Microstructure and mechanical properties of SiO2-BN ceramic and Invar alloy joints brazed with Ag–Cu–Ti + TiH2 + BN composite filler

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Received 7 July 2015; revised 5 October 2015; accepted 21 October 2015
Available online 18 November 2015

Abstract

Ag–Cu–Ti + TiH2 + BN composite filler was prepared to braze SiO2-BN ceramic and Invar alloy. The interfacial microstructure, mechanical properties, and residual stress distribution of the brazed joints were investigated. The results show that a wave-like Fe2Ti-Ni3Ti structure appears in the Invar substrate and a thin TiN-TiB2 reaction layer forms adjacent to the SiO2-BN ceramic. The added BN particles react with Ti to form TiN-TiB fine-particles, which is beneficial to refine the microstructure of the brazing seam and to greatly inhibit the brittle compounds formation. The interfacial microstructure at various brazing temperatures was analyzed, and the mechanism for the interfacial reactions responsible for the bonding was proposed. The maximum shear strength of the joints brazed with the composite filler at 880 °C for 10 min is 39 MPa, which is 30% greater than that brazed with Ag–Cu–Ti alloy. The improvement of the joint strength is attributed to the variation of joint microstructure and the reduction of tensile stresses induced in the SiO2-BN ceramic. The finite element analysis indicates that the peak tensile stress decreases from 230 to 142 MPa due to the addition of BN particles in the ceramic.

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Keywords: SiO2-BN ceramic; Invar alloy; Brazing; Microstructure; Mechanical properties

1. Introduction

Hexagonal BN particles reinforced SiO2-BN ceramic has a low dielectric constant, rather high strength and fracture toughness, and a superior thermal shock resistance. It is thus regarded as a promising structure material for the preparation of thermal protection parts (i.e., radomes, nose tip of aerospace vehicles, and electromagnetic wave transparent windows) [1–3]. It is essential for the practical application of this ceramic to join it to metallic components. For instance, the assembly of radar window requires joining the SiO2-BN ceramic to Invar alloy, which has a low thermal expansion coefficient (CTE) at room temperature [4].

Ceramic-metal joints were fabricated by different bonding methods, such as adhesive bonding, diffusion bonding and various types of brazing. Among the joining techniques available, active metal brazing is a well-established method for the joining of dissimilar materials due to its convenience and good adaptability to the sample shape [5–8]. Near-eutectic Ag–Cu alloys with a small amount of Ti can react with SiO2 [9,10] and BN [11,12] to form a metallurgical reaction layer. It is assumed that SiO2-BN ceramic comprised of amorphous SiO2 and h-BN phase could be well brazed with such a Ti-activated brazing alloy. In some previous work [13,14], the SiO2-BN ceramic and Invar alloy could be brazed using the commercially available Ag–Cu–Ti alloy, and a compact reaction layer formed on the ceramic surface. However, the joint strength decreased as a consequence of the formation of Fe2Ti–Ni3Ti compounds, especially when these brittle compounds accumulated in the vicinity of the SiO2-BN
ceramic. It is important to improve the microstructure of the brazed joints, thereby enhancing the bonding properties.

Like most of ceramic-metal components, it is rather difficult to fabricate a strong joint of ceramics and metals since their different chemical and physical properties. There are two primary factors that impede formation of a mechanically reliable joint, i.e., the CTE mismatch and the difference in the nature of the interatomic bond. The thermal stresses are induced in a joint during cooling from the brazing temperature due to the CTE mismatch and differing mechanical responses of ceramic and metal. In particular, Invar alloy exhibits a dramatic change in the CTE values as the temperature increases (i.e., $1.2 \times 10^{-6}$ K$^{-1}$ at 20 °C; $17.5 \times 10^{-6}$ K$^{-1}$ at 600 °C). As a consequence, a complex residual stress distribution could form in the vicinity of the joining interface, among which the tensile stress induced in the ceramic severely deteriorate the joint properties [15,16]. If the tensile stresses are high enough in the ceramic due to the consequence of operating conditions or the formation of the joining procedure itself, failure can occur [17]. Therefore, it is of vital importance to minimize the residual stresses. Extensive studies reported that the addition or the in situ formation of low CTE fibers or particles into brazing alloys can alleviate the residual stresses effectively. The incorporation of carbon fibers, TiB whiskers, SiC, Si$_3$N$_4$, Mo, W and BN particles can improve the joint strength [18–28]. Song et al. reported that the shear strength of TiAl/Si$_3$N$_4$ joints was increased by 85% when nano-particles of Si$_3$N$_4$ of 3 wt.% were added into Ag–Cu–Ti brazing alloy [23]. A recent work showed that the addition of BN particles into the brazing alloy could improve the bonding properties of Ti/SiO$_2$-BN brazed joints [26]. It was indicated that the improvement of joint properties was primarily attributed to the reduction of residual stresses. However, little work has been done to evaluate the variation of residual stresses caused by the addition of ceramic particles, and thus the reinforcing effect is not well understood.

