Influence of Brazing Filler Metal Diffusion on the Mechanical Strength of SUS304/Cu/Si₃N₄ Composite

by

Nobuhiro SETTSU *, Masafumi MATSUSHITA *, Manabu TAKAHASHI *, Masaki TANIMOTO ** and Hiroaki OHFUJI ***

The effects of brazing filler metal diffusion on the mechanical strength of a ceramic/metal composite are described. First, a specimen of a SUS304/Cu/Si₃N₄ system, including brazing filler metals of AgCu and/or AgCuTi, was prepared by brazing in a vacuum furnace. Next, the vicinity of the joint parts was observed using field emission scanning electron microscopy. The brazing filler metals were found to diffuse into the Cu interlayer and ramify. In addition, a crack due to thermal stress resulting from a mismatch in thermal contraction between the materials present was observed around the AgCuTi/Si₃N₄ boundary. Energy-dispersive X-ray spectroscopic analysis revealed that Ag atoms diffused into the Cu interlayer to form the solid solutions of Ag and Cu. Micro-Vickers hardness tests were conducted on the surface of the Cu interlayer in order to examine the effects of brazing alloy diffusion on the hardening of the Cu interlayer. It was found that the diffusion of the brazing filler metals enhanced the hardness of the Cu interlayer. Finally, numerical simulations were performed to verify the increase in thermal stress due to hardening of Cu, and this behavior was discussed using simple equations. The results of the experiments and numerical simulations showed that the mechanical strength of the SUS304/Cu/Si₃N₄ composite is subjected to the diffusion of brazing filler metals.

Key words: Diffusion, Brazing filler metal, Crack initiation, Cu interlayer, Hardening, Thermal stress

1 Introduction

Various ceramics, such as Al₂O₃, AlN, SiC, and Si₃N₄, have excellent high-temperature strength, corrosion resistance, high electrical resistance and properties that give these ceramics potential application in many fields. However, ceramics are brittle materials with fracture toughness that is far inferior to that of metals. In order to overcome the low toughness of ceramics, joint structures with high toughness metals, i.e., ceramic/metal composites, have been adopted. Ceramic/metal composites can reduce the disadvantages of ceramics while still exploiting their advantages, and have been widely applied in many fields, such as in industrial equipment and electronic devices. However, thermal stress is generated in the structures during the joint-cooling process, due to the mismatch in the thermal expansion of the ceramic and metal. Therefore, much research has been devoted to the reduction of thermal stress in order to maintain structural strength.¹⁻⁵

One particular type of stress reduction technique, metallic insertion, has been widely proposed,⁶⁻⁹ where a relatively-soft metal is inserted between the ceramic and metal to form a metallic interlayer.

Brazing is a well-known diffusion bonding technique, and has been used to bond different materials together, and AgCu alloys have been employed as brazing filler metals.⁶⁻⁷ In particular, AgCuTi alloys have been widely used to bond ceramic and metal, because the addition of an active metal (Ti) in brazing filler metals effectively improves the wettability of the ceramic surface.⁸⁻¹⁰ Brazing and/or active metal brazing are appropriate for high-temperature applications, where bond strength and corrosion resistance are required, so that ceramic/metal composites can be used over a wide range of temperature. However, although the diffusion of brazing filler metals contributes to significant bonding strength, the influence of such diffusion on the mechanical strength (not bond strength, but material strength) of ceramic/metal composites has not yet been systematically studied. Hence, such an investigation is essential to assess the integrity of ceramic/metal composites with brazing alloys.

In this study, we report the effect of brazing filler metal diffusion on the mechanical strength of a ceramic/metal composite using a SUS304/Cu/Si₃N₄ system with AgCu and AgCuTi brazing alloys. Experimental and numerical analyses are carried out as follows. First, electron microscopy and elemental analyses are conducted on the vicinity of the joint parts, in order to investigate the diffusion of brazing alloys into the Cu interlayer. Next, micro-Vickers hardness tests are conducted on the surface of the Cu interlayer to demonstrate Cu hardening due to diffusion.

