



Full length article

Dewetting behavior of Ag in Ag-coated Cu particle with thick Ag shell

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ABSTRACT

With the aim of application as either a conductive filler or a sinter-bonding material with enhanced antioxidation properties, Ag-coated Cu (Cu@Ag) particles with thick Ag shells were fabricated and heated at 220 °C for 10 min in air to observe the dewetting behavior of the thick Ag shell. The fabricated Cu@Ag particles were spherical with the average size of 2 μm, and the Ag shell was 250–400 nm in thickness, comprising a mixed Ag-Cu layer and a dense Ag layer. As the heat-treatment time increased, the Cu@Ag particles were aggregated by forming numerous Ag nodules covering the surface of the particle. Dewetting in the thick Ag shell occurred from 4 min and only in the outer layer of the Ag shell even after 10 min of heat-treatment. In addition, the thickness of the dewetting layer and the mixed Ag-Cu layer were increased because the outward diffusion of Cu and Ag were increased proportionally with the time. However, because the dense Ag layer remained even after the dewetting of the Ag shell and the formation of the mixed Ag-Cu layer, the Cu@Ag particles were not oxidized after heating at 220 °C for 10 min in air.

1. Introduction

With the advantages of Ag paste such as oxidation resistance and superior electrical and thermal conductivities, Ag paste has been widely used in the electronic packaging industry [1–8]. Because the Ag powder used as a filler material directly affects the high cost of the paste, Ag-coated Cu (Cu@Ag) particles with core-shell structures have been studied as an inexpensive alternative to the Ag filler [9–14]. The thickness, uniformity, and coverage of the Ag coating shell on the Cu surface affect the oxidation characteristics of the Cu@Ag particle. In particular, when the shell is thin and the entire surface of core is not covered, which may weaken the oxidation stability [14]. Therefore, it is expected that the electrical and thermal conductivity and long-term stability of the Cu@Ag paste are improved when thicker Ag shells are formed on the Cu cores.

Meanwhile, oxidation of Cu@Ag particles occurs when the core Cu is exposed or some parts of the Ag shell changed into extremely thin by the dewetting of the Ag shell during heating in air at temperatures above 200 °C [15–18]. Ag dewetting is known to be caused by the lattice mismatch of 11.7% between Cu and Ag [19,20] and the instability of the Cu and Ag interface [20]. Meanwhile, several studies have recently reported the use of the dewetting phenomenon of Cu@Ag particles in printed electronics and chip bonding [21–23]; it is expected in these applications that Cu@Ag particles with thick Ag shells could be

utilized with improved antioxidation properties. In particular, Cu@Ag particles are suitable for a high-temperature-endurable bonding material for die-attach with price competitiveness as compared with Ag [23]. In that case, the abundant quantity of Ag dewetted from the shell can fill quickly and easily the voids between the particles with the thick Ag shell under applied external pressure, thus significantly differing from those obtained using thin Ag shells.

Therefore, research on the dewetting behaviors in Cu@Ag particles with thick Ag shells is necessary to evaluate the properties and performance of Cu@Ag particles as either a conductive filler or a bonding material. With this purpose, micrometer-sized Cu@Ag particles with thick Ag shells of 250–400 nm were fabricated in this study and the dewetting behavior was analyzed during heating in air at 220 °C for 10 min.

2. Materials and methods

The spherical Cu particles (CNVISION Co., Ltd.) that served as the core material in the Cu@Ag particles were subjected to a pretreatment process to remove the oxides from the surface [10]. The pretreatment solution was prepared by dissolving 2.09 M of ammonium sulfate ((NH₄)₂SO₄, 99%, Samchun Pure Chemical Co., Ltd.) and 150 mM of ammonium hydroxide (NH₄OH, 28–30%, Samchun Pure Chemical Co., Ltd.) in 100 mL of deionized (DI) water. Cu powder (3 g) was added to

