Pressureless Bonding by Micro-Sized Silver Particle Paste for High-Temperature Electronic Packaging

Myong-Hoon Roh1, Hiroshi Nishikawa1, Seiichiro Tsutsumi1, Naruhiko Nishiwaki2, Keiichi Ito2, Koji Ishikawa2, Akihiro Katsuya2, Nobuo Kamada3 and Mutsuo Saito3

1Joining and Welding Research Institute, Osaka University, Ibaraki 567–0047, Japan
2NHK SPRING CO., LTD, Yokohama 236–0004, Japan
3KAKEN TECH Co., Ltd., Higashiomino 527–0065, Japan

Lead-free bonding in high-temperature electronic components is desirable for realizing eco-friendly technology. A pressureless process is more appropriate for electronic packaging because it enables a more automated manufacturing process and avoids any potential damage caused by application of pressure. Recently, Ag nanoparticles were used without pressure to join materials for high-temperature electronic applications. In this study, a Ag paste of micro-sized particles was proposed for electroless nickel immersion gold (ENIG) finished Cu pressureless bonding owing to its advantages of both cost effectiveness and easy manufacturing process compared to Ag nanoparticle paste. The micro-sized Ag paste was composed of both chestnut-burr-like (CBL) and spherical particles. The weight ratios of CBL to spherical particles were 10:0, 7:3, and 5:5. The bonding process was carried out at 573 K for 60 min in a nitrogen atmosphere. The experimental results showed that all of the sintered layers had an open porous structure. ENIG-finished Cu joint using the Ag paste of the 5:5 weight ratio exhibited the shear strength of 18.6 MPa, which is comparable to that of a conventional Pb-5Sn joint. [doi:10.2320/matertrans.MD201513]

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1. Introduction

Despite environmental regulations such as the Restriction of Hazardous Substances (RoHS) of the European Union, a high lead (Pb) soldering is primarily used even today because a suitable alternative has not been developed for high-temperature electronic packaging.1,2) Recently, Ag has attracted attention as a substitute for high Pb soldering owing to its low-temperature sinterability, maximum electrical and thermal conductivity, and high melting temperature (Tm = 1234 K) after bonding.3,4) Several types of Ag-based paste have been investigated in various studies, such as Ag nanoparticles,1,4–11) Ag micro-sized particles including flakes,12,13) hybrid Ag particles,14) and Ag oxide particles.15) Among these, sintered joints using Ag nanoparticle paste, both with and without pressure, have been the focus of most studies because of the high diffusion coefficient and low melting temperature that are consequences of particle size effects.1,4,5) Hirose’s research group reported the effect of size on bondability of Ag metallo-organic nanoparticle pastes at 573 K for 5 min under pressures of 1 and 5 MPa.6) In their study, a Ag joint using nanoparticle paste, which had particles with an average diameter of 11 nm, showed higher shear strength (25–40 MPa) than joints using a fine particle paste with an average particle diameter of 100 nm (0.5–10 MPa). Ogura et al.7) compared the shear strength of Ag joints sintered at 573 K for 20 min, both with an applied pressure of 1 MPa and no applied pressure, to that of a conventional Pb-5Sn joint. They showed that the Ag joint with an applied pressure had a better shear strength than the Pb-5Sn joint, but the pressureless sintering resulted in a lower shear strength of 11–12 MPa. In order to improve the bonding strength of Ag joints without applying any pressure, various methods such as optimizing the sintering profile,8,9) mixing of trimodal Ag nanoparticles,10) and using a high Ag content in paste11) have also been investigated, with resulting shear strengths in the range of 14 to 28 MPa. However, in spite of the advantage of sinterability, nanoparticles still have the drawbacks of higher manufacturing costs, the requirement of toxic solvents and stabilizers in the preparation process, and an unproven safety record for human health.16)

