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Microstructure evolution of Al_2O_3/Al_2O_3 joint brazed with Ag–Cu–Ti + B + TiH_2 composite filler

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Abstract

Al_2O_3/Al_2O_3 joint was achieved using Ag–Cu–Ti + B + TiH_2 composite fillers at 900 °C for 10 min. The evolution mechanism of interface during brazing was discussed. Effects of Ti and B atoms content on microstructure of joints were investigated. Results show that a continuous and compact reaction layer $Ti_3(Cu,Al)_3O$ forms at Al_2O_3/brazing alloy interface. Ti(Cu,Al) precipitates near $Ti_3(Cu,Al)_3O$ layer. In situ synthesized TiB whiskers evenly distribute in Ag and Cu based solid solution. The higher content of B powders in composite fillers increases TiB whiskers content, but decreases the thickness of $Ti_3(Cu,Al)_3O$ layer, while the higher TiH_2 powders content thickens $Ti_3(Cu,Al)_3O$ layer. Ag and Cu based solid solutions become uniform and fine with the increasing of TiB whiskers content. Ti(Cu,Al) intermetallics content increase and they gradually distribute from Al_2O_3 side to the central of brazing alloy, but the content of Cu based solid solution decreases when the TiH_2 content increases.

Keywords: A. Joining; B. Whiskers; B. Electron microscopy; D. Al_2O_3

1. Introduction

Ceramics are covering a growing application field due to their specific properties such as high temperature stability, corrosion and wear resistance. To construct ceramic parts and components, ceramics have to be machined, and that can be a difficult and time consuming task due to their high hardness and brittleness [1–3]. For the integration of ceramic components into complex shapes, it can be advantageous to use joining techniques such as active brazing. However, the key problem is the present of joints residual stress resulted from the mismatch of thermal expansion coefficient (CTE) and elastic modulus between ceramic and brazing alloy [4]. The solution for above challenge is generally to add low CTE materials, such as powders of superalloys [5,6], ceramics [7–12] or carbon fibers [13–15], into the convention brazing filler metals to form composite fillers. The proposed method has many intrinsic limitations. The reinforcements are difficult to be distributed evenly in brazing alloy and reinforcements always have bad wetting ability with intermetallics [16]. However in situ synthesized low CTE materials originated from brazing process have greater reinforcing effects due to their fine size, uniform distribution, favorable cohesion with matrix, and good wettability. TiB has been identified as possessing the most appropriate balance of thermochemical stability, good mechanical properties and thermal expansion among low CTE materials formed during brazing [17].

The present study was carried out to braze Al_2O_3 using Ag–Cu–Ti + B + TiH_2 composite filler with TiB whiskers as low CTE material. In this paper, TiB whiskers in situ synthesized during brazing process were investigated. The evolution mechanism of interface during brazing was discussed. And the effects of B and Ti content on brazed joints microstructure were examined.

2. Materials and experimental procedures

Al_2O_3 was cut into the specimens with size of 5 mm × 5 mm × 3 mm by diamond discs, and then all specimens were ultrasonically cleaned in acetone. The commercially available Ag–26.4Cu–4.5Ti (wt.%) filler metal was in powder form with an average size of 50 μm. B powders with an average

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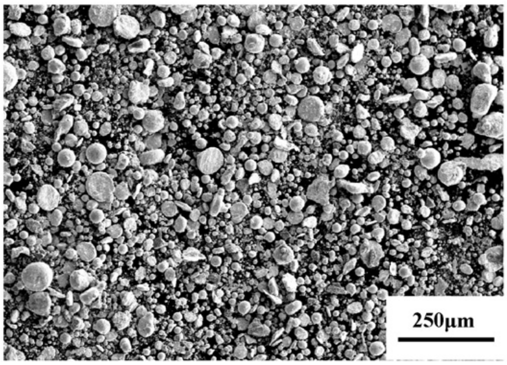

Fig. 1. SEM image of the Ag–Cu–Ti + 1.5 wt.% B + 3 wt.% TiH_2 (wt.%) as-mixed powders.

diameter of 1 μm were added into Ag–26.4Cu–4.5Ti filler metal. 0.35, 0.72 and 1.5 wt.% B powders corresponding to formation of 5, 10 and 20 vol.% TiB in brazing layer were added into composite fillers. Meanwhile, TiH_2 powders were applied as a good replacement in composite fillers, because Ti powders are easy to be oxidized during mechanical milling. TiH_2 powders with an average size of 50 μm were employed to change Ti content in composite fillers. The overall mass fractions of TiH_2 particles in composite fillers were 0, 1, 3 and 5 wt.% respectively. Fig. 1 shows the SEM micrograph taken for the Ag–Cu–Ti + 1.5 wt.% B + 3 wt.% TiH_2 composite filler fabricated by mechanical mixing before brazing.

