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Effects of Joining Conditions on Joint Strength of Cu/Cu Joint Using Cu Nanoparticle Paste

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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 joining conditions on the joint strength of the Cu-to-Cu joint was investigated. Joining using Cu nanoparticle paste was successfully achieved, but the effect of joining conditions such as heating temperature and joining atmosphere on joint strength of the Cu-to-Cu joint was significant.

Keywords: Cu nanoparticle paate, joint strength, joining atmosphere, high-temperature joining.

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 process. 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 procedure still requires relatively high joining temperature, although the sintering temperature of metal particle is below its melting point. Furthermore, two strategies exist for lowering the sintering temperature even further: the use of pressure and the use of nanoparticles. Pressure increases the sintering driving force [9], and application of external pressure is believed to increase densification by compressing/deforming and thus eliminating some fraction of pores, which increases the contact area between particles. On the other hand, 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. Computer simulations, particularly atomistic simulations, reveal the fundamental mechanisms of nanoparticle sintering and offer a convenient and practical way to investigate small scale phenomena. Many attempts have been made to model nanoparticle sintering using molecular dynamics simulations [12-14].

Furthermore, the sintering behavior of metallic nanoparticles has been exploited to write electronic circuits and join components to substrate [15-20]. For example, Ide *et al*. [16] 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*. [19] 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*. [20] reported using Cu nanoparticles as ink to print a conductive Cu pattern directly on flexible polyimide substrate 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 research

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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 joining conditions on the strength of a Cu-to-Cu joint formed using Cu nanoparticle paste has been investigated to obtain high joint strength.

EXPERIMENTAL

The paste used in this study consisted of Cu nanoparticles and organic solvent, for a metal content of 60 mass%. Cu nanoparticles were synthesized by a chemical reduction method in solution. 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 nitrogen atmosphere.

Fig. (**1a**) shows the two different-sized oxygen-free Cu specimens used for the joining experiment. The faying surfaces of the specimens were polished with with 2000-grit SiC paper and 1 μm 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 φ10 mm Cu specimen to a thickness of 150 μm, and then the φ3 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 one of two ways: one-step heating or two-step heating. For one-step heating, specimens were heated for 300 s under joining pressure of 15 MPa at the following temperatures: 553, 593, 633, and 673 K. For two-step heating, specimens were preheated for 300 s under normal pressure at the following temperatures: 363, 393, 423, 453, 483, 513, and 543 K; then they were heated for 300 s under joining pressure of 15 MPa at 673 K. The joining atmosphere was variously air, nitrogen, or a nitrogen/oxygen mixture (N_2:O_2 = 5:1, 10:1, 50:1, and 100:1).

Fig. (**1b**) shows the shear test method used to investigate 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).

RESULTS AND DISCUSSION

Fig. (**2**) shows DTA and TG curves for Cu nanoparticle paste during heating at a rate of 0.17 K/s in air and under nitrogen atmosphere. For heating both in air and under nitrogen atmosphere, a first mass loss is evident in 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.

Firstly, one-step heating process was examined. The Cu-to-Cu disc joints using Cu nanoparticle paste were made for 300 s at the various heating temperatures under joining pressure of 15 MPa in air and under nitrogen atmosphere. Fig. (**3**) shows the effect of the heating temperature by one-step heating on the shear strength of the disc joints. For joining both in air and under nitrogen atmosphere, shear strength of the disc joints increases with increasing temperature; at 553 and 593 K it is <20 MPa and at 673 K, which is higher than the decomposition temperature of the protective agent, it is ~40 MPa. In the case of 633 and 673 K, shear strength is higher for heating under nitrogen atmosphere than for heating in air. This may be because oxidation of the nanoparticle is prevented under nitrogen atmosphere. The relatively large effect of heating temperature on shear strength may be attributable to decomposition of the protective agent in the nanoparticle paste. In other words, the thermal characteristics of the paste strongly affect the relationship between heating temperature and joint strength. These results demonstrate the success of Cu-to-Cu joining using Cu nanoparticle paste.

To investigate the difference of the joint strength related to the heating temperature, the fracture surface after the shear test was observed. Fig. (**4**) shows SEM images of the fracture surface of disc joints after one-step heating followed by shear testing. For heating both in air and under nitrogen

