Microstructure and mechanical properties of inconel 600/ZrB$_2$-SiC joints brazed with AgCu/Cu-foam/AgCu/Ti multi-layered composite filler

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ABSTRACT

A set of AgCu/Cu-foam/AgCu/Ti multi-layered composite fillers was designed and employed to braze the Inconel 600 alloy and ZrB$_2$-SiC ceramic. Microstructures, formation mechanism and shear strengths of the joints were investigated in detail with and without the addition of Ti foil. The shear strengths of the brazed joints were improved substantially with the presence of Ti foils. A maximum gain of 150 % was reached from 77 MPa to 198 MPa after introducing the Ti foil and brazing the joint at a 1173 K for 15 min. The mechanical property enhancement is attributed to a newly formed TiC phase, release of residual stress, and barrier effect of Cu foam to inhibit formation of Ti-Ni intermetallic compounds.

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1. Introduction

Modern ceramics are labelled with high strength and hardness, low thermal expansion, good oxidation and thermal shock resistances, and especially higher high temperature properties. Thanks to these materials uniqueness, they have been widely used in electronics, aerospace, precision machinery areas and energy industries [1,2]. As a typical modern ceramic, the ZrB$_2$-SiC is endowed with good chemical and mechanical stabilities at ultra high temperatures, yet employed for thermal protections [3,4]. However, poor processability of this ceramic restricts its industrial applications.

Therefore, self-connection of the ZrB$_2$-SiC or joining it to metals has been envisaged for extensions of its application scopes.

Brazing is considered as an effective method to join ceramic materials thanks to high-performance joints, facile processes and low processing costs [5,6]. However, two main obstacles turn out when brazing ceramics with metals. Firstly, high residual stresses at the brazed joints are created during the cooling process as a result of large mismatches between thermal expansion coefficients of the ceramics and metals. Secondly, joint performances are greatly reduced due to formations of brittle intermetallic compounds within the joints [7]. However, it has been noticed that the residual stress of joints could be alleviated through introducing metal foams. Sun et al. reported the microstructural evolution and thermal stress relaxation of Al$_2$O$_3$/1Cr18Ni9Ti brazed joint with Ni...
foam. The thermal stress was reduced from 450 MPa to 75 MPa after brazing with the Ni-foam-added AgCuTi filler [8]. The Cu foam was employed as an interlayer material to improve the brazed joint of Zirconia toughened alumina/Ti6Al4V alloy. The shear strength of the joints reached a maximum value of 84.5 MPa, displaying a 95 % increase compared to the joints without the foam [9]. In our previous work, the Cu foam and graphene reinforced Cu foam were used for brazing Inconel 600 alloy with ZrB2-SiC ceramic. An obvious reduction of residual stress was also found by adding Cu foam. As a result, the joint strength was improved [10,11].

As one of the most widely used fillers for metal-ceramic brazing, the conventional AgCuTi has been used to braze ceramic and Ni-based superalloy, such as Inconel 600 alloy. Therein, the Ni element in Inconel 600 alloy strongly dissolves into the molten filler at the brazing temperature. The Ti and Ni will be alloyed due to a large negative enthalpy of mixing between the Ti and Ni (~35 kJ/mol) [12]. Consequently, the reactivity of the Ti will be reduced, and reliable connections from the Ti to the ceramic prevented. At the same time, the excessive Ni element dissolved in the brazing joint can react with ceramic and form a large quantity of brittle intermetallic compounds. As a result, the joint strength is decreased. The AgCuTi filler was also reported to braze Si3N4 and Invar alloy, and the resulted Fe2Ti+Ni3Ti intermetallic compounds were found harmful to the mechanical properties of the brazed joint [13]. The brazing mechanism of the filler was studied when joining the Inconel 600. A stronger Ti-Ni interaction than the Ti-Cu one was found as a key factor influencing formation behaviours. The formed Ni3Ti and NiTi2 strongly affected the joint performance [14]. Under the premise of wettability, the investigation of regulate of TiNi intermetallic compounds in the brazed joint is of great significance.

In this work, a trilayer composite filler of AgCu/Cu foam/AgCu/Ti foil was designed to improve joint performance. The filler was then employed to braze Inconel 600 alloy and ZrB2-SiC ceramic. A Ti foil was placed in the ceramic side to maintain the wettability of ceramic and metals. The Cu foam was used to relief the thermal residual stress. It also acted as a separator between the Ti and Inconel 600 alloy to prevent formation of Ti-Ni intermetallic compounds. We systematically studied the microstructures and mechanical properties of the joint. A large gain of shear strength was reached after introduction of the Ti foil, and the origin of the property enhancement was explored.