The composite filler was mixed by binder to make into paste. Then the brazing paste was placed between two Al_2O_3 samples and then the assembly was brazed in a vacuum furnace with a pressure of 3.0×10^{-4} Pa. During brazing, the specimen was first heated to 450 °C at a rate of 20 °C/min, and held for 20 min to volatilize the organic glue and ensure that the brazing surfaces were clean. Then the specimen was heated to 750 °C at a rate of 10 °C/min, held for 30 min at the temperature to ensure that TiH_2 could be thoroughly decomposed and then heated to the brazing temperature of 900 °C at a rate of 5 °C/min. After being held at 900 °C for 10 min, the specimen was cooled down to 400 °C at 5 °C/min and then cooled in the furnace without power.

To characterize microstructure of the joints, the polished cross-section of the brazed joints was examined by means of scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS).

3. Results and discussion

3.1. Microstructure of the Al_2O_3/Al_2O_3 joint

Fig. 2 shows the microstructure and the corresponding element area distribution of the Al_2O_3/Al_2O_3 joint brazed with Ag–Cu–Ti + 1.5 wt.% B + 3 wt.% TiH_2 composite filler. 20 vol.% TiB whiskers in situ synthesize in joint. The brazing layer exhibits sound bonding between Al_2O_3 and brazing alloy as shown in Fig. 2(a). The joint consists of three layers: continuous reaction Layer I with thickness of 2.5 μm next to Al_2O_3, discontinuous Layer II comprised of black particle E near Layer I, and Layer III containing fine Phase C, bright phase A and grey phase B.

Fig. 2(b) presents magnified back-scattered micrograph of Area α in Fig. 2(a). It can be clearly seen that TiB is a needle-like compound, which forms during brazing process. Neither pores nor voids appear at the interface between TiB whiskers and bright based solid solution or grey based solid solution, indicating a good wettability and closely bonding between in situ synthesized TiB whiskers and bright based solid solution or grey based solid solution. As the TiB eutectic temperature of 1540 °C (much higher than the brazing temperature), B powders contacted with the liquid system would react with Ti element as well, and the forming of TiB follows the diffusion-mechanism. TiB reaction phase forms according to the following reactions:

$$Ti + B \rightarrow TiB \tag{1}$$

$$\Delta G = -163,197 + 6.71T$$

or

$$Ti + 2B \rightarrow TiB_2 \tag{2}$$

$$Ti + TiB_2 \rightarrow 2TiB \tag{3}$$

$$\Delta G = -182,765 + 12.55T$$

According to the literature [18], although the ΔG of formation for TiB_2 reportedly is the most negative in above three reactions, Ti and TiB_2 can further react to form TiB due to the small negative of the free energy of Eq. (3). Meanwhile, the free energy of formation for TiB is negative at the brazing temperature ranging from 779 to 900 °C, based on Eqs. (1)–(3), indicating formation of TiB from both reactions Eqs. (1) and (3) is possible.

Fig. 2(c) shows a continuous Ti layer close to Al_2O_3, indicting that Ti, as an active element, has diffused towards Al_2O_3, due to concentration gradient and adsorption affinity between O and Ti atoms. According to composition analysis listed in Table 1, the continuous reaction layer should be $Ti_3(Cu,Al)_3O$, for the reason that Al (released during the reaction with the Al_2O_3 surface) is intersoluble with Cu (and, to a more limited extent, with Ti) in Ti_3Cu_3O, which is given by the following equation [19,20]:

$$4Ti + 2Cu + \frac{1}{2}O_2 \rightarrow Ti_4Cu_2O \tag{4}$$

$$\Delta G(Ti_4Cu_2O) = RT[4\ \ln\ a_{Ti} + 2\ \ln\ a_{Cu} + 0.5\ \ln\ P_{O_2}]$$

$$3Ti_4Cu_2O \rightarrow 2Ti_3Cu_3O + 6Ti + \frac{1}{2}O_2 \tag{5}$$

$$\Delta G(Ti_3Cu_3O) = \frac{3}{2}\Delta G(Ti_4Cu_2O) - RT\left[3\ \ln\ a_{Ti} + \frac{1}{4}\ln\ P_{O_2}\right]$$