Key words: Diffusion, Brazing filler metal, Crack initiation, Cu interlayer, Hardening, Thermal stress
fusión of the brazing alloys. Finally, finite element analyses are performed to discuss the increase in thermal stress due to Cu hardening.

2 Experimental and Stress Analysis

A specimen of a SUS304/Cu/Si3N4 system, including brazing filler metals of AgCu and AgCuTi, was fabricated as follows. Figure 1 shows a schematic drawing of the specimen assembly. The specimen consisted of several thin layers. A 50-μm-thick Ag59.6Cu40.4 (wt.%) brazing filler was inserted between a 300-μm-thick SUS304 layer and a 300-μm-thick Cu interlayer. A 50-μm-thick Ag67.8Cu30.6Ti1.6 (wt.%) brazing filler was inserted between the interlayer and a 300-μm-thick Si3N4 layer. The SUS304/Cu/Si3N4 system was heated to the melting point of the AgCuTi alloy (850°C) at a pressure of 1.3 × 10^-4 Pa using a vacuum furnace and held at this temperature for 15 min. After heating, the structure was cooled to room temperature in the furnace. The surface of the Cu interlayer was analyzed using field emission scanning electron microscopy (FE-SEM), and was examined by energy-dispersive X-ray spectroscopic (EDS) analysis. The vicinity of the AgCuTi/Si3N4 interface was also analyzed using FE-SEM. In addition, micro-Vickers hardness tests were conducted on the surface of the Cu interlayer at a constant indentation load of 0.25N. Indentations were then formed as shown in Fig. 2, and the sizes of the indentations were measured using an optical microscope. The micro-Vickers hardness Hv is given by 

\[ Hv = \frac{0.1891F}{d^2} \]

where \( F \) is the indentation load and \( d \) is the indentation size. From the above experiments, the effect of brazing filler metal diffusion on the hardening of the Cu interlayer was discussed.

Residual thermal stresses under temperature reduction based on the joint-cooling process were calculated for the SUS304/Cu/Si3N4 composite using two-dimensional finite-element (FE) analysis code and the room temperature material properties listed in Table 1. A 2-D model was developed for each of the materials on the basis of the sample shown in Fig. 1, and the five-layer model was formed into a 100-mm square, see Fig. 3 (a). Because of the symmetry of the structure, only one quarter of it needed to be simulated. The model consisted of four-noded plane stress quadrilateral elements, because its thickness was much smaller than the width and the length of the model. The total number of elements was 2000. The thickness of each layer model was set to be 0.004. The thickness of each layer model was set to be experimental value. The initial temperature of the model was set to be 850°C. As a thermal condition, the temperature of the model was lowered to 20°C. The temperature was assumed to be uniform because of the extremely small thickness, and hence all surfaces of the model were assumed to be thermally isolated. The following mechanical boundary conditions were set. The normal displacement of each of the symmetric lines was restrained. All layer models were tied together in order to prevent tangential relative movements between the materials present, see Fig. 3 (b). Cu, AgCuTi and SUS304 were assumed to behave as elastic-plastic materials, and their plastic deformation behaviors were assumed to obey the linear strain hardening rule. In order to discuss the effect of Cu hardening on the thermal stress behavior, the residual thermal stresses were calculated under the following three types of conditions:

![Fig. 1 Schematic of the test sample.](image1)

![Fig. 2 Schematic of indentations at the surface of the AgCu/Cu/AgCuTi system.](image2)