2. Experimental

In the present work, the ZrB2-SiC ceramic was provided by Institute of Advanced Structure Technology at Beijing Institute of Technology. ZrB2 powder with particle size of 2 μm and SiC powder with particle size of 1 μm were used. The purity of ZrB2 and SiC powders were both 99 %. The mixed powder at a volume ratio of 4:1 was obtained by ball milling in ethanol for 8 h. In order to minimize segregation of mixed powder, a rotating evaporator was used to remove ethanol at 353 K. Then, the achieved mixed powder was carefully sieved through a mesh with the hole size of 200 μm. Finally, the ZrB2-SiC ceramic were prepared by hot-pressed with the as-received powder at 2223 K for 3600 s in vacuum. During hot-pressed processing, a pressure of 30 MPa was applied. The nominal composition of Inconel 600 alloy was Ni-15.5Cr-8Fe-1Mn-0.5Cu-0.5Si-0.1C, (wt. %), in line with the one reported previously [15].

Samples for microstructural observation and shear strength testing were cut into pieces of 4 mm × 4 mm × 4 mm (ZrB2-SiC)/4 mm × 4 mm × 4 mm (Inconel 600) and 4 mm × 4 mm × 4 mm (ZrB2-SiC)/10 mm × 10 mm × 4 mm (Inconel 600) by wire electrical discharge machining, respectively. The thickness of each AgCu filler metal is 50 μm, and 1 mm and 20 μm for Cu foam and Ti foil, respectively. Figs. 1a and 1c depict schematic diagrams of the brazing assembly. Fig. 1b exhibits the morphology of Cu foam whose average pore size is 400 μm.

Brazing experiments were carried out in a vacuum brazing furnace (JVLF211) with the pressure < 6.0 × 10⁻³ Pa. Heating rates were set to 10 K/min during brazing processes. A holding period of 10 min at 973 K after the brazing temperature was implemented to reach a uniform temperature distribution in specimens. Subsequently, the second heating process was continued until 1173 K, at which the holdings were taken place at different times. The microstructure and phase of joints were characterized by scanning electron microscope (SEM, SU-8010) with an energy-dispersive X-ray spectrometer (EDS), and X-ray diffraction (XRD, Bede D1). Shear strength of joints were measured on an Instron 5500 machine. The measurements were done three times to obtain average results.

3. Results and discussion

Fig. 2a shows a typical microstructure of the Inconel 600/AgCu/Cu foam/AgCu/ZrB2-SiC joint brazed at 1173 K for
15 min. Figs. 2b and 2c demonstrate the zoomed regions of a reaction layer at the Inconel 600 side and ZrB$_2$-SiC side, respectively. The chemical composition of each marked phase was shown in Table 1. Spots 1 and 2 in the brazing seam are mainly consisted of Cu and Ag. Thus, phases 1 and 2 can be interpreted as an Ag-rich solid solution (Ag(s, s)) and Cu-rich solid solution (Cu(s,s)), respectively. Elements in phase 3 are Ni, Fe and Cr, similar to the Inconel 600 alloy. Due to the solution of Inconel 600 alloy during brazing processing, phase 3 can be inferred as a Ni-Fe-Cr phase. The main elements of phase 4 are Fe, Cr and C. The ratio of Fe + Cr to C is about 7:3. When Cr / C equivalence ratio reaches a certain value, the Cr is apt to react with the C to form a $M_2$C$_3$ (M = Fe, Cr) [16]. Based on the Fe-Cr-C ternary diagram and previous results [17,18], phase 4 was inferred as (Fe, Cr)$_2$C. Therefore, the reaction products of Inconel 600/AgCu/Cu foam/AgCu/ZrB$_2$-SiC joint brazed in the joint were deduced to Cu(s, s), Ag(s, s), Ni-Fe-Cr and (Fe, Cr)$_2$C.