Thermodynamic calculations from ΔG for Ti_3Cu_3O (Eq. (5)) confirm that it is more stable than Ti_4Cu_2O when the brazing

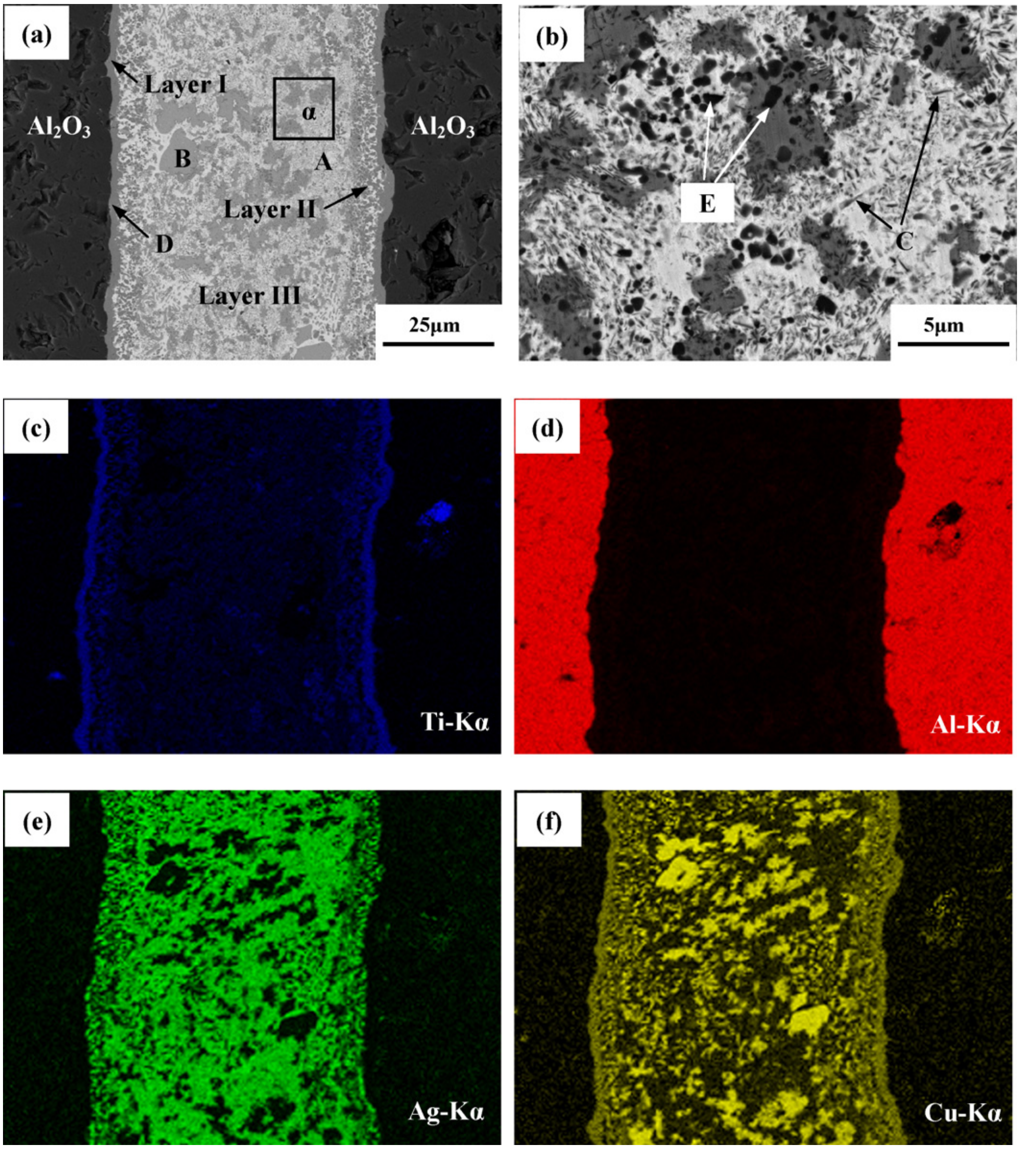

Fig. 2. Morphology and elemental analysis of the Al_2O_3/Al_2O_3 brazed with Ag–Cu–Ti + 1.5 wt.%B + 3 wt.% TiH_2 (20 vol.% TiB whiskers) composite filler at 900 °C for 10 min.