In this paper, BN particles were added in Ag–Cu–Ti alloy for brazing SiO$_2$-BN ceramic and Invar alloy to improve the microstructure and reduce the residual stress of the brazed joint. The effect of brazing temperature on the interfacial microstructure and mechanical properties of brazed joints was investigated. The mechanism for the interfacial reactions responsible for the bonding was proposed. In addition, a finite element modeling was also used to calculate the magnitude and distribution of the residual stresses induced in the brazed joints to reveal the reinforcing effect of the BN particles modified composite filler.

2. Experimental and modeling procedures

2.1. Brazing and characterization of the joints

Invar alloy with a composition of Fe-36wt.-%Ni and SiO$_2$-BN ceramic fabricated by hot pressing of h-BN + SiO$_2$ mixed powder were used in the experiments. The SiO$_2$-BN ceramic was provided by Institute for Advanced Ceramics in Harbin, China. The volume fraction of h-BN was 60% and the density of the sintered ceramic was 2.1 g/cm$^3$. The microstructure of SiO$_2$-BN ceramic was comprised of amorphous fused silica and hexagonal boron nitride. The amorphous fused silica formed a continuous phase in the sintered SiO$_2$-BN ceramic, and the h-BN existed as a disperse phase. The sizes of SiO$_2$-BN ceramic and Invar alloy brazing sample were 5 mm × 4 mm × 3 mm and 25 mm × 10 mm × 3 mm, respectively. The surfaces to be brazed were firstly polished and then ultrasonically cleaned in acetone for 10 min. The composite filler was consisted of commercial available Ag-27.5Cu-4.5Ti (wt.%) brazing alloy powder, TiH$_2$ powder and h-BN powder. The average particle sizes of TiH$_2$ and h-BN were 70 μm and 0.5 μm, respectively. The content of h-BN powder in the composite filler was 3 wt.%. The TiH$_2$ content was calculated in terms of the reaction of 2Ti + BN $\rightarrow$ TiB + TiN. The mixture was milled in argon atmosphere for 1 h using a model QM-4H planetary ball mill with alumina balls at a rotational speed of 300 rpm. Fig. 1 shows the morphology of the as-milled Ag–Cu–Ti + TiH$_2$ + BN composite filler.

The as-milled composite filler was mixed with a small amount of cellulose nitrate and octylacetate to prepare a composite brazing paste. During the brazing process, the binder was volatilized in a vacuum furnace at a low temperature, which is lower than the brazing temperature. The brazing paste was firstly coated on the bonding surface of SiO$_2$-BN ceramic and then sandwiched between Invar alloy and the ceramic substrate. The thickness of the coated paste was 200–300 μm. Fig. 2a shows the assembly structure of the brazing samples. During the brazing experiments, the assembly structure was maintained by a graphite jig and a small load of 0.6 MPa was applied to keep the specimens in close contact. The brazing experiments were carried out in a vacuum furnace with a pressure of 3.0 $\times$ 10$^{-3}$ Pa at 860–900 °C for 10 min. The heating rate was 10 °C/min and the cooling rate was set to be 5 °C/min.