Fig. 3 shows element distributions of Inconel 600/AgCu/Cu foam/AgCu/ZrB$_2$-SiC joint brazed at 1173 K for 15 min. The Zr, B, Si and C from ZrB$_2$-SiC ceramics are mainly concentrated on the ceramic side. The Fe, Ni and Cr from the Inconel 600 alloy are not only enriched on the metal side but also diffused into the brazed weld where the (Fe, Cr)$_2$C was formed. The Ag and Cu from the filler were massively diffused and distributed in the whole joint.

Fig. 4 demonstrates a typical microstructure of the Inconel 600/AgCu/Cu foam/AgCu/Ti/ZrB$_2$-SiC joint brazed at 1173 K for 15 min. The brazed joint was well joined and no defects were detected. The thickness of the brazed joint is around 60 µm, much larger than the original size of multi-layered composite filler. This is attributed to sufficient infiltration of the molten filler metal into the pressed Cu foam at 1173 K. In the overview, the joint is mainly consisted of three regions. In Fig. 4a, red lines were drawn to guide eyes and separate these regions: 1) A continuous reaction layer (10 µm thickness) was formed adjacent to the Inconel 600 alloy side; 2) The central part of the joint is composed of white and grey phases, also some dark phase varied in size and morphology distributed in the brazing seam; 3) A thin reaction layer was formed adjacent to the ZrB$_2$-SiC ceramic side.

Figs. 4b and 4c show zoomed images of reaction layers at the Inconel 600 alloy and ZrB$_2$-SiC sides, respectively. The compositions of the phases A–H are tabulated in Table 1. According to EDS results, the element compositions of phase A and phase B are mainly consisted of Cu and Ag. Their total contents are over 80 % of the total fractions. Thus, they were confirmed as Cu(s, s) and Ag(s, s), respectively, as typical features of ceramic brazed joint with AgCu filler metal [19,20]. The black phase C contains Ti and Fe at an approximate atomic ratio of 1:2. It is likely to be the TiFe$_2$ phase from the reaction of Ti +2Fe → TiFe$_2$. The formation enthalpy of TiFe$_2$ was reported to −54 kJ/mol, indicating a strong formation tendency of TiFe$_2$ [21,22]. For phase D with a large proportion in the reaction layer at the Inconel 600 side, the ratio of Ti to Cu is about 1:1. It is assigned to the TiCu phase resulted from the reaction of Ti +Cu → TiCu based on the Ti-Cu binary diagram. This result is in line with the reported Ref [11]. The element composition of phase E is mainly Ag. Thus, phases E also can be indicated as Ag(s, s). Phase F with a thin dark grey layer located in the Inconel 600 sides was detected, as shown in Fig. 4b. It was mainly composed of Ni, Cr and Fe, which is similar to the Inconel 600 alloy. Due to the solution of Inconel 600 alloy during brazing process, phase F thus became a ternary Ni-Fe-Cr phase. The composition of G was mainly composed of Ti, C and Si. It is reported that Ti is likely to react with the SiC to form TiC and Ti$_5$Si$_3$ phases form the reaction of Ti +SiC→Ti$_5$Si$_3$ + TiC. In ZrB$_2$-SiC side, some TiFe$_2$ phases were also detected, as shown of phase H. Thus, the microstructure of joint brazed with AgCu/Cu foam/AgCu/Ti multi-layered composite filler was Inconel 600/Ni-Fe-Cr + Ag(s, s) + TiCu/TiFe$_2$ + Cu(s, s) + Ag(s, s)/TiC + Ti$_5$Si$_3$/ZrB$_2$-SiC ceramic.

Fig. 5 shows the element distribution of Inconel 600/AgCu/Cu foam/AgCu/Ti/ZrB$_2$-SiC joint which was brazed at 1173 K for 15 min. The Zr, B, Si and C originated from the ZrB$_2$-SiC ceramic were mainly enriched on parent metal’s side. The Fe, Ni and Cr originated from the Inconel 600 alloy were enriched both on metal’s side, and diffused into the brazing seam, resulting in the formation of TiFe$_2$ and Ni-Fe-Cr. Due to the chemical compatibility between the Cu and Ni, a homogenous distribution of the Ni was detected in the brazing seam, as shown in Fig. 5g. A large number of Ag(s, s) and Cu(s, s) were formed in the brazing seam due to the use of AgCu filler and Cu foam [23,24]. Fig. 5k clearly shows that Ti is mainly enriched in the reaction layer and brazing seam. The reaction between Ti and ZrB$_2$-SiC, and Ti and Inconel 600 alloy offered the driving force for Ti diffusion and migration. As a result, the TiFe$_2$, TiC and Ti$_5$Si$_3$ were formed.