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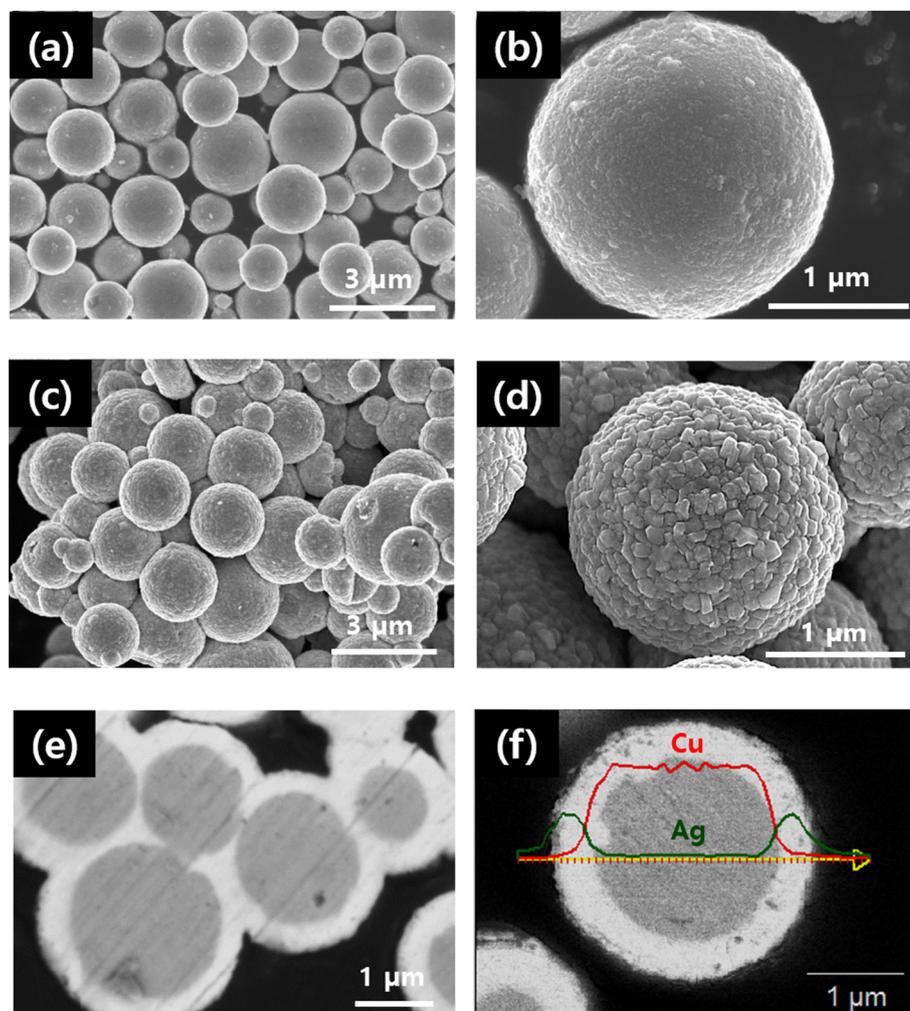


Fig. 1. (a, c) Low- and (b, d) high-magnification SEM images of (a, b) Cu particles used in this study and (c, d) fabricated Cu@Ag particles. (e) Cross-sectional BSE image and (f) EDS line profiles of the Cu@Ag particles.