Table 1
The EDS analysis results of Al_2O_3/Al_2O_3 joint brazed with Ag–Cu–Ti + B + TiH_2 at 900 °C for 10 min (at.%).

Phases	O	Al	Ag	Ti	Cu	B	Possible phase
A	–	–	92.49	–	7.51	–	Ag(s.s)
B	–	12.09	2.10	3.60	82.21	–	Cu(s.s)
C	–	3.79	0.90	43.56	9.92	41.82	TiB
D	17.76	16.15	0.45	37.71	27.93	–	$Ti_3(Cu,Al)_3O$
E	–	17.31	2.50	48.64	31.55	–	Ti(Cu,Al)

temperature ranges from 779 ($\Delta G(Ti_3Cu_3O) = -440.5$ kJ/mol) to 900 °C ($\Delta G(Ti_3Cu_3O) = -502.5$ kJ/mol).

Moreover, a number of Ti uniformly distribute in bright Ag based solid solution (Ag(s.s)) (marked by A), which is inconsistent with the Ag–Ti interactions: $\Delta H^{\infty}_{Ag(Ti)} = 25$ kJ/mol [21]. This further proves that the addition of B powders results in TiB whiskers (marked by C) forming first.

In Fig. 2(d), Al can distribute in the whole brazing joint and present higher concentration near Al_2O_3, implying that Al decomposed from Al_2O_3 has diffused towards the liquid brazing alloy. Black Ti(Cu,Al) particles (marked by E) form near Layer I, and then make up Layer II. In Fig. 2(e) and (f), combining with the EDS analysis, the central part of the joint is mainly composed of bright Ag based solid solution and grey Cu

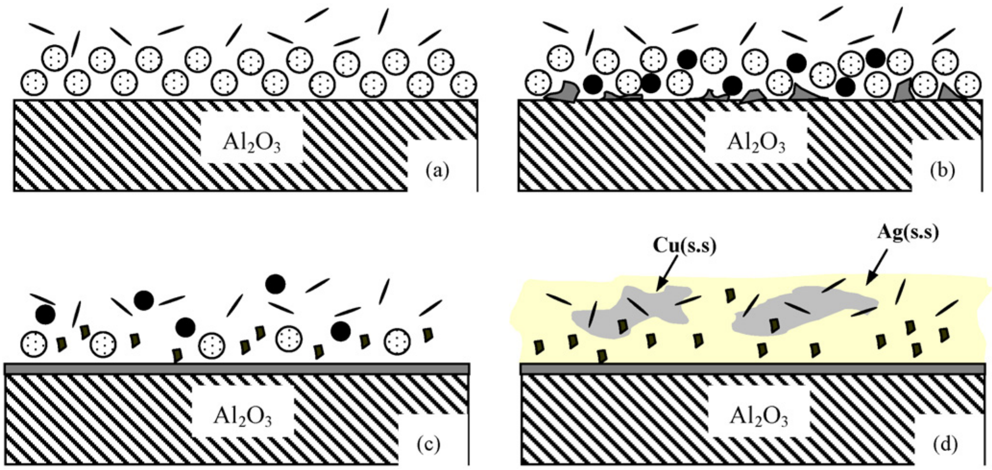

Fig. 3. Schematic diagrams showing the formation processes of the brazing alloy/Al_2O_3 interface. (a) TiB whiskers in situ synthesize and Ti atoms aggregate at the brazing alloy/Al_2O_3 interface, (b) $Ti_3(Cu,Al)_3O$ form and Al atoms liberate by interfacial reaction, (c) $Ti_3(Cu,Al)_3O$ layer and Ti(Cu,Al) form, (d) $Ti_3(Cu,Al)_3O$ layer thickens and size of Ti(Cu,Al) increases, together with Ag(s.s) and Cu(s.s) solidify (● Al atom; ⊙ Ti atom; ╱ TiB whisker; ◢ $Ti_3(Cu,Al)_3O$; ▮ Ti(Cu,Al)).

based solid solution (marked by A), on which a large number of TiB whiskers distributed.