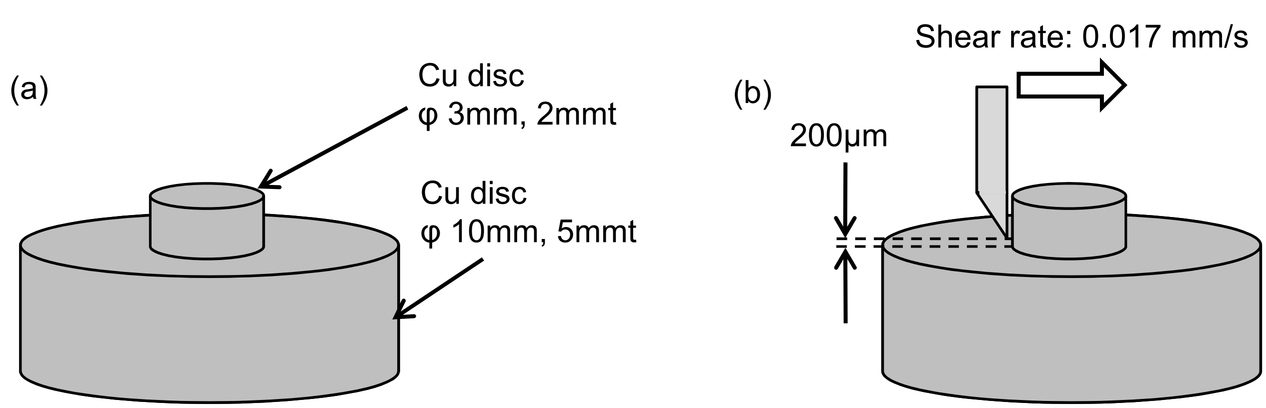

Fig. (1). Schematic diagram of test sample specification (**a**) and shear test method (**b**).

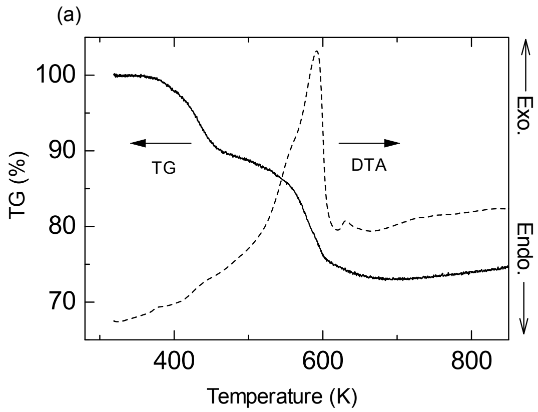

Fig. (2). DTA and TG curves of Cu nanoparticle paste under heating rate of 0.17 K/s in Air (**a**) and N_2 (**b**).

atmosphere, distinctive fracture surfaces are evident in joints bonded at 553 and 673 K. At 553 K, the spherical shape of the nanoparticles is retained for both cases. At 673 K, especially for heating under nitrogen atmosphere, the nanoparticles have sintered, and an elongated dimple structure is partially observable on the fracture surface of the joints. This result suggests that nanoparticle sintering progresses effectively at 673 K.

To improve the shear strength of the disc joints, two-step heating process was examined. To clarify the effect of preheat temperature of two-step heating on the joint strength, the disc joints using Cu nanoparticle paste were made for 300 s under normal pressure at various preheat temperatures. All joining was performed under nitrogen atmosphere. Fig. (**5**) shows the relationship between the preheat temperature and the shear strength of the disc joints. For preheat temperature <500 K have no effect on shear strength. For preheat temperatures of 513 and 543 K, shear strength

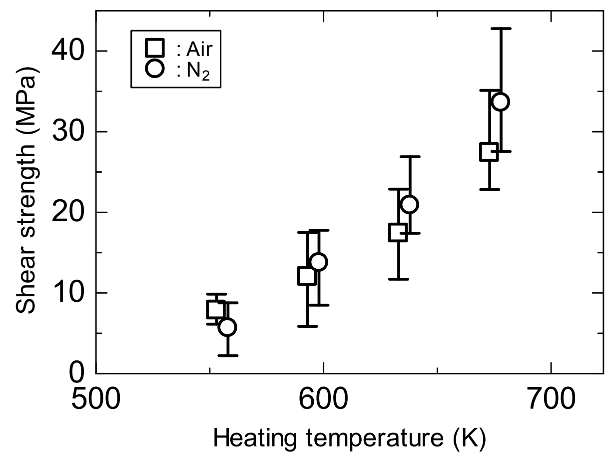

Fig. (3). Effect of heating temperature for 300 s on shear strength of joints using Cu nanoparticle in air and N_2. (One-step heating, joining pressure: 15MPa).