The cross-section of Invar/SiO$_2$-BN brazed joint was characterized by a model S-4700 scanning electron
microscope (SEM, Hitachi Ltd., Japan) equipped with an energy dispersive X-ray spectroscopy (EDS). The reaction phase in the joint was confirmed by an X-ray diffraction instrument (D/max-RB, Ricoh Ltd., Japan) using a Cu Kα radiation source. The Vicker hardness of the reactants formed in the joint was measured by a model DUH-W201S dynamic ultramicro hardness tester under a load of 100 g for a loading time of 10 s. Shear tests were carried out at a constant speed of 0.5 mm/min by a model INSTRON-1186 universal testing machine. Fig. 2b shows the schematic diagram of shear testing. The average shear strength was determined from three joints that were achieved under the same experimental conditions.

2.2. Estimation of residual stress in the joints

The distribution of the residual stress, yielded in the brazed joint during cooling from brazing temperature due to a mismatch in the coefficient of thermal expansion (CTE), was simulated by finite element modeling (FEM). The continuum models were used to evaluate the stress in the joints. The stress-free temperature was set at 780 °C, which is the melting point of Ag–Cu eutectic. It was assumed that a sound joint could be formed during brazing and remained throughout the cooling process. The computation was conducted using the FEM solver, Marc-2010. As seen in Fig. 3, a three-dimensional thermal elasto-plastic model was created, whose dimension was equal to the brazing samples. The mesh was refined nearby the bonding interfaces where the greater residual stress could generate. The boundary condition was that the nodes on the bottom of Invar alloy did not displace in the Z-direction and no external loads were used in these simulations.

Table 1 shows the physical and mechanical properties of materials used in the computation. The interfacial microstructure of brazed joints at room temperature was taken into consideration. For the joints brazed with BN particles modified composite filler, the elastic modulus of brazing seam was determined by nanoindentation tests [26]. The coefficient of thermal expansion of the brazing seam was calculated by Ref. [29].

\[
\alpha = \alpha_m \left(1 - \sum V_f\right) + \sum \alpha_f V_f
\]  

### Table 1

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature (°C)</th>
<th>Elastic modulus (GPa)</th>
<th>Yield stress (MPa)</th>
<th>CTE (×10⁻⁶ K⁻¹)</th>
<th>Poisson's ratio</th>
</tr>
</thead>
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<tr>
<td>SiO₂-BN</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>0.18</td>
</tr>
<tr>
<td>Invar</td>
<td>20</td>
<td>143</td>
<td>310</td>
<td>1.2</td>
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<td></td>
<td>200</td>
<td>141</td>
<td>115</td>
<td>7.8</td>
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<td></td>
<td>400</td>
<td>138</td>
<td>90</td>
<td>17.1</td>
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<td>600</td>
<td>120</td>
<td>75</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>AgCuTi</td>
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<td>100</td>
<td>230</td>
<td>19.0</td>
<td>0.36</td>
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<tr>
<td></td>
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<td>170</td>
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<td>600</td>
<td>67</td>
<td>25</td>
<td>20.5</td>
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<tr>
<td>TiN</td>
<td>–</td>
<td>350</td>
<td>–</td>
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<td>–</td>
<td>371</td>
<td>–</td>
<td>8.6</td>
<td>0.28</td>
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<tr>
<td>Composite filler</td>
<td>–</td>
<td>130</td>
<td>–</td>
<td>15.0</td>
<td></td>
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</tbody>
</table>
where \( \alpha \) is the CTE of the brazing seam, \( \alpha_m \) and \( \alpha_f \) are the CTEs of Ag-based solid solution and reinforcing particles respectively, \( V_f \) is the volume fraction of \textit{in situ} synthesized reinforcing particles.

3. Results and discussion

3.1. Microstructure of Invar/SiO\textsubscript{2}-BN brazed joints

Fig. 4 shows a typical interfacial microstructure of Invar/SiO\textsubscript{2}-BN joint brazed with Ag–Cu–Ti + TiH\textsubscript{2} + BN composite filler at 880 °C for 10 min. In Fig. 4a, the joint was completely filled without any pores or micro-cracks. The formation of such a sound joint indicates that the flow of the liquid composite filler is adequate and that sufficient liquid–solid interaction occurs during the process of brazing. Table 2 shows the average chemical compositions of each phase measured by EDS, which can indicate the possible phases produced in the joint.