According to the experimental results and thermodynamic analysis above, an evolution of the forming process for the Al_2O_3/brazing alloy interface is presented as shown in Fig. 3. After brazing filler melting, B powders contacted with the liquid system react with Ti, thus TiB whiskers form in brazing layer during heating first by diffusion mechanism. The mixing enthalpies (kJ/mol) are calculated as B–Ti: −42 and Cu–Ti: −17. The interaction of B with Ti is very strong based on ΔG of the formation for TiB and the mixing enthalpies [22]. The addition of B powders makes the total mixing enthalpy more negative and stabilizes the super cooled liquid region. Then excessive Ti atoms aggregate at the Al_2O_3/brazing alloy interface (Fig. 3(a)), due to the interaction of Ti and Ag, and Ti and O as well. $Ti_3(Cu,Al)_3O$ intermetallics form near Al_2O_3 when the concentration of Ti at the Al_2O_3/brazing alloy interface is large enough (Fig. 3(b)). With the increasing of heating temperature, a continuous $Ti_3(Cu,Al)_3O$ layer forms and thickens on Al_2O_3 surface, together with the concentration of Ti decreases and Al increases. When $Ti_3(Cu,Al)_3O$ layer reaches a certain thickness, Ti(Cu,Al) phase nucleates and forms, appearing mainly near $Ti_3(Cu,Al)_3O$ layer and distributing around Cu(s.s) (Fig. 3(c)). It can be believed that Ti atoms dissolved from Cu(s.s) react with Cu forming Ti–Cu compounds, when the solid solution degree of Ti atoms in Cu(s.s) reaches limit. Ti(Cu,Al) subsequently forms for Al atoms from Al_2O_3 dissolving in Cu. From the location and shape of Ti(Cu,Al) intermetallics it may be concluded that they precipitate at the brazing temperature, not during cooling. After that Ag(s.s) and Cu(s.s) solidify in the end during cooling, and TiB whiskers locate in them (Fig. 3(d)).

3.2. *Effect of B powders content on microstructure of the brazed joints*

This effect is investigated using composite filler with four compositions: 0, 0.35, 0.72 and 1.5 wt.% B powders, corresponding to in situ synthesize 0, 5, 10 and 15 vol.% TiB in joints during brazing, when the addition of TiH_2 content is 3 wt.%. There are no different reaction phases forming with B content increasing from 0.35 to 1.5 wt.% as shown in Fig. 4. TiB whiskers distribute uniformly throughout the brazing layer. Ag(s.s) and Cu(s.s) become increasingly uniform and fine when B content increases, because new phase in the melt usually prefers to precipitate around impurity. Thus in situ synthesized TiB whiskers act as nucleation site for Ag(s.s) and Cu(s.s) during brazing. The higher content of TiB whiskers in brazing layer is, the more nucleation center will be supplied for Ag(s.s) and Cu(s.s).

Another remarkable phenomenon is that the increase in B content leads to a decrease in the thickness of reaction layer $Ti_3(Cu,Al)_3O$. It can be inferred that excessive B powders consume a large number of Ti atoms, and the concentration of Ti atoms near Al_2O_3 decreases. The consumption of Ti atoms may lead to insufficient reaction between Ti and Al_2O_3. The too thin interfacial reaction layer is adverse to the joint quality. Therefore, a definite amount of Ti will be supplied to the brazing filler for compensating Ti consumed by B powders. Integrated joints could be achieved with appropriate Ti content in brazing composite filler.

3.3. *Effect of TiH_2 content on microstructure of brazed joints*

Fig. 5 provides the morphology of Al_2O_3/Al_2O_3 joints brazed using composite filler with four compositions: 0, 1, 3, and 5 wt.% TiH_2, in addition to commercially available Ag–Cu–Ti filler containing 4.5 wt.% Ti, when TiB in situ synthesize 10 vol.% in joints during brazing.