![Fig. 3 Analysis conditions: (a) FE analysis model and (b) tying between the materials present. Note that the dashed lines indicate the symmetrical axes.](image3)

| Table 1 Material properties at room temperature for numerical simulations. |
|------------------|------------------|------------------|------------------|------------------|
| Material   | Young’s modulus \( E \) [GPa] | Poisson’s ratio \( \nu \) | Thermal expansion coefficient \( \alpha \) \( \times 10^{-6}, \text{K}^{-1} \) | Yield strength \( \sigma_y \) [MPa] | Hardening modulus \( H \) [MPa] |
| Cu          | 120.4            | 0.34             | 16.7            | 63.2             | 515.1            |
| AgCuTi      | 90.6             | 0.35             | 18.5            | 490.2            | 1171.4           |
| SUS304      | 196.9            | 0.3              | 16.6            | 257.2            | 440.2            |
| Si3N4       | 304              | 0.27             | 3.4             | —                | —                |
(σ_{yCu} : 63.2MPa, H_{Cu} : 515.1MPa), (2σ_{yCu}, 2H_{Cu}) and (3σ_{yCu}, 3H_{Cu}). Although material properties should depend on temperature, these were assumed to be constant for the simplicity.

### 3 Results and Discussion

Figure 4 (a) shows an FE-SEM micrograph of the Cu interlayer surface after bonding. The brazing filler metals were found to diffuse into the Cu interlayer and ramify. The amount of AgCuTi diffusion was somewhat larger than that of AgCu. The micrograph in Fig. 4 (b) shows a magnified view of part A in Fig. 4 (a). The primary Cu phases (B) and a network-like solid solution of Ag and Cu (C) were evident, particularly around the Cu/Si₃N₄ joint including the brazing filler of AgCuTi alloy with active metal (Ti) content. The active metal is considered to promote the solute effects, in addition to enhancing metal diffusion. Figure 5 shows the distributions of (a) Ag, (b) Cu, (c) Ti and (d) N at the Cu interlayer surface, obtained by EDS analysis. The magnified views in Figs. 5 (a) and (b) indicate the solid solutions of Ag and Cu. Figure 5 (c) indicates the diffusion of Ti atoms toward the boundary between AgCuTi and Si₃N₄, i.e., interfacial segregation. In addition, Figs. 5 (c) and (d) imply the generation of a TiN layer at the boundary. It is well known that Ti atoms easily combine with N atoms of Si₃N₄ to form TiN. In addition, the syntheses of some nitrides, such as M₂N (M : Ti, Si, Ag, Cu), have also been reported.

Figure 6 shows crack initiation at the surface of Si₃N₄ around the boundary between AgCuTi and Si₃N₄. This is considered to be due to the thermal stress, which results from a mismatch of the coefficient of thermal expansion between the materials present. Ceramics are typically inferior to metals in fracture toughness, which explains the crack propagation through Si₃N₄. Hence, the fracture strength of the SUS304/Cu/Si₃N₄ composite depends on the thermal stress at Si₃N₄. The origin of the crack was observed at the boundary, and two types of potential origins are considered. The first is an accumulation of vacancies, namely cavity formation, resulting from interface diffusion of AgCuTi. It has been reported that stress-induced vacancy diffusion occurs at the inter-

---

![Fig. 4](image-url)  
**Fig. 4** FE-SEM micrographs: (a) the Cu interlayer surface, and (b) a magnified view of part A indicated in (a). The parts denoted as B and C indicate the primary Cu phase and a network-like solid solution of Ag and Cu, respectively.

![Fig. 5](image-url)  
**Fig. 5** Results of componential analysis: distributions of (a) Ag, (b) Cu, (c) Ti and (d) N at the Cu interlayer surface by EDS analysis.

![Fig. 6](image-url)  
**Fig. 6** Crack initiation at the surface of Si₃N₄ in the vicinity of the AgCuTi/Si₃N₄ interface.
face between two materials, which results in some accumulations of vacancies.\textsuperscript{15}−\textsuperscript{17} The other phenomenon is the generation of reactive layer (TIN) due to the interfacial segregation of Ti atoms. Such a layer is well known as a brittle material that has a number of defects. If thermal stresses act on such cavities and/or defects, then stress concentrations occur due to their singularity, which becomes the driving force for crack growth through SUS304.

