

## Effect of Zn-Al Brazing Filler Composition on the Interfacial Structure and Properties of Cu/Zn-Al/Al Brazed Joints Postprint

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**Date:** 2023-03-19T00:00:00+00:00

### Abstract

Cu/Al joints were fabricated by brazing with Zn-15Al, Zn-22Al, Zn-28Al, Zn-37Al, and Zn-45Al filler metals, respectively. The influence of Zn-Al filler metal composition on the Cu base metal/brazing seam interface structure in Cu/Al joints was investigated using SEM, EDS, and XRD, and the relationship among Zn-Al filler metal composition, joint interface structure, and joint shear strength was systematically elucidated. The results revealed that the Cu base metal/brazing seam interface structure in the Cu/Zn-15Al/Al joint consisted of Cu/Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub>, with the Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub> interfacial layer being relatively thin at 2-3 μm, and the joint exhibited a high shear strength of 66.3 MPa. As the Al content in the filler metal increased, the thickness of the Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub> interfacial layer at the Cu/Zn-22Al/Al joint interface gradually increased, and even trace amounts of CuAl<sub>2</sub> appeared near the Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub> interfacial layer in the Cu/Zn-28Al/Al joint, while the joint shear strength progressively decreased. When brazing Cu/Al joints with the higher Al-content Zn-37Al filler metal, the Cu base metal/brazing seam interface structure transformed to Cu/Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub>/CuAl<sub>2</sub>; the formation of the brittle CuAl<sub>2</sub> layer caused a substantial reduction in joint shear strength to 34.5 MPa. When brazing Cu/Al joints with the highest Al-content Zn-45Al filler metal, the Cu base metal/brazing seam interface structure transformed to Cu/CuAl<sub>2</sub>, and the joint shear strength was the lowest, at 31.6 MPa.

## Full Text

### Influence of Zn-Al Filler Metal Composition on Interfacial Structure and Properties of Cu/Zn-Al/Al Brazed Joints

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**Supported by:** Guangdong Provincial Science and Technology Project (No. 2010A080402014)

**Manuscript received:** 2014-09-24, in revised form 2014-11-29

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#### Abstract

Cu/Al dissimilar metal joints are composite structures that can effectively reduce manufacturing costs and product weight while integrating the advantages of both metals. Due to their excellent comprehensive properties, Cu/Al dissimilar metal joints have broad application prospects in air conditioners, refrigerators, cables, electronic components, solar collectors, and other fields. Brazing is considered a promising method for joining Cu/Al dissimilar metals because of its lower residual stress, lower cost, higher precision, and better adaptability to joint structures. Meanwhile, Zn-Al filler metals are regarded as relatively ideal filler materials due to the superior properties of Cu/Zn-Al/Al joints. However, the influence of Zn-Al filler metal composition on the interfacial structure near the Cu substrate and the properties of Cu/Al joints has not been investigated.

In this work, Cu/Al joints were brazed using Zn-15Al, Zn-22Al, Zn-28Al, Zn-37Al, and Zn-45Al filler metals, respectively. The effects of Zn-Al filler metal composition on the interfacial structure near the Cu substrate in Cu/Al joints were investigated using SEM, EDS, and XRD, and the relationships between Zn-Al filler metal composition, interfacial structure, and joint shear strength were systematically elucidated.

The study revealed that the interfacial structure of the Cu/Zn-15Al/Al brazed joint was Cu/Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub>, with a thin Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub> interfacial layer measuring 2-3 μm, resulting in a high shear strength of 66.3 MPa. As the Al content in the filler metal increased, the thickness of the Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub> interfacial layer at the Cu/Zn-22Al/Al joint interface gradually increased, and even a small amount of CuAl<sub>2</sub> appeared near the Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub> interfacial layer in the Cu/Zn-28Al/Al joint, leading to a gradual decrease in shear strength.

When using the higher Al-content Zn-37Al filler metal, the Cu substrate/filler interface structure transformed to  $\text{Cu}/\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}/\text{CuAl}_2$ ; the appearance of the brittle  $\text{CuAl}_2$  layer caused a significant drop in shear strength to 34.5 MPa. With the highest Al-content Zn-45Al filler metal, the interface structure changed to  $\text{Cu}/\text{CuAl}_2$ , yielding the lowest shear strength of 31.6 MPa.

**Keywords:** Cu/Al joint, brazing, interfacial structure, intermetallic compound, shear strength

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## Experimental Methods

The interfacial structure and fracture morphology of the brazed Cu/Al joints were examined using a Quanta 250 scanning electron microscope (SEM). The phase composition in the interfacial zones of the Cu/Al joints was analyzed using a STOE/STADI P ( $\text{CuK}\alpha$ ) X-ray diffractometer (XRD). Prior to XRD analysis, the Al substrate side of the Cu/Al joint was removed, and the remaining portion was ground down to near the Cu substrate/filler interface to prepare the XRD sample.