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Table 1 – EDS results of marked phase in Fig. 2.

<table>
<thead>
<tr>
<th>Spot</th>
<th>Ag</th>
<th>Cu</th>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>Zr</th>
<th>B</th>
<th>C</th>
<th>Si</th>
<th>Possible phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.71</td>
<td>70.14</td>
<td>2.05</td>
<td>1.06</td>
<td>1.62</td>
<td>1.21</td>
<td>1.54</td>
<td>18.94</td>
<td>0.73</td>
<td>Cu(s, s)</td>
</tr>
<tr>
<td>2</td>
<td>76.35</td>
<td>4.20</td>
<td>1.07</td>
<td>0.25</td>
<td>1.44</td>
<td>0.24</td>
<td>0.97</td>
<td>15.20</td>
<td>0.28</td>
<td>Ag(s, s)</td>
</tr>
<tr>
<td>3</td>
<td>0.55</td>
<td>0.47</td>
<td>50.76</td>
<td>26.31</td>
<td>18.34</td>
<td>0.09</td>
<td>1.15</td>
<td>1.28</td>
<td>1.05</td>
<td>Ni-Fe-Cr</td>
</tr>
<tr>
<td>4</td>
<td>1.21</td>
<td>3.46</td>
<td>0.44</td>
<td>13.09</td>
<td>52.04</td>
<td>1.18</td>
<td>0.74</td>
<td>26.35</td>
<td>1.49</td>
<td>(Fe, Cr)$_2$C$_3$</td>
</tr>
</tbody>
</table>
Besides, melting temperature, the molten AgCu filler metal flowed into the pores of Cu foam which was pressed at the same time. The Ag-Cu eutectic consisting of Ag(s,s) and Cu(s,s) was then formed in the joint, as a typical microstructural characteristic when using the AgCu filler [27–29]. In Fig. 6c, the temperature was further elevated to the brazing temperature, the molten AgCu filler continuously penetrated the Cu foam, and a strengthened TiCu phase was produced via Ti + Cu → TiCu reaction at the Inconel 600 alloy side. During this process, TiFe2 was also formed through Fe + 2Ti → TiFe2 due to a strong reaction tendency between the Fe and Ti. Meanwhile, blocky Cu (s, s) was also formed and distributed in the joint as a result of the dissolved Cu from the Cu foam. Fig. 6d demonstrates the microstructure of the joint after brazing. The newly formed Cu (s, s), TiFe2 and TiC distributed homogeneously in the joint. Then Cu(s,s) owns good plasticity and can relieve residual stress effectively, while TiFe2 and TiC particles act as reinforcing phases. Therefore, the joint strength was greatly improved.

Shear strength of samples brazed at different treatment conditions are shown in Fig. 7. The joints brazed with AgCu/Cu foam/AgCu/Ti composite filler exhibited much higher shear strength than those brazed without the Ti foil, regardless the brazing time. Extensive research shows that the shear strength
of the joint increased when the brazing time increased from 5 min to 15 min. However, the strength decreased when brazing time was further prolonged to 25 min. The maximum shear strengths were 198 MPa and 77 MPa for the joints brazed with and without Ti foil, respectively. This demonstrates a significant increase of the mechanical properties of the joint after addition of Ti foil. Such an increase of shear strength can be explained as follows. Firstly, the soft Ti foil was sandwiched between filler and ZrB2-SiC ceramics. It can improve the wetability of ceramic and alloys and reduce the thermal residual stress of joint. Later, the Ti reacted with ZrB2-SiC ceramic substrate and formed a large number of reaction products that benefit interfacial bonding properties. Secondly, the Cu foam can act as a barrier and prevent direct contact between Ti and Ni from Inconel 600 alloy. The formation of Ti-Ni intermetallic compounds was prohibited. This result agreed with the data shown in Fig. 4 and Table 1 where Ti-Ni intermetallic compound was not detected in the joint. Thirdly, the TiC was formed and distributed uniformly in the brazed joint, which was conductive to the strengthen of the joint. The TiC exhibited a positive effect on refinement of the crystal microstructure of the brazed fillers [30]. The coefficient of thermal expansions of TiC, ZrB2-SiC ceramic and AgCuTi brazing filler were reported to 6.52 × 10⁻⁶ K⁻¹, 4.0 × 10⁻⁶ K⁻¹ and 18.2 × 10⁻⁶ K⁻¹, respectively [23,31]. Difference in coefficient of thermal expansion between TiC and ZrB2-SiC was

Fig. 5 – EDS images of Inconel 600/AgCu/Cu foam/AgCu/Ti/ZrB2-SiC joint brazed at 1173 K for 15 min: a) microstructure of joint, b)-k) elements distribution.
Fig. 6 – Schematic diagram of the formation of brazed joint.

