min and 930 °C/30 min. As the brazing parameter is 930 °C/30 min, the joint shear strength reaches the maximum of 74.11 MPa. It can be attributed to the formation of ductile-rigid-ductile multi-layer structure. When the joint is brazed at 970 °C/10 min, the multi-layer structure does not appear, and Ti₂(Cu,Al) phases randomly distribute in the whole joint. Thus the joint shear strength is only 40.30 MPa, which is almost not improved. The variation of joint room shear strength is associated with the joint microstructure, and they are mainly decided by the content of Ti atoms dissolved in joint.

3.5.2. High temperature properties

The effect of in situ synthesized TiB on high temperature shear strength of Al₂O₃/Ti-6Al-4V alloy joints is investigated as shown in Fig. 8. The shear strength of joint with 30 vol.% TiB brazed at 930 °C/10 min is compared with that of joint without TiB at high temperature, i.e. 400 °C, 500 °C, 600 °C, 700 °C and 800 °C. It indicates that the high temperature shear strength of joint with 30 vol.% TiB can be maintained above 70 MPa, and all of that are higher than

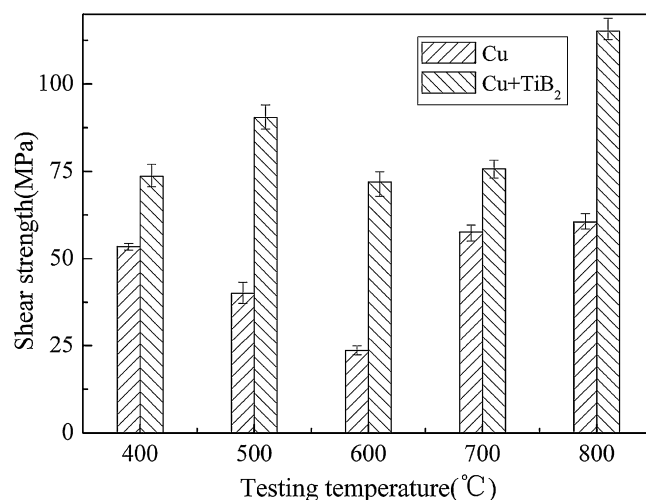


Fig. 8. Summary of the high temperature shear strength results of Al₂O₃/Ti-6Al-4V alloy joints.

joints without TiB. The high temperature shear strength of joint without TiB is higher than the room temperature shear strength of the joint. As can be seen that the shear strength of joints without TiB decreases firstly, and then increases as the temperature rises. Because brazing alloy increasingly softens with the increasing of load testing temperature, subsequently leading to the decrease in load-carrying. When the testing temperature ranges from 700 to 800 °C, the increase in joint shear strength can be attributed to the residual stress release and increase in adhesive force between brazed seam and based materials.

The high temperature shear strength of joint with 30 vol.% TiB is lower than room temperature shear strength of the joint. The joint shear strength increases to 90.39 MPa at 500 °C, decreases to 71.99 MPa at 600 °C, and then increases to 115.16 MPa at 800 °C, which is about 118% in room temperature shear strength. It can be attributed to that TiB acted as ceramic skeleton exists in joints owing to its high melting point. Therefore, the joint containing TiB phases will be less likely to fail at high temperature.

4. Conclusions

With regard to using Cu + TiB₂ composite filler to braze Al₂O₃ and Ti-6Al-4V alloy, the effect of in situ synthesized TiB content, brazing temperature and holding time on joint microstructure and shear strength is investigated. Furthermore, the joint microstructure evolution is particularly interpreted.

- (1) The typical microstructure of Al₂O₃/Ti-6Al-4V alloy joint brazed at 930 °C/10 min is Al₂O₃/Ti₄(Cu,Al)₂O/Ti₂Cu + Ti₃Al + Ti₂(Cu,Al)/Ti₂(Cu,Al) + AlCu₂Ti/Ti₂Cu + AlCu₂Ti + Ti₃Al + Ti₂(Cu,Al) + TiB/Ti + Ti₂Cu/Ti-6Al-4V alloy.
- (2) The addition increasing of TiB₂ leads to an increase in both the volume fraction of TiB and the dissolution of Ti from Ti-6Al-4V alloy. Moreover, the generation amount of Ti₂(Cu,Al) intermetallics increases and the location of them mainly assembles in Al₂O₃ side. Meanwhile, AlCu₂Ti intermetallics disappear in Area III as TiB₂ content rises.
- (3) The content of Ti₂(Cu,Al) intermetallics increases in joint containing 10 vol.% TiB brazed at high brazing parameter, but decreases in joint containing 30 vol.% TiB brazed at high brazing parameter. Likewise, area III of joint moves to Ti-6Al-4V alloy side in former joint, but moves to Al₂O₃ side at the latter joint.
- (4) Based on the compositional variation and the formed phase morphology, the joint microstructure evolution at