In Fig. 4b, some block-like Fe\textsubscript{2}Ti + Ni\textsubscript{3}Ti compounds form nearby the Invar alloy. The formation of Fe\textsubscript{2}Ti + Ni\textsubscript{3}Ti is accompanied by the dissolution of Invar substrate. This phenomenon can be speculated from the uneven interface of Invar brazing alloy. Moreover, the dissolved Fe and Ni atoms can react with the active Ti to form brittle intermetallics [30], which favors the dissolution of Invar during brazing process. Noted that compared to the microstructure of the joint brazed with single Ag–Cu–Ti alloy [14], the formation of brittle Fe\textsubscript{2}Ti + Ni\textsubscript{3}Ti compounds is decreased when the BN particles modified composite filler is added. This is because partial Ti in the liquid filler is captured by the added BN particles, the Ti concentration is not sufficient to further react with Fe or Ni dissolved from the Invar alloy. Also, these compounds primarily appear nearby the Invar alloy and do not move to reinforcing particles.

In Fig. 4c, there is the magnified microstructure of the brazing seam with the massive black fine-particles distributed on Ag- and Cu-based solid solutions. Fig. 5a shows the XRD pattern of the brazing seam. It is seen that TiB and TiN exist in the joint besides Ti\textsubscript{3}Cu\textsubscript{4} and TiCu\textsubscript{4}. The formation of TiN–TiB fine particles demonstrates that the BN particles can react with the active Ti atoms from the liquid composite filler during brazing process. The calculated Gibbs free energy of 2Ti + BN→TiB + TiN at 880 °C is −236.6 kJ/mol, indicating this reaction can occur spontaneously. The \textit{in situ} synthesized TiB–TiN fine-particles could act as the nucleating centers for Ti–Cu compounds [26]. Therefore, Ti–Cu compounds such as TiCu\textsubscript{4} and Ti\textsubscript{3}Cu\textsubscript{4}, are formed in the joint when BN particles are added in the composite filler.

In Fig. 4d, a homogeneous, featureless and compact reaction layer with a thickness of about 1.5 \( \mu \text{m} \) appears adjacent to the SiO\textsubscript{2}-BN ceramic. According to the composition analysis (see Table 1) and XRD result (see Fig. 5b), the reaction layer determined is TiN–TiB\textsubscript{2}, which is consistent with that brazed with Ag–Cu–Ti alloy [13]. It is assumed that the amorphous SiO\textsubscript{2} in the SiO\textsubscript{2}-BN ceramic could not react during brazing, while h-BN phase could react with Ti to form TiN–TiB\textsubscript{2} layer bordering the SiO\textsubscript{2}-BN ceramic.

A thin TiN–TiB\textsubscript{2} reaction layer, which plays a critical role in obtaining a strong joint, is formed adjacent to SiO\textsubscript{2}-BN ceramic. The BN particles in the composite filler react with active Ti to form TiB–TiN fine particles in the brazing seam.

Fig. 4. Microstructure of Invar/SiO\textsubscript{2}-BN joint brazed with Ag–Cu–Ti + TiH\textsubscript{2} + BN composite filler at 880 °C for 10 min: (a) the whole joint; (b) Invar/filler interface; (c) magnification of brazing seam; (d) filler/SiO\textsubscript{2}-BN interface.
The modification of the joint microstructure is beneficial to refine the microstructure of the brazing seam and to greatly inhibit Fe$_2$Ti + Ni$_3$Ti formation. Moreover, these brittle compounds are primarily distributed nearby the Invar substrate and do not appear at ceramic side due to the addition of BN particles.