The first effect of Ti content is $Ti_3(Cu,Al)_3O$ layer thickening, with the increasing of TiH_2 content from 0 to 3 wt.%. However, the increase in the average thickness of $Ti_3(Cu,Al)_3O$ layer is not accompanied by a significant increase in Ti content ranged from 3 to 5 wt.%. It can be believed that the content of Al and O from Al_2O_3 is definite, although Ti

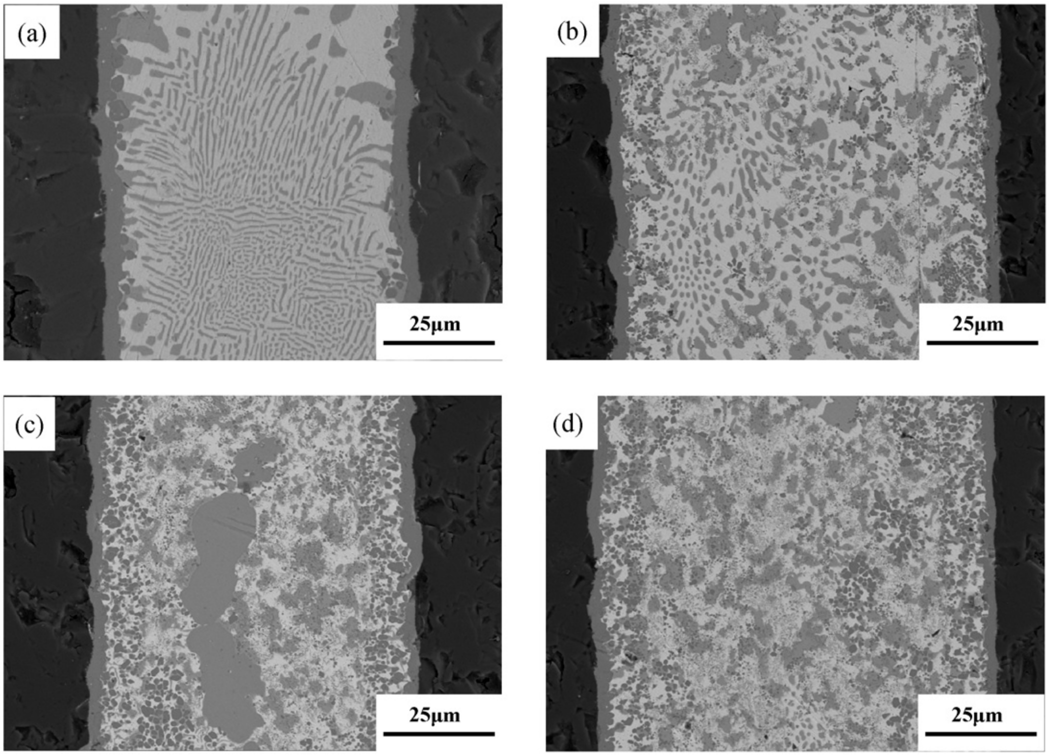

Fig. 4. SEM backscatter images showing the microstructure in different content of B (wt.%) (a) 0, (b) 0.35, (c) 0.72 and (d) 1.5 versus the volume fraction of TiB whiskers (vol.%) (a) 0, (b) 5, (c) 10 and (d) 20.