930 °C/10 min is divided into four stages: (1) formation of interfacial $Ti_4(Cu,Al)_2O$ in Al_2O_3 side, (2) formation of Ti_2Cu and Ti_3Al in Al_2O_3 side, together with TiB, Ti_2Cu , and $AlCu_2Ti$ in Ti–6Al–4V alloy side, (3) formation of $Ti_2(Cu,Al)$ and $AlCu_2Ti$, (4) formation of Ti + Ti_2Cu hypereutectoid organization adjacent to Ti–6Al–4V alloy.

- (5) When the tests are performed at room temperature, the shear strength of joint with 30 vol.% TiB reaches the maximum of 96.76 MPa at 930 °C/10 min, and the shear strength of joint containing 10 vol.% TiB reaches the maximum of 74.11 MPa at 930 °C/30 min. When the tests are performed at high temperature, the high temperature shear strength of joint with 30 vol.% TiB was 115.16 MPa at 800 °C, which is about 118% in room temperature shear strength of joint, because TiB can serve to ceramic skeleton in joints at high temperature.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (NSFC, Grant number 50975062, 51105107 and 51021002), and the Fundamental Research Funds for the Central Universities (Grant No. HIT.BRET1. 2010006, HIT.NSRIF.2010119 and HIT.NSRIF. 201135).

References

- [1] R.K. Shiue, S.K. Wu, Y.T. Chen, C.Y. Shiue, *Intermetallics* 16 (2008) 1083–1089.
- [2] R. Asthana, M. Singh, *J. Eur. Ceram. Soc.* 28 (2008) 617–631.
- [3] M. Paulasto, F.J.J. van Loo, J.K. Kivilahti, *J. Alloys Compd.* 220 (1995) 136–141.
- [4] A. Levy, *J. Am. Ceram. Soc.* 74 (1991) 2141–2147.
- [5] Y.M. He, J. Zhang, Y. Sun, C.F. Liu, *J. Eur. Ceram. Soc.* 30 (2010) 3245–3251.
- [6] Z. Zhong, Z. Zhou, C. Ge, *J. Mater. Process. Technol.* 209 (2009) 2662–2670.
- [7] G.B. Lin, J.H. Huang, *Powder Metall.* 49 (2006) 345–348.
- [8] P. He, M.X. Yang, T.S. Lin, Z. Jiao, *J. Alloys Compd.* 509 (2011) L289–L292.
- [9] M. Brochu, M.D. Pugh, R.A.L. Drew, *Ceram. Int.* 30 (2004) 901–910.
- [10] G. Blugan, J. Kuebler, V. Bissig, J. Jancazk-Rusch, *Ceram. Int.* 33 (2007) 1033–1039.
- [11] M.X. Yang, T.S. Lin, P. He, Y.D. Huang, *Mater. Sci. Eng. A* 528 (2011) 3520–3525.
- [12] O. Kozlova, M. Braccini, R. Voytovych, N. Eustathopoulos, P. Martinetti, M.F. Devismes, *Acta Mater.* 58 (2010) 1252–1260.
- [13] J.G. Lee, G.H. Kim, M.K. Lee, C.K. Rhee, *Intermetallics* 18 (2010) 529–535.
- [14] T.S. Lin, M.X. Yang, P. He, C. Huang, F. Pan, Y.D. Huang, *Mater. Des.* 32 (2011) 4553–4558.
- [15] S. Gorsse, J.P. Chaminade, Y. Le Petitcorps, *Compos. A: Appl. Sci. Manuf.* 29 (1998) 1229–1234.
- [16] X.H. Wang, D. Li, L.D. Lu, X. Wang, *J. Alloys Compd.* 237 (1996) 45–48.
- [17] X.L. Wang, C.R. Hubbard, S. Spooner, S.A. David, B.H. Rabin, R.L. Williamson, *Mater. Sci. Eng. A* 211 (1996) 45–53.
- [18] Z.H. Jiang, J.S. Lian, D.Z. Yang, S.L. Dong, *Mater. Sci. Eng. A* 248 (1998) 256–275.
- [19] M.X. Yang, T.S. Lin, P. He, Y.D. Huang, *Brazing of Al_2O_3 to Ti-6Al-4V alloy with in situ synthesized TiB-whisker-reinforced active brazing alloy*, *Ceram. Int.* 37 (2011) 3029–3035.
- [20] H. Xiong, C. Wan, Z. Zhou, *J. Mater. Process. Technol.* 75 (1998) 137–142.