Figure 7 shows the distribution of hardness at the surface of the AgCu/Cu/AgCuTi system. It should be noted that the term $x$ shown in the transverse axis denotes the distance from the boundary between SUS304 and AgCu. Hardening of the Cu interlayer was demonstrated in the ranges of about 50-100$\mu$m and 300-350$\mu$m (diffusion regions). Figures 4 (a) and (b) indicate that the diffusion regions consist of AgCu solid solutions and primary Cu phases. The results of further hardness tests (performed on surfaces of the AgCu solid solutions and primary Cu phases) revealed that primary Cu phases were relatively hard compared to the AgCu solid solutions ($H_{\text{Cu}} : 113-127$, $H_{\text{AgCu}} : 72-90$). The values of $H_{\text{Cu}}$ are approximately twice as large as the experimental results for a Cu plate (64-67).

The phenomenon of Cu hardening in the diffusion regions may be due to crystal lattice strain resulting from the penetration of Ag atoms into the Cu interlayer. Based on these results, diffusion of the brazing filler metals caused hardening of the Cu interlayer, i.e., loss of ductility, and should result in an increased yield stress and an increased hardening modulus. According to other research, the hardening modulus of Cu is raised by the addition of Ag.\textsuperscript{18}

Residual thermal stresses were evaluated with a focus on Si$_3$N$_4$, because the fracture strength of the SUS304/Cu/Si$_3$N$_4$ composite should depend on the thermal stress at Si$_3$N$_4$. The crack initiation is considered to be due to shear stress around the AgCuTi/Si$_3$N$_4$ boundary, because the crack growth occurs along the boundary. In the present analysis, no shear stress, however, was generated because of the isotropic elasto-plasticity of the layers and no tangential relative motions between the materials present. In contrast, shear stresses are considered to be generated in the real sample. This can be explained by the crystal anisotropy in each layer. Materials are generally polycrystalline structures composed of randomly-oriented grains and an elastic principal axis of each of the grains disagrees with a loading direction; therefore, the materials are assumed to be isotropy from a macroscopic viewpoint, while they are assumed to be anisotropy from a microscopic viewpoint. If normal thermal stresses due to isotropy (macroscopic stresses) are caused to the sample by a joint-cooling process, then shear stresses (microscopic stresses) occur due to crystal anisotropy. In other words, the normal thermal stresses induce the shear stresses which become the driving force for crack growth; therefore, a normal stress was applied for evaluation of the thermal stress. Table 2 shows the residual thermal stresses at Si$_3$N$_4$ for the three types of yield stresses and hardening moduli. The Si$_3$N$_4$ layer was negatively stressed, because its coefficient of thermal expansion was much lower than any of the other layers.

The increase in thermal stress due to the increases in the yield stress and hardening modulus of Cu. These results provide an explanation for reduction in strength of the structure, because an increase in thermal stress enhances the driving force for crack growth.

The increase in thermal stress due to the increases in the yield stress and hardening modulus is discussed using the simple model shown in Fig. 8. From the results of the stress analyses, it was found that all-metal

![Fig. 7](image_url) Fig. 7 Hardness as a function of $x$ at the surface of the AgCu/Cu/AgCuTi system. The term $x$ is the distance from the boundary between SUS304 and AgCu. Note that the red line indicates the hardness of a Cu plate.

![Fig. 8](image_url) Fig. 8 Simplified model showing the multilayer, and the thermal stress for each of the layers.