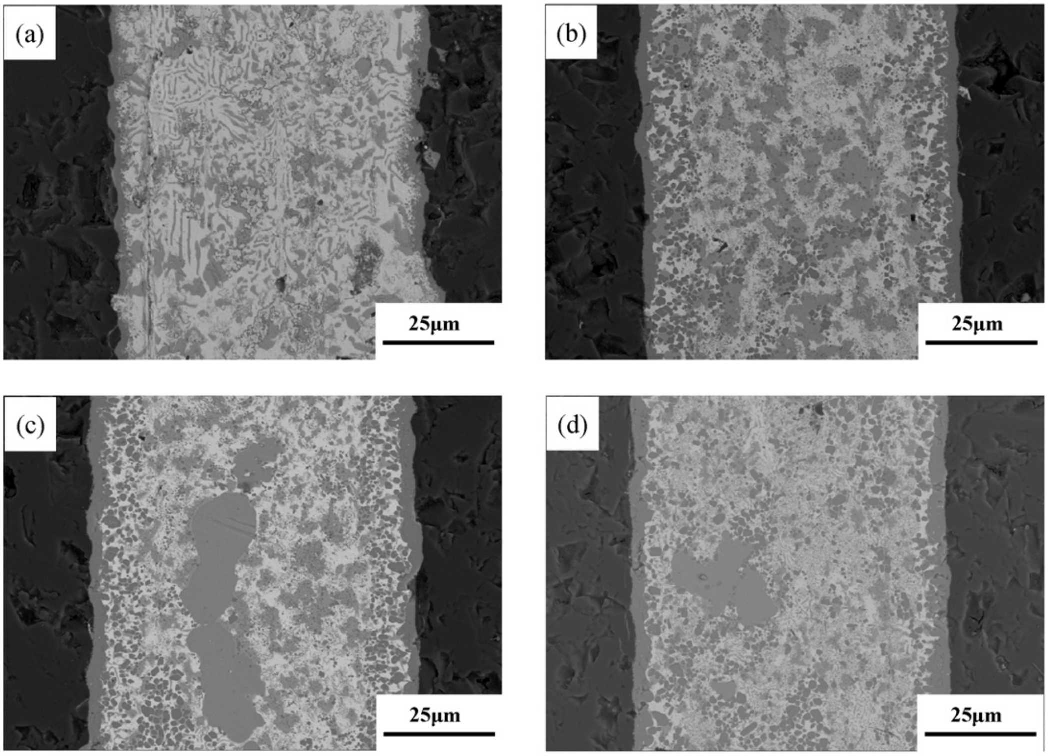

Fig. 5. SEM backscatter images showing the microstructure in different content of TiH_2 (wt.%) (a) 0, (b) 1, (c) 3 and (d) 5.

excessively concentrates on Al_2O_3 side. The residual Ti atoms available in the liquid brazing alloy are trapped by Ti(Cu,Al) intermetallics forming at the brazing temperature. The number of Ti(Cu,Al) intermetallics increase and Cu(s.s) decrease with the increasing of Ti content in brazing alloy. Meanwhile, for TiH_2 content ranging from 0 to 3 wt.%, Ti(Cu,Al) mainly distributes near Al_2O_3 and around Cu(s.s), as can be seen from Fig. 5(a)–(c). When TiH_2 content increases to 5 wt.%, the distribution of Ti(Cu,Al) is more uniform in Layer III, not just at Al_2O_3 side as displayed in Fig. 4(d). This is a predictable result given the formation mechanism of Ti(Cu,Al) and the interaction of Cu–Ti (−17 kJ/mol). Meanwhile, the refinement of Ag(s.s) decreases the exclusion of Ag and Ti.

4. Conclusions

The Al_2O_3/Al_2O_3 joint is successfully brazed using Ag–Cu–Ti + B + TiH_2 composite fillers at 900 °C for 10 min. The joint consists of $Al_2O_3/Ti_3(Cu,Al)_3O$/Ti(Cu,Al)/Ag(s.s) + Cu(s.s) + TiB/Ti(Cu,Al)/$Ti_3(Cu,Al)_3/Al_2O_3$.

The interface evolution process can be divided into four stages: (1) after Ag–Cu–Ti alloy melting, TiB whiskers in situ synthesizing in brazing layer; (2) $Ti_3(Cu,Al)_3O$ reaction layer forming; (3) $Ti_3(Cu,Al)_3O$ reaction layer thickening and Ti(Cu,Al) forming; (4) Ag(s.s) and Cu(s.s) solidifying.

B powders contacted with the liquid system react with Ti, forming TiB whiskers first during heating by diffusion mechanism. Then TiB whiskers uniformly distribute in Ag(s.s) and Cu(s.s). The higher content of B in brazing layer is, the lower thickness of reaction layer $Ti_3(Cu,Al)_3O$, as well as more uniform and fine Ag(s.s) and Cu(s.s) will be. With the increasing of TiH_2 content, reaction layer $Ti_3(Cu,Al)_3O$ thicken, together with the number of Ti(Cu,Al) intermetallics increasing and Cu(s.s) decreasing. Ti(Cu,Al) distributes uniformly in the center of brazing layer, not just in Al_2O_3 side when TiH_2 content is 5 wt.%.

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