On the other hand, micro-sized Ag particle paste has made it possible to sinter at temperatures of 453–573 K by controlling the pressure and the particle shape.12,13,17) A higher applied pressure of 40 MPa has been shown to contribute to a reduction of the sintering time and temperature.17) Chestnut-burr-like (CBL) Ag particles with an average diameter of 3 μm were used for Cu/Cu bonding under a pressure of 10 MPa.13) Sintering under a low pressure of 0.4 MPa was also attempted using Ag flake fillers with an average diameter of 8 μm and average thickness of 80 nm.13) Although applying pressure enabled the creation of Ag joints using micro-sized particles, a pressureless process is more preferable for automated manufacturing processes. However, it is difficult to find studies of pressureless bonding using micro-sized Ag particle paste because there is no size-effect to induce the driving force for sintering. Thus, pressureless sintering by micro-sized CBL Ag particle paste was investigated in this study to expand on existing research. The shape of a micro-sized CBL particle features minute spikes that extend radially outwards and has lots of sharp edges such as needle and knife. Due to a large diffusion-potential gradient at sharp edges, the atoms on the edges are easily diffused for reducing the surface energy which is the basic mechanism of sintering driving force.18,19) We believe that CBL particle with many sharp edges has more potential than spherical particle for atom diffusion in the micro-sized particle system. Additionally, the effect of the addition of smaller spherical Ag particles in the CBL Ag paste was studied for ENIG-finished Cu bonding. The shear strength and microstructure of the resulting joint were also characterized.
2. Experimental Procedures

The micro-sized Ag paste with CBL and spherical particles was provided by KAKEN TECH Co. Ltd. for the ENIG-finished Cu joint. The paste composed of a glycol ether-base solvent, Ag particles, and minor SiO$_2$ particles. The average diameter of the CBL particles was 3 $\mu$m and the spherical particles had an average diameter of 1 $\mu$m. Three kinds of Ag pastes differing in the weight ratio of the two particles were prepared as shown in Table 1. The weight ratios of CBL and spherical particles were 10:0, 7:3, and 5:5. The pastes were designated as MA0, MA3, and MA5 based on the percentage of spherical particles. The addition of more than 50 mass% of the smaller particles in the mixed paste can reduce the effect of not only the shape of CBL particles but also the particle packing density of the mixture.$^{20}$ Additionally, one of the authors has previously studied the effect of the mass fraction of micro-sized and nano-scale Ag particles on joint shear strength using mixed particle paste.$^{21}$ The results showed that the shear strength improved as the content of nano-scale Ag particles in mixed paste increased to 50 mass%, and then decreased. Thus, we used a maximum spherical particle content of 50 mass% in this experiment. Figure 1 shows the morphology of the Ag pastes dried for 24 h at room temperature in air.

The shear strength of the Ag joint was evaluated using disc joint specimens as shown in Fig. 2 (a). Cu discs were metalized with electroless nickel immersion gold (ENIG). The upper and bottom discs had diameters of 3 mm and 10 mm and thicknesses of 2 mm and 5 mm, respectively. The Ag paste was screen printed on the bottom ENIG-finished Cu disc ($\Phi = 10$ mm) with a metal mask ($\Phi = 5$ mm, $t = 150$ $\mu$m), and the upper disc ($\Phi = 3$ mm) was set on top of it. The prepared disc specimens were pre-heated at 403 K for 5 min and then sintered at 573 K for 60 min in a nitrogen atmosphere. After bonding, the shear strength was measured at a crosshead speed of 1 mm/min using a shear tester (STR-1000, Rhesca Co.).

The morphology of the Ag particles and the microstructures of the joints were observed using field emission scanning electron microscopy (FE-SEM, SU-70; Hitachi Ltd.). To investigate the relationship between microstructure and joint properties, the Ag area and bonding ratios were analyzed by FE-SEM images of the cross-section. The bonded samples were mounted in an epoxy molding resin and polished with 1 $\mu$m diamond paste for observing a cross-section. The Ag area ratio was defined as the Ag area to total area and the bonding ratio was calculated as the sum of Ag joint lengths to the total length of the joint cross-section (See Fig. 2(b)). Thermo gravimetric differential thermal analysis (TG-DTA,

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight ratio of Ag particles (mass%)</th>
<th>Viscosity (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CBL$^1$</td>
<td>Spherical</td>
</tr>
<tr>
<td>MA0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>MA3</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>MA5</td>
<td>50</td>
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$^1$CBL: Chestnut-burr-like particle

Fig. 1 Morphology of micro-sized Ag particle paste according to weight ratio of chestnut-burr-like and spherical particles. (a) 10:0, (b) 7:3, and (c) 5:5.

Fig. 2 Schematics of (a) Cu/Cu joint for shear strength and (b) the measurement of Ag area and bonding ratios.
ST 7200, Hitachi High-Tech Sciences) was used to measure the thermal properties of Ag paste. The fracture surface and cross-section analysis was conducted by electron probe micro-analysis (EPMA).