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$\rho_{\text{Cu}}$ [MPa]</th>
<th>$\rho_{\text{AgCu}}$ [MPa]</th>
<th>Thermal stress [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>63.2</td>
<td>515.1</td>
<td>-510.2</td>
</tr>
<tr>
<td>2</td>
<td>126.4</td>
<td>1030.2</td>
<td>-581.7</td>
</tr>
<tr>
<td>3</td>
<td>189.6</td>
<td>1545.3</td>
<td>-652.2</td>
</tr>
</tbody>
</table>
layers were positively stressed. The thermal stress at each layer is indicated by $\sigma_i (i = 1, 2, 3, 4)$. The term $s$ denotes the Si$_3$N$_4$ layer, and the numbers 1, 2, 3 and 4 denote the AgCuTi, Cu, AgCu and SUS304 layers, respectively. In addition, the thickness of each layer is indicated by $t_i$. The strain, $\epsilon_i$, is approximately described by the sum of the elastic, plastic and thermal components. If we consider a material with a plane stress and a linear stain hardening, then the strain $(\epsilon_i)$ is given by

$$\epsilon_i = \frac{\sigma_{iy}}{E_i (1 - \nu_i)} + \frac{\sigma_{iy} - \sigma_{iy}^*}{2H_i} + \alpha_i (T_i - T_b), \quad (1)$$

where $E_i$, $\nu_i$, $\sigma_{iy}$, $H_i$, $\alpha_i$, $T_b$ and $T_H$ are Young’s modulus in the longitudinal direction, Poisson’s ratio, the yield stress, the hardening modulus, the coefficient of thermal expansion, the room temperature and the temperature before joint-cooling process, respectively. The yield stress ($\sigma_{iy}$) of Si$_3$N$_4$ is set to $\sigma_s$ because of the elastic material; therefore, the plastic strain is set to zero. In contrast, all-metal layers had plastic strains in the present analyses. The strains at all layers are equal because of zero tangential relative motions between the materials present. A requisite condition for the equilibrium of force, namely zero external force, gives the stress $\sigma_i$:

$$\sigma_i = \sum_{j=1}^{4} H_{ij} [(\sigma_{ij} - \sigma_{ij}^*) (T_j - T_b) - \beta_i]$$

(2)

with

$$\beta_i = \left( \frac{1}{2H_i} - \frac{1 - \nu_i}{E_i} \right) \sigma_{iy}^*, \quad (3)$$

These imply that the increase in yield stress accelerates the increase in compressive-thermal stress. The values of $\alpha_i$ against yield stress $\sigma_{iy} (= \gamma \sigma_{iy})$ and/or hardening modulus $H_i (= \gamma H_{Cy})$ were obtained using the material properties listed in Table 1, Eqs. (2) and (3). It should be noted that the term $\gamma$ is the multiplicative factor with respect to the yield stress and hardening modulus of Cu.

Figure 9 shows the compressive-thermal stresses from FE analysis and the above equations. The theoretically-obtained model agrees well with analysis results. This agreement emphasizes that the Cu hardening enhances the residual thermal stress in the SUS304 layer.

The experiments results and FE analyses indicate that diffusion of the brazing filler metals reduces the mechanical strength of the SUS304/Cu/Si$_3$N$_4$ composite. Although diffusion techniques have been widely utilized to bond ceramic and metal due to significant bonding strength, diffusion relaxation is required to minimize reduction of the mechanical strength in ceramic/metal composite. Therefore, it is necessary to maintain a balance between bonding and mechanical strength.

4 Conclusions

The effects of brazing filler metal diffusion on the mechanical strength in a ceramic/metal composite were studied using a SUS304/Cu/Si$_3$N$_4$ system with brazing alloys of AgCu and AgCuTi. Cracking was generated around the boundary between AgCuTi and Si$_3$N$_4$ due to thermal stress. The crack origin was most likely a cavity, due to interface diffusion of AgCuTi or a defect in the reactive layer formed as a result of the interfacial segregation of Ti atoms. The brazing filler metals diffuse into the Cu interlayer during the joint-cooling process and this phenomenon causes hardening of the interlayer. The thermal stress at Si$_3$N$_4$ increases as the yield stress and hardening modulus of Cu are increased. The results indicate that the diffusion of brazing filler metals does reduce the mechanical strength of the SUS304/Cu/Si$_3$N$_4$ composite. It was found that diffusion relaxation is required to minimize reduction of the mechanical strength in ceramic/metal composite.

References