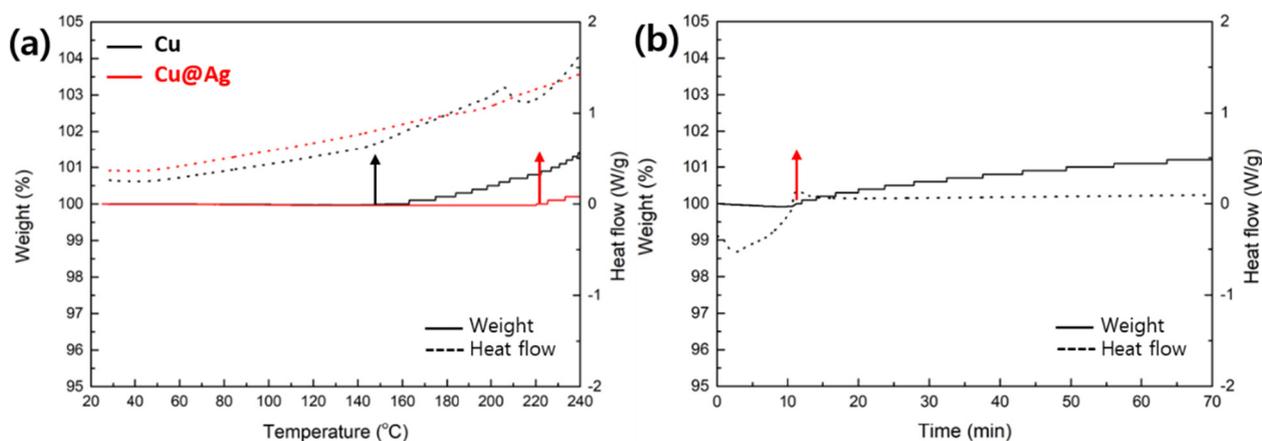


Fig. 2. TG-DSC results of (a) Cu and Cu@Ag particles during dynamic heating up to 240 °C at a heating rate of 10 °C/min in air and (b) Cu@Ag particles during isothermal heating at 220 °C for 70 min in air.

the pretreatment solution and stirred at 200 rpm for 2 min at room temperature (RT). After removing oxides from the Cu surface, the Cu powder was washed with DI water three times and prepared by dispersing in 100 mL DI water.

The Ag coating solution was prepared by completely dissolving 3.56 M of sodium hydroxide (NaOH, 97.0%, Deajung Chemicals & Metals Co., Ltd.), 0.89 M of ethylenediaminetetraacetic acid (EDTA,

$C_{10}H_{16}N_2O_8$, 99.0%, Samchun Pure Chemical Co. Ltd.), and 0.11 M of silver nitrate ($AgNO_3$, 99.8%, Hojeonable Inc.) in 100 mL of DI water. During the Ag coating process, the Ag coating solution was injected dropwise into the Cu solution at a rate of 10 mL/min with continuous stirring at RT. After completing the injection, the mixed solution was stirred for 5 min to complete the Ag coating reaction. The fabricated Cu@Ag particles were washed with DI water two times and with methyl