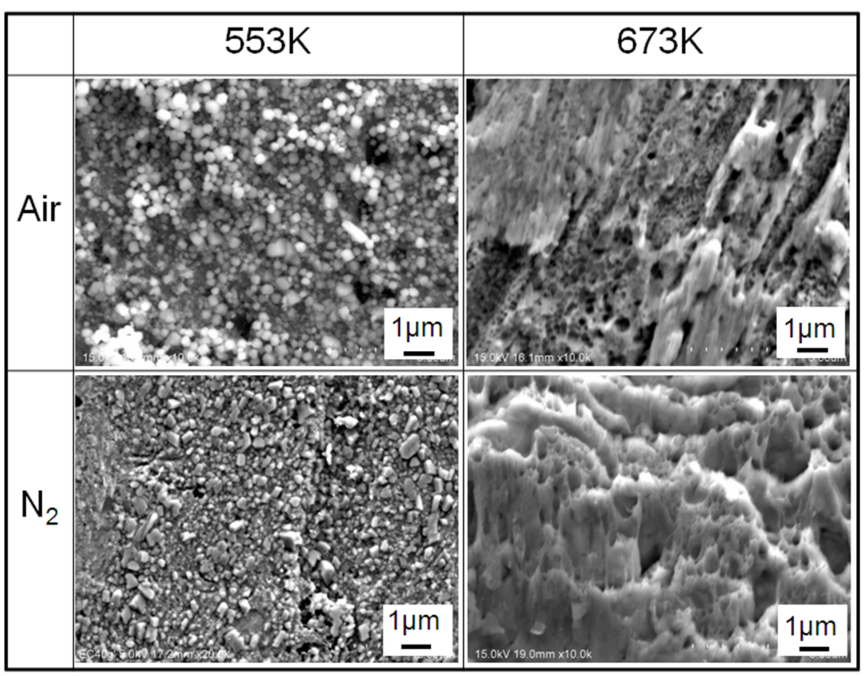

Fig. (4). SEM images of the typical fracture surface of joints using Cu nanoparticle in air and N_2. (One-step heating, heating time: 300s, joining pressure: 15MPa).

clearly decreases relative to its values at lower temperatures. This result may be attributable to gradual nanoparticle sintering during preheating, causing them to assume a size that prevents subsequent sintering during the second heating step at 673 K.

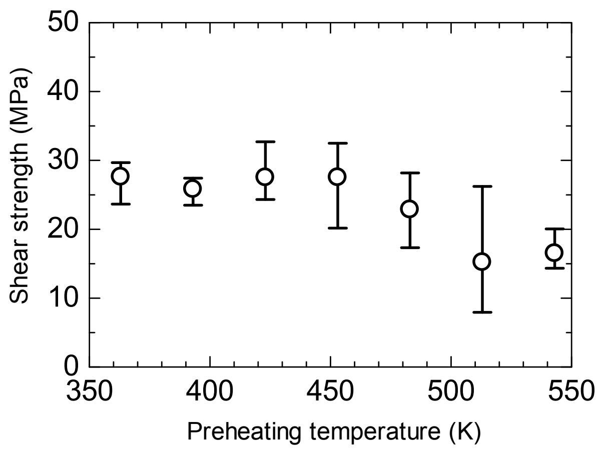

Fig. (5). Effect of preheating temperature for 300s on shear strength of joints using Cu nanoparticle in N_2 (Two-step heating, heating temperature: 673 K, heating time 300 s, bonding pressure: 15 MPa).

Then, to investigate the effect of joining atmosphere on the joint strength, the disc joints using Cu nanoparticle paste were made in various joining atmospheres. Fig. (**6**) shows the effect of joining atmosphere on the shear strength of the disc joints. All preheating was performed for 300 s under normal pressure at 423 K, and then all heating was performed for 300 s at 673 K. Shear strength was highest, ~40 MPa, for joining in a N_2:O_2 = 10:1 atmosphere. This result suggests that the joining process requires a certain amount of oxygen. Therefore, the amount of oxygen must be carefully determined, as an excess amount causes the nanoparticles to oxidize and an insufficient amount causes organic substances from the solvent and the protective agent to remain in the sintered layer.

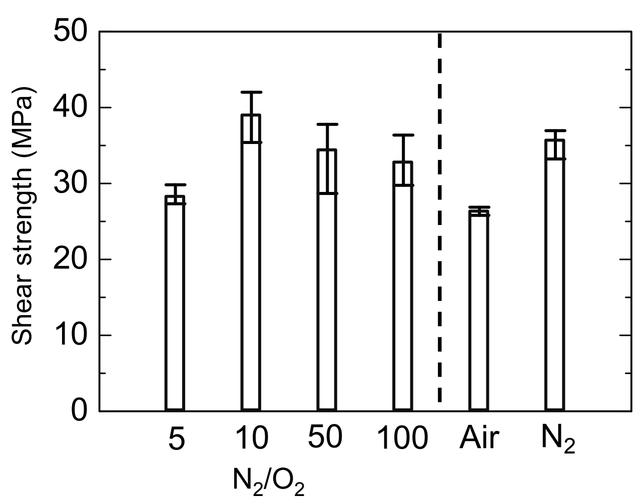

Fig. (6). Effect of joining atmosphere on shear strength of joints using Cu nanoparticle in N_2 (Two-step heating, preheating temperature: 423 K, preheating time 300 s, heating temperature: 673 K, heating time 300 s, bonding pressure: 15 MPa).

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. The effect of joining conditions on the shear strength of Cu-to-Cu disc joints formed using Cu nanoparticle paste was investigated. The main results are as follows:

1. Joints that were bonded at 673 K for 300 s under a joining pressure of 15 MPa showed high shear strength (~40MPa), demonstrating the successful use of Cu nanoparticle paste to form joints.
2. Joining conditions such as heating temperature and joining atmosphere significantly affect the shear strength of a joint. The joining process using Cu nanoparticle also needs a certain amount of oxygen, best achieved by use of a mixed nitrogen/oxygen joining atmosphere.
3. In joints that showed high shear strength, the nanoparticles in the paste became effectively sintered, forming an elongated dimple structure that was partially observable on the fracture surface of the joint.

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