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## Results and Discussion

**2.2 Influence of Zn-Al Filler Metal Composition on Shear Strength of Cu/Al Brazed Joints** Variations in Zn-Al filler metal composition significantly affect both the type and thickness of intermetallic compound layers at the Cu/Zn-Al/Al brazed joint interface. This transformation in interfacial structure inevitably exerts a pronounced influence on the mechanical properties of Cu/Al joints. Figure 4 [Figure 4: see original paper] presents the shear strengths of Cu/Al joints brazed with the five different Zn-Al filler metals.

The results demonstrate that, under the experimental conditions of this study, the shear strength of Cu/Zn-Al/Al brazed joints gradually decreases with increasing Al content in the filler metal. The Cu/Zn-15Al/Al joint exhibits a high shear strength of 66.3 MPa. The Cu/Zn-22Al/Al joint follows with a strength of 59.8 MPa, while the Cu/Zn-28Al/Al joint shows a lower strength of 50.9 MPa. Notably, all three joints achieve shear strengths exceeding 50 MPa, which corresponds to more than 72.5% of the Al substrate strength. However, when using higher Al-content Zn-37Al and Zn-45Al filler metals, the shear strengths drop dramatically to 34.5 MPa and 31.6 MPa, respectively—substantially lower than those of the Cu/Zn-15Al/Al, Cu/Zn-22Al/Al, and Cu/Zn-28Al/Al joints.

**3. Analysis and Discussion** Changes in Zn-Al filler metal composition distinctly alter the interfacial structure at the Cu substrate/filler interface in Cu/Zn-Al/Al joints. As the Al content in the filler metal increases, the interface structure gradually transitions from  $\text{Cu}/\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  to  $\text{Cu}/\text{CuAl}_2$ .

This transformation arises from the sequential precipitation and interaction of  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  and  $\text{CuAl}_2$  at the interface.

Generally, to reduce nucleation difficulty, intermetallic compounds tend to precipitate at existing interfaces, such as the Cu substrate surface in this study. According to literature [10, 12, 24-26],  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  is more likely to precipitate on the Cu substrate surface than Al-Cu compounds (such as  $\text{CuAl}_2$ ,  $\text{CuAl}$ , and  $\text{Cu}_9\text{Al}_4$ ) due to its lower formation energy—a conclusion that this study reaffirms. When brazing Cu/Al joints with the lowest Al-content Zn-15Al filler metal,  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  precipitates first on the Cu substrate surface and grows perpendicular to the interface into the filler, forming a continuous intermetallic layer with fine protrusions (Figure 2a). At this stage, the Cu/Zn-15Al/Al joint interface forms a  $\text{Cu}/\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  structure.

When using Zn-22Al filler metal, the relative Al content in the liquid filler increases, intensifying  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  precipitation on the Cu substrate surface [12] and thickening the  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  layer. Simultaneously, another compound— $\text{CuAl}_2$ —begins to precipitate in the filler near the Cu substrate/filler interface (Figure 2b). In the Cu/Zn-28Al/Al joint,  $\text{CuAl}_2$  precipitation is enhanced, with small amounts even appearing on the surface of the interfacial  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  layer (Figure 2c). Although the interfaces of Cu/Zn-22Al/Al and Cu/Zn-28Al/Al joints remain primarily composed of  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$ , the emergence of  $\text{CuAl}_2$  gradually initiates changes in the interfacial structure.

This transition becomes particularly evident when brazing Cu/Al joints with Zn-37Al and Zn-45Al filler metals. At the Cu substrate/filler interface of the Cu/Zn-37Al/Al joint, abundant  $\text{CuAl}_2$  precipitates directly on the  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  layer, forming a connected compound layer and transforming the interface structure to  $\text{Cu}/\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}/\text{CuAl}_2$ . Moreover, the substantial presence of  $\text{CuAl}_2$  suppresses  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  precipitation, even causing fracture of large  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  protrusions and hindering their growth into the filler (Figure 2d).

In the Cu/Zn-45Al/Al joint, the further increased relative Al content in the filler promotes additional  $\text{CuAl}_2$  precipitation near the interface, which further suppresses the nucleation and growth of  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  on the Cu substrate surface. The  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  layer becomes thinner and cannot form a continuous layered distribution. In some interfacial regions,  $\text{CuAl}_2$  begins to connect directly with the Cu substrate, ultimately transforming the interface structure to  $\text{Cu}/\text{CuAl}_2$  (Figure 2e).

Thus, increasing Al content in Zn-Al filler metals promotes  $\text{CuAl}_2$  precipitation at the Cu substrate/filler interface, while the precipitated  $\text{CuAl}_2$  inhibits the nucleation and growth of  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  on the Cu substrate surface, thereby inducing the interfacial structure evolution from  $\text{Cu}/\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7} \rightarrow \text{Cu}/\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}/\text{CuAl}_2 \rightarrow \text{Cu}/\text{CuAl}_2$ .

The transformation from a fine  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  layer to a thick, coarse  $\text{CuAl}_2$  layer at the Cu/Al joint interface inevitably deteriorates the joint shear strength

[27,28]. The influence of interfacial structure on shear strength is directly reflected in the fracture morphology. Figure 5 [Figure 5: see original paper] shows the fracture surfaces on the Cu substrate side of Cu/Al joints brazed with the five Zn-Al filler metals. All joints fractured at the Cu substrate/filler interface.