3. Results and Discussion

The TG-DTA curves of Ag pastes in N₂ for the three weight ratios of CBL to spherical particles are shown in Fig. 3. The solid line indicates the relative weight by TG analysis and the dotted line represents the DTA. The relative weights of all Ag pastes, regardless of the weight ratio, decreased with increasing temperature to 423 K, corresponding to the evaporation of the solvent. The weight losses of the MA0, MA3, and MA5 pastes were 19.2 mass%, 15.5 mass%, and 13.1 mass%, respectively. This means that a lesser amount of solvent was needed as the weight ratio of CBL particles in Ag paste decreased. As shown in Fig. 1, the surface area of the CBL particles is larger compared to that of the spherical particles. In order to obtain a similar viscosity for all three pastes for screen printing, a larger amount of solvent was required as the weight ratio of CBL particles increased. However, large amounts of solvent could potentially interfere with the improvement of bondability since organic materials like solvents have been shown to have a detrimental effect on the sintering process.11) On the other hand, the exothermic peaks were observed at about 523 K in the DTA curves of all three Ag pastes. These exothermic peaks indicated the decomposition of residual solvents. The decomposition of residual solvents has an important role, since the solvents on particle surface can interfere with the metal to metal contact for sintering. Thus, the sintering was carried out at 573 K, which was higher than the temperature of exothermic peaks in this study.

Figure 4 shows FE-SEM images exhibiting the morphologies of Ag paste sintered at 573 K for 60 min in N₂. All of the sintered Ag pastes exhibited an open porous structure. Comparison of Fig. 1 (a) and 4 (a) showed that the CBL particles have changed to a more spherical shape. Connections between particles were also observed in Fig. 4 (a) even though the paste was composed of only CBL particles. However, the some particles retained hint of the original CBL shape after sintering. The CBL shape was reduced as the amount of smaller spherical particles increased (see Fig. 4(b) and (c)). Most notably, the MA5 paste formed a well-connected network compared to the MA0 and MA3 paste.

Figure 5 shows the shear strength of sintered Ag joints using MA0, MA3, and MA5 pastes and also represents the Ag area and bonding ratios in the joint layer. The shear strength of the ENIG-finished Cu joint was clearly improved as the weight ratio of spherical particles in Ag paste increased. The shear strength using MA0 paste composed only of CBL particles was 1.7 MPa. However, the shear strength of the joint using MA5 paste reached 18.6 MPa, which was comparable to the values for Ag nanoparticle paste and Pb-5Sn.7,8,10,11,22,23) On the other hand, the Ag area and bonding ratios in the joint layer also increased with an increased weight ratio of spherical particles. In other words, this means that the addition of spherical particles in the Ag paste resulted in the increase of both Ag area and bonding ratios, causing an improvement of strength in the joint.

Typical cross-section observations of the joint area after sintering are shown in Fig. 6. The joint area of MA0 revealed the separated structure of Ag. When MA0 paste was used for Cu to Cu bonding with pressure in our previous study, the Ag joint had a shear strength of over 20 MPa because the contact area between the particles as well as particles and substrate was improved by the applied pressure.12) In the case of pressureless sintering, one does not to expect a large contact area. However, an increasing number of connections between the particles were observed as spherical particles were added and the Ag network was formed, as shown in Fig. 6(b) and (c). The Ag area ratio in the joint layer also increased from 45.4% to 62.9% as the amount of spherical particles increased (see
This result is thought to be a consequence of the relatively high packing density that occurs with the addition of spherical particles which had a three times smaller diameter than that of the CBL particles. The improvement of fractional packing density obtained from a mix of CBL and spherical particles must be effective in forming a connected Ag network.

Figure 7 represents the schematics of particle packing structure in only CBL particle paste and mixed paste. Like conventional other paste, Ag paste with only CBL particles would have a more open packing structure than the close packed structure as shown in Fig. 7 (a). When the smaller particles were added in this open packing structure, the probability that they are positioned at an open site would increase and the packing density could be improved as shown in Fig. 7 (b). The improved packing density with smaller particles would help the sintering behavior. As a result, the Ag joint layer using MA5 exhibited a higher Ag area ratio and well-connected network than that using MA0 after sintering.