Fig. 7 – Shear strength of brazed joint with AgCu/Cu foam/AgCu/Ti) multi-layered composite filler.

much smaller than that between AgCuTi brazing filler and ZrB₂-SiC. The mismatch of thermal expansion coefficient was greatly reduced. Consequently, the joint strength was improved.

The microstructure of Inconel 600 alloy/ZrB₂-SiC ceramic joints brazed with different brazing time at 1173 K are shown in Fig. 8. Obviously, the weld width was gradually decreased. Three characteristic zones clearly turned out in all samples with different brazing time, as shown in Figs. 8a, 8d, and 8g. However, changes also appear in each region following the increase of brazing time. In the Inconel 600 alloy side, the thickness of the reaction layer increased from ~3 µm to ~10 µm, along with the brazing time from 5 min to 25 min. When the brazing time was 5 min, the insufficient diffusion of atoms led to an insufficient reaction between filler and ZrB₂-SiC ceramic substrate. This is not conducive to the joint strength and resulting in a minimum shear strength, as shown in Fig. 7. For the 15 min case, the size and amount of Ni-Cr-Fe ternary phase and TiCu phase increased with the brazing time. A continuous TiCu layer blocked the atomic diffusion between Inconel 600 alloy and the filler. Instead, an aggregation of Ag(s, s) phase was formed in the TiCu layer, as shown in Fig. 8e. Such a composite structure is beneficial to the bonding strength of the interface, leading to improved mechanical properties of the joint. For 25 min, micro-cracks were observed at the Inconel 600 alloy side (Fig. 8g). The existence of the cracks is harmful to the mechanical properties, resulting in the reduced shear strength. The Ag(s, s) and Cu(s, s) are the main phases in the middle of joints. However, at the 25 min brazing time, the Cu foam has more obvious softening problems than at other time. Some areas collapsed and formed a large area of Cu-based solid solution, as shown in Fig. 8g. This is harmful to maintain a high shear strength at the joints. In ZrB₂-SiC ceramic side, the thickness of the reaction layer did not change significantly. At 5 min of brazing, no obvious reaction product was observed. However, for 15 min brazing, a large number of dispersed precipitates TiC and Ti₅Si₃ appear in the joint, as shown in Figs. 4c and 8f. Moreover, the brazing time of 25 min results in the formation of larger quantity
of TiC and Ti₅Si₃ in the interface. Due to the intrinsic brittleness of Ti₅Si₃ and TiC, these larger brittle intermetallic compounds damage the plastic deformation of the joint and are unbeneﬁcial to the relaxation of residual stress of the joint [32].

4. Conclusions

To conclude, the ZrB₂-SiC ceramic was successfully brazed to Inconel 600 alloy with a AgCu/Cu-foam/AgCu/Ti multi-layered composite ﬁller at 1173 K. The typical microstructures of the brazed joint with an addition of Ti foil were In 600 alloy/TiCu/Ti₅Si₃/Cu(α,γ) + Ag(α,γ)/TiC + Ti₅Si₃/ZrB₂-SiC ceramic. Meanwhile, compared with the joint without Ti foil, the additions of Ti foils increase the shear strength. The maximum shear strength reached 198 MPa in the presence of the Ti foil and brazing time of 15 min. This value is 150 % more than the one of the joint brazed without Ti foil. The additive Ti foil can improve the wettability of ceramic and metals, and reacts with ZrB₂-SiC ceramic to form TiC and Ti₅Si₃ reaction products. The TiC formation played a positive role in strength reinforcements and reduced the mismatch of thermal expansion coefﬁcient of brazing ﬁller and ceramic. Meanwhile, the Cu foam can act as a barrier to separate Ti and Ni, and also effectively release thermal residual stress. The above effects greatly enhance the shear strength of the brazed joint.

Conflict of interest

None.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2020.01.080.

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