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Citation	Transactions of JWRI. 2011, 40(2), p. 33-36
Version Type	VoR
URL	<a href="https://doi.org/10.18910/5952">https://doi.org/10.18910/5952</a>
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# Bonding process of Cu/Cu joint using Cu nanoparticle paste<sup>†</sup>

NISHIKAWA Hiroshi\*, HIRANO Tomoaki\*\*, TAKEMOTO Tadashi\*\*\*

## Abstract

*High-temperature bonding, or joining, is a key technology for electronic component assembly and other high-temperature applications. Recently, focusing on the sintering behavior of nanoparticles, the joining process using a nanoparticle paste has been proposed as an alternative to soldering for high-temperature applications. In this study, Cu nanoparticle paste was used to join two Cu discs, and the effect of heating conditions on the joint strength of the Cu-to-Cu joint was investigated. Joining using Cu nanoparticle paste was successfully achieved, and joints that were bonded at 673 K for 300 s under nitrogen atmosphere showed high shear strength.*

**KEY WORDS:** (High-temperature joining), (Cu nanoparticle paste), (Cu-to-Cu joint), (Shear strength), (high-temperature applications)

## 1. Introduction

The European Restriction of Hazardous Substances (RoHS) directive currently exempts the used of high-lead-containing solders for high-temperature soldering, as high-temperature soldering is a key technology for electronic component assembly and other high-temperature applications. However, there is no guarantee that the exemption will last. A strong drive thus exists to find lead-free alternatives for high-temperature joining processes. Research is needed to establish and characterize a new joining process for high-temperature applications. Several materials and joining processes have been proposed as alternatives to high-lead-containing solders. For example, Au-, Zn- and Bi-based alloys have been investigated for use as lead-free solder, but their widespread use is unlikely because of their inferior properties and high costs [1-8]. New joining processes involving thin film joining process using evaporated films and sintering process using particles have also been proposed as solder alternatives [9-11].

Metals such as Ag, Cu and Au have high electrical and thermal conductivities and exhibit limited fatigue. These metals tend to have high melting points. These properties make them suitable for high-temperature joining process. For instance, one candidate process that might be applicable for joining at lower temperature is sintering. Standard sintering procedures still require relatively high joining temperatures, although the sintering temperature of a metal particle is below its

melting point. Related to using nanoparticles, it is well known that metal nanoparticles sinter and melt at temperatures lower than that for the bulk metal. The sintering behavior of nanoparticles is of significant interest.

Furthermore, the sintering behavior of metallic nanoparticles has been exploited to write electronic circuits and join components to substrate [12-17]. For example, Ide et al. [13] reported achieving Cu-to-Cu joining using Ag metallo-organic nanoparticles at a low bonding temperature (573 K) and a bonding pressure of 1 or 5 MPa; the shear strength of the resulting joints was 25-40 MPa. Bonding was believed to occur because of the large surface energy contributed by the nanoparticles. As the latest work for low temperature bonding using Ag nanoparticles, Hu et al. [16] reported that robust bonding of Cu wire to Cu pads on polyimide was achieved at 373 K through solid state sintering of Ag nanoparticle and metallic bonding of Ag to Cu substrates. Using the sintering behavior of Cu nanoparticles, Jang et al. [17] reported using Cu nanoparticles as ink to print a conductive Cu pattern directly on flexible polyimide substrates using their own functional materials and printing system. However, the microstructure in the bottom of the film was not completely dense and the achieved line exhibited higher resistance than a conventional conductive line.

Cu nanoparticles seem particularly promising for joining materials because of their low resistivity, low cost and good electromigration performance. Accordingly, our

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Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

research group has proposed a joining process for high-temperature applications that uses Cu nanoparticle paste as an alternative to solder. In this study, the effect of heating conditions on the joint strength of a Cu-to-Cu joint formed using Cu nanoparticle paste has been investigated to obtain high joint strength.

## 2. Experimental

The paste used in this study consisted of Cu nanoparticles and organic solvent, for a metal content of about 60 mass%. Cu nanoparticles were synthesized by a chemical reduction method in solution. A glycol system was used as organic solvent to prevent oxidation of Cu nanoparticles. Nanoparticle diameters were in the ranges of 10 to 20 nm. The thermal characteristics of the paste were measured by differential thermal analysis (DTA) and thermogravimetry (TG) at a heating rate of 0.17 K/s in air and under a nitrogen atmosphere.

The two different-sized oxygen-free Cu specimens were used for the joining experiment. The faying surfaces of the specimens were polished with 2000-grit SiC paper and 1  $\mu\text{m}$  diamond paste, then soaked in ethanol solution for 300 s. Just before bonding, the specimens were soaked in hydrochloric acid and cleaned with distilled water and ethanol solution. Cu nanoparticle paste was applied to the faying surface of the  $\phi 10$  mm Cu specimen to a thickness of 150  $\mu\text{m}$ , and then the  $\phi 3$  mm Cu specimen was set on top.