Figure 8 shows the typical fracture surface of a Ag joint by SEM and EPMA after shear test. The white color in the EPMA analysis represents a high Ag and Au content on the
fracture surface. In Fig. 8 (a), a small amount of Ag partially remained on the fracture surface. The Ag area on the fracture surface increased as the amount of spherical particles increased (Fig. 8 (b) and (c)). Above, we discussed how the addition of spherical particles leads to an increase in fractional packing density. Similarly, it was considered that the Ag contact area on the surface of the substrate was improved with the addition of the smaller particles. It appeared that the Ag bonding ratio was closely related to the shear strength of the Ag joint (see Fig. 5). The shear strengths of the Ag joint sintered with MA0, MA3, and MA5 paste were 1.7 MPa, 7.7 MPa, and 18.6 MPa when the bonding ratios were 12.5%, 37.2%, and 67.7%, respectively. Thus, the bonding ratio between the Ag layer and substrate was an important factor in joint strength as much as the Ag area ratio and the interconnection of particles in this study.

EPMA line scanning analysis of the ENIG-finished Cu joint using MA5 paste was conducted to investigate the interfacial reaction between Ag and ENIG. Based on EPMA data shown by the dotted line in Fig. 9, it was confirmed that Au diffused into Ag to a depth of about 1 μm, whereas the diffusion of Ag and Ni was negligible. It is known that Ag and Au form a solid-solution over the whole composition range of the Ag-Au phase diagram. In general, the solid-solution formation is accompanied by solid-solution strengthening owing to increased resistance to dislocation movement. Suzuki reported that the Ag-Au alloy also had its solution hardening and critical shear stress increase until Au content reached 50 at%. In this study, the solid solution strengthening by Au diffusion into Ag would have occurred at the interface. As a result, the bonding strength at the interface would be higher than inside the layer, which was composed of pure Ag. Thus, the joint sintered with MA5 paste showed a layer fracture almost entirely of Ag, as shown in Fig. 8 (c).

Figure 10 presents the actual strength as calculated by the effective bonding area. The effective bonding area was calculated using the original area of the joint and the bonding ratio, which was closely related to shear strength. The actual strength was recomputed from the effective bonding area and the force measured in the shear test. As shown in Fig. 10, the actual strengths in the effective bonding area of MA0, MA3, and MA5 paste were 13.3 MPa, 20.6 MPa, and 27.5 MPa, respectively. Compared with the shear strength in Fig. 5, a large increase of strength in MA0 was found and the difference between the strengths using MA0 and MA5 paste was reduced by about half. Generally, if process parameters such as type of material, substrate and sintering conditions for the joint are the same, the actual strength would have a similar value. However, there were differences between the three pastes, even though the active element, Ag, was the same in each case. In particular, the two kinds of Ag particle might...
exhibit different behavior during bonding, such as different diffusion characteristics between Ag particles or between particles and substrate, and further studies are needed to establish the mechanism.

Although the actual strength using the paste with only CBL particles was greater than 10 MPa over the effective bonded area, practical application for high temperature electronic packaging without pressure will be difficult. The sintering using only CBL particle paste made possible the interconnection between the micro-sized Ag particles, but the bonding behavior exhibited a limit because of the small contact area between the thin arms of the CBL particle and surface. The addition of smaller micro-sized spherical particles in the paste was one solution to improve the bonding ratio as well as fractional packing density, and, as a result, the shear strength also increased in this study.

4. Conclusions

Pressureless bonding using micro-sized Ag paste composed of chestnut-burr-like (CBL) and spherical particles was investigated for high-temperature electronic packaging. The micro-sized CBL particles made it possible to sinter without pressure and the addition of the smaller spherical particles improved the bonding properties. The results can be summarized as follows.

(1) When the weight ratio of CBL and spherical particles was 5:5, joining by micro-sized Ag paste was successfully achieved at 573 K for 60 min under no applied pressure. The resulting joint had a shear strength of 18.6 MPa.

(2) The shear strength, Ag area ratio, and bonding ratio showed higher values when the content of spherical particles in the paste increased. The addition of the smaller spherical particles in the paste contributed to the improvement of the particle packing density.

(3) The bonding ratio was determined to be a major factor on the shear strength of Ag joints sintered with micro-sized paste.

(4) Au coated on a Ni/Cu substrate was diffused into the Ag during sintering but the diffusion of Ag and Ni was insignificant.

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REFERENCES