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>Ti</th>
<th>Ag</th>
<th>Cu</th>
<th>Si</th>
<th>O</th>
<th>N</th>
<th>B</th>
<th>Possible phase</th>
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<tr>
<td>A</td>
<td>54.04</td>
<td>11.75</td>
<td>27.71</td>
<td>2.52</td>
<td>3.3</td>
<td>0.68</td>
<td></td>
<td></td>
<td></td>
<td>Fe$_2$Ti</td>
</tr>
<tr>
<td>B</td>
<td>8.70</td>
<td>58.25</td>
<td>21.75</td>
<td>2.94</td>
<td>7.75</td>
<td>0.61</td>
<td></td>
<td></td>
<td></td>
<td>Ni$_3$Ti</td>
</tr>
<tr>
<td>C</td>
<td>2.03</td>
<td>2.18</td>
<td>0.56</td>
<td>2.50</td>
<td>92.57</td>
<td>0.43</td>
<td></td>
<td></td>
<td></td>
<td>Cu(s.s)</td>
</tr>
<tr>
<td>D</td>
<td>2.19</td>
<td>1.28</td>
<td>1.05</td>
<td>85.18</td>
<td>9.60</td>
<td>0.70</td>
<td></td>
<td></td>
<td></td>
<td>Ag(s.s)</td>
</tr>
<tr>
<td>E</td>
<td>1.86</td>
<td>1.86</td>
<td>32.09</td>
<td>—</td>
<td>1.91</td>
<td>4.95</td>
<td>5.19</td>
<td>10.39</td>
<td>41.75</td>
<td>TiN + TiB$_2$</td>
</tr>
</tbody>
</table>

3.2. Effect of brazing temperature on joint microstructure

Fig. 6 shows the effect of brazing temperature on the interfacial microstructure of Invar/SiO$_2$-BN joints brazed with the BN particles modified composite filler, and the joint microstructure is affected by the brazing temperature. The microstructure of the brazing seam and reaction layer adjacent to SiO$_2$-BN ceramic is shown in Fig. 5.

![Fig. 5. XRD patterns of (a) brazing seam and (b) reaction layer adjacent to SiO$_2$-BN ceramic.](image)

![Fig. 6. Effect of brazing temperature on the microstructure of Invar/SiO$_2$-BN joints brazed with the composite filler for 10 min: (a–c) 860 °C; (d–f) 900 °C.](image)
microstructure obtained at 880 °C for 10 min (see Fig. 4). It can be observed that a similar interfacial structure is formed, though the microstructure of the brazing seam and the thickness of the reaction layer vary slightly.

In Fig. 6a, Ag–Cu eutectic microstructure appears in the brazing seam at the brazing temperature of 860 °C. The Ag–Cu eutectic gradually disappears and is replaced by Ag-based solid solution (see Figs. 4a and 6d) when the temperature increases. As a result, more Cu atoms are consumed to form Ti–Cu compounds. The formation of Ti–Cu compounds as well as TiB–TiN fine-particles needs Ti atoms to participate in the reactions, and thus the Ti concentration is not sufficient to further react with Fe or Ni dissolved from the Invar alloy. Consequently, the increase of Fe2Ti + Ni3Ti compounds with increasing the brazing temperature is not significant (see Figs. 4b, 6a and d). Also, the thickness of TiN–TiB2 layer increases from about 1 μm to 2 μm when the brazing temperature increases from 860 °C to 900 °C. The growth of TiN–TiB2 reaction layer is initially controlled by the rate of chemical reaction, which primarily depends on the reaction temperature [31]. Hence, the increase of the brazing temperature can favor the growth of the TiN–TiB2 reaction layer. Nevertheless, the growth is affected by the diffusion barrier of an already formed reaction layer when an appreciable thickness of the reaction layer is formed. In this case, the diffusion time becomes the most important factor to maintain the chemical reaction. Therefore, it is reasonable that the variation of the thickness of TiN–TiB2 layer as a function of brazing temperature is not evident.

Based on the above microstructure analysis, Fig. 7 shows the formation mechanism of the joint brazed with the BN particles modified composite filler. It can be divided into the following four stages.

(a) In Fig. 7a, when the heating temperature is 780 °C, Ag–Cu eutectic melts, Ti begins to dissolve in the liquid phase. Then, active Ti atoms diffuse and accumulate beside BN particles and SiO2-BN ceramic under the driving force of chemical potential difference. At the same time, Invar alloy dissolves into the liquid filler, resulting in the strong interaction between Ti and Ni or Fe atoms.