Cu-to-Cu disc specimens so created were bonded by heating in a furnace. Bonding was performed in a two-step heating process. For two-step heating, specimens were preheated for various times (60, 300, 600, 1800 s) under normal pressure at the following temperatures: 363, 393, 423, 453, 483, 513, and 543 K; then they were heated for various heating times (60, 300, 1800, 3600 s) under joining pressure of 15 MPa at the following temperatures: 553, 593, 633, and 673 K. The joining atmosphere was air or a nitrogen atmosphere.

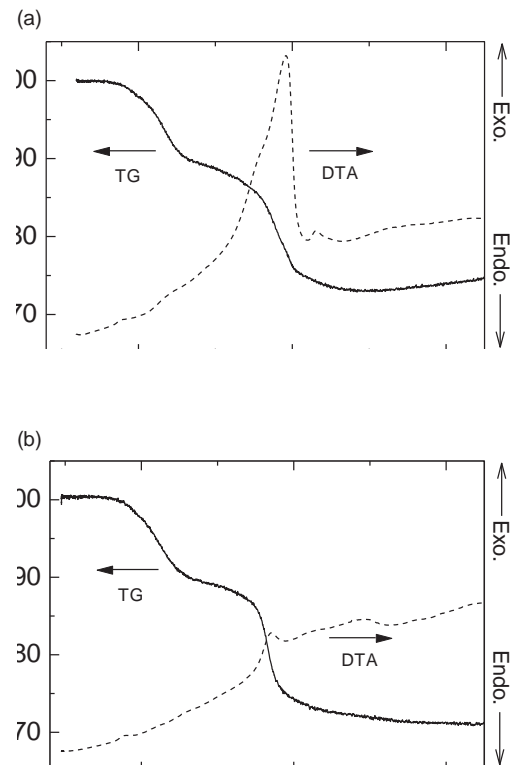
The shear test method was used to investigate the joint strength of the disc joints. The shear strengths of three joints for each joining condition were measured at a shear strain rate of 0.017 mm/s. The strength was estimated by the average of three trials. After shearing, the fracture surfaces were observed by scanning electron microscopy (SEM).

## 3. Results and discussion

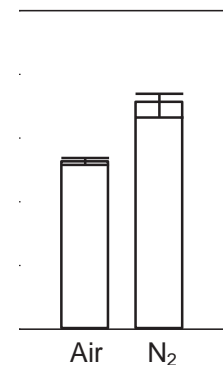
Figure 1 shows DTA and TG curves for Cu nanoparticle paste during heating at a rate of 0.17 K/s in air and under a nitrogen atmosphere. For heating both in air and under nitrogen atmosphere, a first mass loss is evident at 380–450 K, attributable to decomposition of the solvent, and a second loss of mass is evident at around 570 K. The DTA curves show clear exothermal behavior, at much higher intensity in air than under nitrogen atmosphere. The second loss of mass can be attributed to decomposition of the protective agent that was present in the nanoparticles to prevent self-cohesion. The TG curves in air and under nitrogen atmosphere are

essentially identical until 670 K, after which a gain in mass is evident in air but not under nitrogen atmosphere, perhaps attributable to oxidation of the nanoparticles.

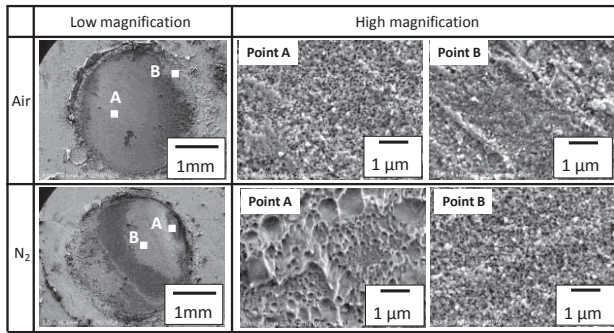
The Cu-to-Cu disc joints using Cu nanoparticle paste were made using two-step heating process. To investigate the effect of joining atmosphere on the joint strength, the disc joints using Cu nanoparticle paste were made in air and under a nitrogen atmosphere. Figure 2 shows the effect of joining atmosphere on the shear strength of the disc joints. The preheating was performed for 300 s under normal pressure at 423 K, and then heating was performed for 300 s at 673 K. The shear strength under



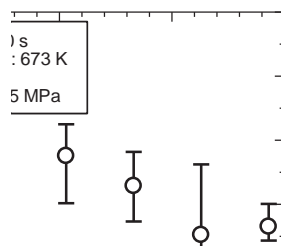
**Fig. 1** DTA and TG curves of Cu nanoparticle paste under heating rate of 0.17 K/s in Air (a) and N<sub>2</sub>(b).