The fracture morphology of the Cu/Zn-15Al/Al joint (Figure 5a) consists of fine dimples (J) and cleavage planes (K) resulting from brittle fracture. EDS analysis indicates that the dimple region J contains 53.9Al-36.92Cu-9.18Zn (at%), which, combined with the intermetallic compound analysis in Section 2.1, identifies these dimples as intergranular fracture of  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$ . The cleavage plane K contains 46.27Al-44.64Cu-9.1Zn, corresponding to transgranular fracture at the root of the  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  layer. The thin (2-3  $\mu\text{m}$ )  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  interfacial layer with fine protrusions requires greater energy for crack propagation, which is the primary reason for the observed ductile intergranular fracture and the high shear strength of the Cu/Zn-15Al/Al joint.

For the Cu/Zn-22Al/Al joint (Figure 5b), the increased thickness of the  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  layer (5-6  $\mu\text{m}$ ) results in significantly fewer dimples and larger brittle cleavage planes compared to the Cu/Zn-15Al/Al joint, leading to reduced shear strength. The Cu/Zn-28Al/Al joint fracture morphology (Figure 5c) shows a further increase in cleavage area due to the thicker  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  layer and the presence of small amounts of brittle  $\text{CuAl}_2$  at the interface, which decreases the energy required for crack propagation and makes the joint more susceptible to brittle fracture, further reducing its strength.

The fracture morphology of the Cu/Zn-37Al/Al joint (Figure 5d) exhibits, in addition to cleavage planes (L) from brittle fracture of the  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  layer, a new cleavage plane (M). EDS analysis shows that region M contains 63.91Al-32.78Cu-3.31Zn, identifying it as fractured  $\text{CuAl}_2$ . Since the interfacial structure of the Cu/Zn-37Al/Al joint has transformed to  $\text{Cu}/\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}/\text{CuAl}_2$ , the extremely brittle  $\text{CuAl}_2$  facilitates crack initiation and propagation [13,14], causing a substantial decrease in shear strength compared to joints brazed with Zn-15Al, Zn-22Al, and Zn-28Al filler metals.

The Cu/Zn-45Al/Al joint fracture morphology (Figure 5e) shows a completely brittle cleavage fracture. EDS analysis of cleavage plane (N) reveals a composition of 65.70Al-31.17Cu-3.13Zn, confirming it as  $\text{CuAl}_2$ . The thick, coarse  $\text{CuAl}_2$  layer at the Cu substrate/filler interface serves as a crack source, further degrading the joint's mechanical properties.

Based on the results regarding interfacial structure, mechanical properties, and fracture morphology of Cu/Zn-Al/Al joints, Zn-Al filler metal composition significantly influences both the Cu substrate/filler interfacial structure and the joint shear performance. When the Al content in the filler metal is 15%-28%, the Cu/Zn-Al/Al joint interface structure is  $\text{Cu}/\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$ , and the relatively thin  $\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$  layer is beneficial for shear strength. At 37% Al content, the interfacial structure becomes  $\text{Cu}/\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}/\text{CuAl}_2$ , and the appearance of the thick, brittle  $\text{CuAl}_2$  layer causes a sharp decline in shear

strength. When Al content further increases to 45%, the interface structure transforms to Cu/CuAl<sub>2</sub>, resulting in the poorest shear performance. Therefore, when selecting Zn-Al filler metals for brazing Cu/Al joints, the Al content should not exceed 28%.

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## Conclusions

1. When the Al content in Zn-Al filler metal is 15%-28%, the Cu/Zn-Al/Al joint interface structure is Cu/Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub>. At 37% Al content, the interface structure transforms to Cu/Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub>/CuAl<sub>2</sub>. When Al content further increases to 45%, the interface structure becomes Cu/CuAl<sub>2</sub>. This evolution is caused by the sequential precipitation and interaction of Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub> and CuAl<sub>2</sub> at the interface.
2. The Cu/Zn-15Al/Al joint, with its thin (2-3 μm) Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub> interfacial layer, exhibits high shear strength of 66.3 MPa. When brazing Cu/Al joints with Zn-37Al filler metal, the interface structure changes to Cu/Al<sub>4.2</sub>Cu<sub>3.2</sub>Zn<sub>0.7</sub>/CuAl<sub>2</sub>, and the appearance of the thick, brittle CuAl<sub>2</sub> layer causes a significant drop in shear strength to 34.5 MPa. The Cu/Zn-45Al/Al joint, with its Cu/CuAl<sub>2</sub> interface structure, shows the lowest shear strength of only 31.6 MPa.
3. The Cu substrate/filler interfacial structure is the primary factor affecting the mechanical properties of Cu/Al brazed joints. Once a continuous CuAl<sub>2</sub> layer forms at the Cu substrate/filler interface, the joint strength drops sharply. Therefore, when selecting Zn-Al filler metals for brazing Cu/Al joints, the Al content should not exceed 28%.

*Note: Figure translations are in progress. See original paper for figures.*

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