(b) When the atomic concentration is sufficient to trigger the chemical reactions, a series of reactants produces in the liquid filler. In Fig. 7b, Fe2Ti + Ni3Ti compounds form nearby Invar alloy, TiN–TiB fine-particles are in situ synthesized around BN particles, and TiN–TiB2 layer appears adjacent to SiO2-BN ceramic.

(c) As the chemical reactions continue, active Ti atoms are partially consumed at the reaction interface, leading to a gradient of Ti concentration in the liquid filler. The gradient would in turn facilitate the diffusion of Ti and make the chemical reactions continue to proceed. Consequently, there are more fine-particles synthesized in the liquid filler, as well as the formation of Fe2Ti + Ni3Ti compounds. The migration of the wave-like compounds in the liquid filler is inhibited by TiB–TiN fine-particles (see Fig. 7c). In addition, the increase of the thickness of TiN–TiB2 reaction layer is not obvious since Ti atoms have to across the already formed reaction layer to maintain the interfacial reaction.

(d) During the cooling process, Ag- and Cu-based solid solutions are formed from the remaining liquid, and then a sound joint is obtained (see Fig. 7d). The in situ synthesized fine-particles are uniformly distributed over the brazing seam, forming a fine and homogeneous microstructure in the joint. Furthermore, a wave-like Fe2Ti + Ni3Ti structure appears near the Invar alloy, and a thin TiN–TiB2 layer is formed adjacent to the SiO2-BN ceramic.

3.3. Mechanical properties of Invar/SiO2-BN brazed joint

Fig. 8 shows the effect of brazing temperature on the shear strength of Invar and SiO2-BN joints brazed with Ag–Cu–Ti + TiH2 + BN composite filler, and its comparison with the joint strength obtained with single Ag–Cu–Ti alloy. For the joints brazed with Ag–Cu–Ti alloy, the bonding area and test conditions are the same as the joints brazed with the composite filler.

Clearly, the maximum shear strength of 39 MPa is obtained when the joint is brazed with the composite filler at 880 °C for 10 min, which is 30% greater than that brazed with Ag–Cu–Ti alloy. The average shear strength of the joints brazed with both Ag–Cu–Ti alloy and Ag–Cu–Ti + TiH2 + BN composite filler firstly increases and then decreases with increasing the brazing temperature from 860 °C to 900 °C. In contrast, for the composite filler, the variation of joint strength as a function of brazing temperature is not significant, and the shear strength of the joints is greater than 30 MPa. Moreover, the average joint strength brazed with the composite filler is greater than that brazed with Ag–Cu–Ti alloy in a wide range of brazing temperature. These results indicate that the BN particles modified composite filler exhibit a good adaptability to braze Invar alloy and SiO2-BN ceramic.

The improvement of joint strength is primarily attributed to the variation of joint microstructure and the reduction of residual stresses. When the BN particles modified composite filler are used to braze SiO2-BN and Invar, Fe2Ti + Ni3Ti compounds are greatly inhibited and replaced by Ag- and Cu-based solid solutions. Compared to the solid solution microstructure, Fe2Ti + Ni3Ti compounds are rather brittle [32]. Moreover, the hardness of Fe2Ti + Ni3Ti (670 HV) is greater than that of Ag (s.s) (115 HV) and Cu (s.s) (140 HV), which means the plasticity and toughness of Ag (s.s) and Cu (s.s) are better than that of Fe2Ti + Ni3Ti. As a result, the reduction of brittle Fe2Ti + Ni3Ti compounds is beneficial to release the residual stresses through plastic deformation of the brazing seam. Also, the in situ formed brittle TiB–TiN fine-particles with a low coefficient of thermal expansion (CTE) could reduce the CTE of the brazing seam. The CTE reduction of brazing seam was estimated by the Formula (1). The result
indicates that the CTE of the brazing seam can be reduced by 21% when BN particles of 3 wt.% are added. Therefore, a favorable stress distribution could form in the brazed joint. The residual stresses yielded in the brazed joint could be calculated by finite element modeling.