**Fig. 2** Effect of joining atmosphere on shear strength of joints using Cu nanoparticle paste. (Preheating temperature: 423 K, preheating time 300 s, heating temperature: 673 K, heating time 300 s, bonding pressure: 15 MPa)



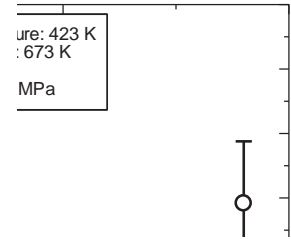
**Fig. 3** SEM images of typical fracture surface of joints in air and  $N_2$ . (Preheating temperature: 423 K, preheating time 300 s, heating temperature: 673 K, heating time 300 s, bonding pressure: 15 MPa)



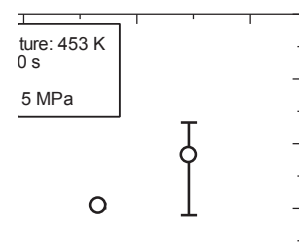
**Fig. 4** Effect of preheating temperature for 300 s on shear strength of joints in  $N_2$ . (Preheating time: 300 s, heating temperature: 673 K, heating time: 300 s, bonding pressure: 15 MPa)

the nitrogen atmosphere was higher than that in air. The strength is  $\sim 40$  MPa. This result suggests that it is important to prevent oxidation of Cu nanoparticles during heating. To investigate the difference of the joint strength related to the atmosphere, the fracture surface after the shear test was observed. **Figure 3** shows SEM images of the fracture surface of disc joints in air and under the nitrogen atmosphere. For heating both in air and under the nitrogen atmosphere, distinctive fracture surfaces are evident in joints bonded at 673 K. Especially for heating under the nitrogen atmosphere, the nanoparticles have sintered, and an elongated dimple structure is partially observable on the fracture surface of the joints. On the other hand, for heating in air, the spherical shape made from Cu nanoparticles is retained in all area. This result suggests that Cu nanoparticle sintering progresses effectively under nitrogen atmosphere.

The Cu-to-Cu disc joints using Cu nanoparticle paste were made under the various preheating and heating conditions under a nitrogen atmosphere. **Figure 4** shows the effect of the preheating temperature on the shear strength of the disc joints. The preheating was performed for 300 s under normal pressure at various temperatures, and then heating was performed for 300 s at 673 K. For



**Fig. 5** Effect of preheating time at 423 K on shear strength of joints in  $N_2$ . (Preheating temperature: 423 K, heating temperature: 673 K, heating time: 300 s, bonding pressure: 15 MPa)

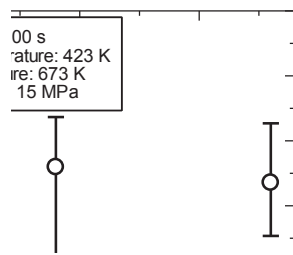


**Fig. 6** Effect of heating temperature for 300 s on shear strength of joints in  $N_2$ . (Preheating temperature: 453 K, preheating time: 300 s, heating time: 300 s, bonding pressure: 15 MPa)

preheat process, the temperature  $< 500$  K have no effect on shear strength. For preheat temperatures of 513 and 543 K, shear strength clearly decreases relative to its values at lower temperatures. This result may be attributable to gradual nanoparticle sintering during preheating process, causing them to assume a size that prevents subsequent sintering during the second heating step at 673 K. **Figure 5** shows the effect of the preheating time on the shear strength of the disc joints. The preheating was performed for various times under normal pressure at 423 K, and then heating was performed for 300 s at 673 K. The maximum shear strength was found at 300 s. For preheat time of 1800 s, shear strength clearly decreases relative to its values at shorter time. This result may be also attributable to gradual nanoparticle sintering during preheating process.

**Figure 6** shows the effect of the heating temperature on the shear strength of the disc joints. The preheating was performed for 300 s under normal pressure at 453 K, and then heating was performed for 300 s at various temperatures. The shear strength of the disc joints increases with increasing heating temperature; at 553 and 593 K it is  $< 15$  MPa and at 673 K, which is higher than the decomposition temperature of the protective agent, it

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**Fig. 7** Effect of heating time at 673 K on shear strength of joints in  $N_2$ . (Preheating temperature: 423 K, preheating time: 300 s, heating temperature: 673 K, bonding pressure: 15 MPa)

is  $< 35$  MPa. The thermal characteristics of the paste strongly affect the relationship between heating temperature and joint strength. **Figure 7** shows the effect of the heating time on the shear strength of the disc joints. The preheating was performed for 300 s under normal pressure at 423 K, and then heating was performed for various times at 673 K. the heating time  $> 60$  s have little effect on shear strength.

### 4. Conclusions

In this study, a joint process using Cu nanoparticle paste was developed as a replacement for high-lead containing solder for high-temperature applications. Especially, the effect of heating conditions on the shear strength of Cu-to-Cu disc joints using Cu nanoparticle paste was investigated. The main results are as follows:

- (1) Joints that were bonded under a nitrogen atmosphere at 673 K for 300 s under a joining pressure of 15 MPa showed high shear strength ( $\sim 40$  MPa), demonstrating the successful use of Cu nanoparticle paste to form joints. Under the nitrogen atmosphere, the nanoparticles in the paste became effectively sintered, forming an elongated dimple structure that was partially observable on the fracture surface of the joint.
- (2) Joining conditions such as preheating temperature and heating temperature significantly affect the shear strength of a joint.

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