### 3.4. Estimation of residual stress in the brazed joint

To better understand the reinforcing effect caused by the addition of BN particles, the magnitude and distribution of the residual stresses in the joints brazed with both Ag–Cu–Ti and Ag–Cu–Ti + TiH₂ + BN were analyzed. Fig. 9a shows the distribution of equivalent von mises stress in Invar/SiO₂-BN joints brazed with single Ag–Cu–Ti alloy. It is clearly seen that the residual stress is constrained around the substrates/filler metal interfaces. The peak residual stress of 230 MPa is generated in the SiO₂-BN ceramic close to filler metal, and decreased from the interface. However, the maximum residual stress is only 142 MPa when the BN particles modified composite filler is used (see Fig. 9b). It should be noted that the distribution of the peak residual stress is different. For the joint brazed with composite filler, its distribution is not homogeneous along the interface, and a bowed distribution of the maximum residual stress appears in the ceramic substrate.

During the cooling process, Invar alloy and SiO₂-BN ceramic both should contract. However, Invar alloy should shrink more than SiO₂-BN ceramic under the same temperature gradient since the CTE for Invar alloy is greater than that of SiO₂-BN ceramic. Therefore, the lower expansion ceramic has a compressive stress on the whole, and the larger expansion metal is in tension. In order to balance those internal stresses, the tensile stress should occur at the edge of SiO₂-BN ceramic, while the compressive stress forms in the Invar alloy. Most ceramic can bear compressive stress, but exhibit a poor ability in enduring the tensile stress [33]. Therefore, the bonding properties of the brazed joints would be deteriorated, resulting in the formation of a tensile stress in the ceramic substrate, and the initiation of the cracks could occur in the edge of SiO₂-BN ceramic nearby the interface during shear test.

Fig. 10 shows the computed results of the distribution of residual stress in the perpendicular cross-section (Z-direction) of the brazed joints. Clearly, a tensile state of stress is
produced in the SiO$_2$-BN ceramic nearby the interface, and the compressive stress is found in the Invar alloy. Moreover, the peak tensile stress generated in the SiO$_2$-BN ceramic is decreased from 230 MPa to 142 MPa when the BN modified composite filler is used. The simulated results indicate that the reduction of the tensile stress in the SiO$_2$-BN ceramic substrate can improve the shear strength of the joints, which are in a reasonable agreement with the experimental results.

4. Conclusions

Ag–Cu–Ti + TiH$_2$ + BN composite filler was prepared to braze SiO$_2$-BN ceramic and Invar alloy. According to the results obtained, the following conclusions could be drawn:

1. BN particles in the composite filler reacted with active Ti to form fine TiN–TiB particles, which was beneficial to refine the joint microstructure and greatly inhibit the formation of brittle Fe$_2$Ti–Ni$_3$Ti compounds. A wave-like Fe$_2$Ti–Ni$_3$Ti structure only appeared nearby the Invar alloy, and a thin TiN–TiB$_2$ reaction layer formed adjacent to the SiO$_2$-BN ceramic.

2. The microstructure of the brazing seam became more fine and homogeneous when the brazing temperature increased. The amount of Fe$_2$Ti + Ni$_3$Ti compounds and the thickness of TiN–TiB$_2$ reaction layer increased slightly when the brazing temperature from 860 °C to 900 °C.

3. The maximum shear strength of the joints brazed with the composite filler at 880 °C for 10 min was 39 MPa, which was 30% greater than that brazed with Ag–Cu–Ti alloy. The shear strength of the brazed joint was great in a wide range of brazing temperature, indicating that the BN particles modified composite filler exhibited a good adaptability to braze Invar alloy and SiO$_2$-BN ceramic.
The improvement of joint strength was primarily attributed to the variation of joint microstructure and the reduction of residual stresses. When the BN particles modified composite filler was applied, fine-particles were formed in the brazed joints. In addition, the calculated results by finite element modeling revealed that the peak tensile stress in the SiO$_2$-BN ceramic decreased from 230 MPa to 142 MPa due to the addition of BN particles.

Acknowledgments

This project was supported by the National Natural Science Foundation of China (No. 51405332).

References