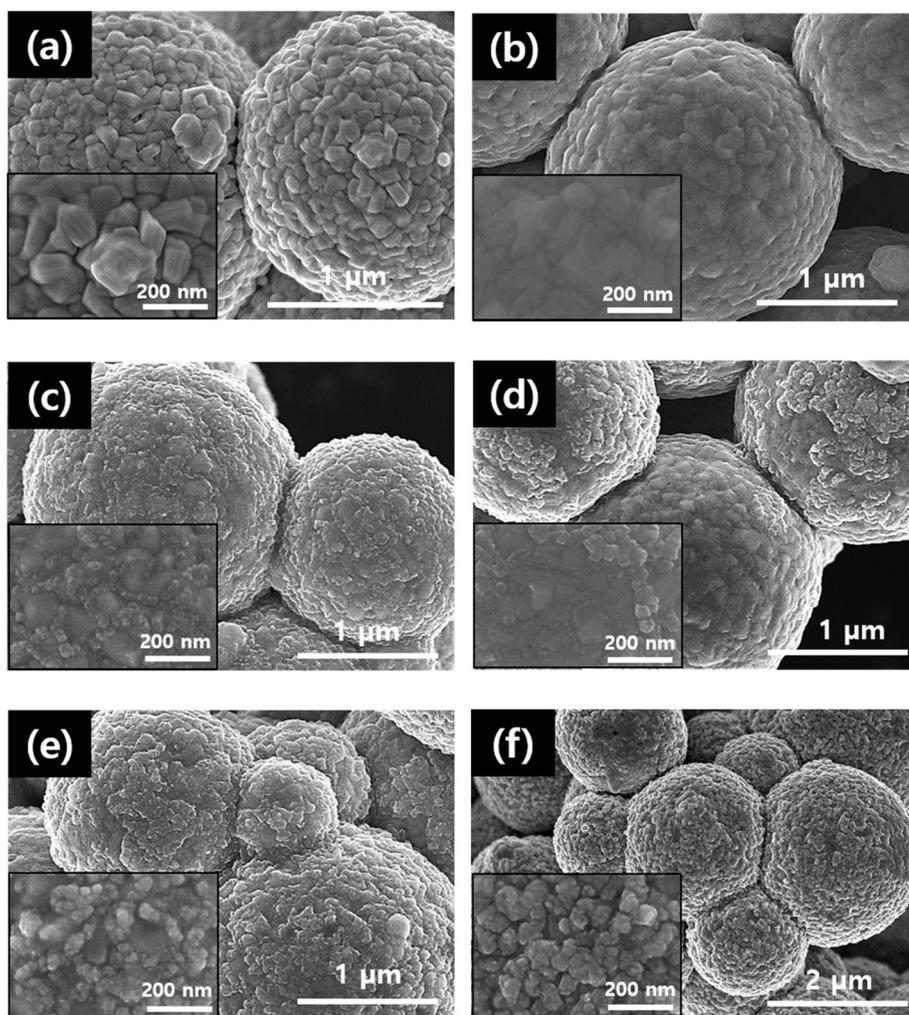


Fig. 3. SEM images of Cu@Ag particles with thick Ag shells during heat-treatment at 220 °C in air for (a) 0, (b) 2, (c) 4, (d) 6, (e) 8, and (f) 10 min.

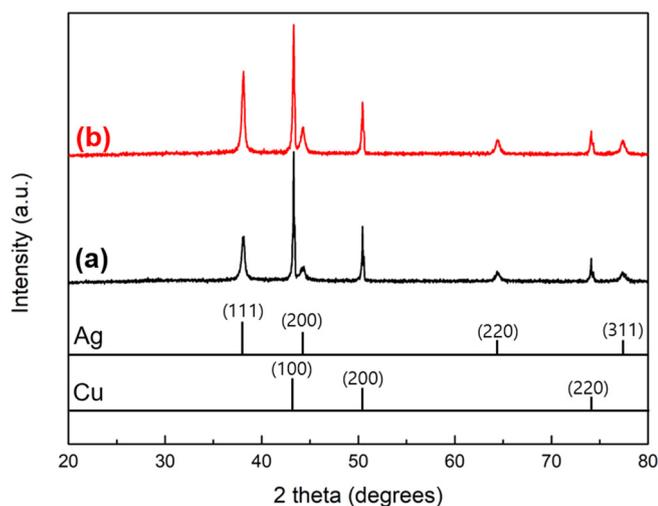


Fig. 4. XRD results of Cu@Ag particles (a) before and (b) after heating at 220 °C for 10 min in air.

alcohol (CH₃OH, 95%, Hanwha Chemical Co.) two times and then vacuum-dried at RT.

To investigate the dewetting behavior of the Cu@Ag particles, 0.5 g of the fabricated Cu@Ag particles were placed on a slide glass located a hot plate and heated at 220 °C for 10 min in air. The surface

morphology of the Cu@Ag particles was observed using a high-resolution scanning electron microscope (HR-SEM, SU8010, Hitachi) and the cross-section of the Cu@Ag particles was observed with back-scattered electron (BSE) images. Energy-dispersive X-ray spectroscopy (EDS, 4502A-3UES-SN, Thermo Scientific) was used to measure the Ag content of the Cu@Ag particles and perform elemental mapping and line analysis. With the aim of measuring exact Ag content in the Cu@Ag particles, inductively coupled plasma atomic emission spectrometry (ICP-AES, JY 138 Ultrace, Jobin Yvon) was also performed. To evaluate the oxidation properties, thermogravimetric-differential scanning calorimetry (TG-DSC, Q600, TA Instruments, installed in KBSI PH407 Pusan) was conducted in air. In addition, phase analysis of the Cu@Ag particles was conducted with X-ray diffraction (XRD, DE/D8 Advance, Bruker).

3. Results and discussion

Fig. 1 shows the SEM images of the Cu particles used in this study and the fabricated Cu@Ag particles with thick Ag shells. The Cu particles have spherical shapes with the d_{50} size of 2 μm and smooth surfaces. The fabricated Cu@Ag particles have rough surfaces with dense and uniform Ag shells. Aggregation between the particles is slightly increased by the formation of the thick Ag shells. In the EDS measurement, the average amount of Ag in the Cu@Ag particles was analyzed as 49.83 wt%, which exceeded the amount of Ag added (40 wt% of the Cu weight). This is because characteristic of the EDS measurement inducing an overstatement of the surface component and small

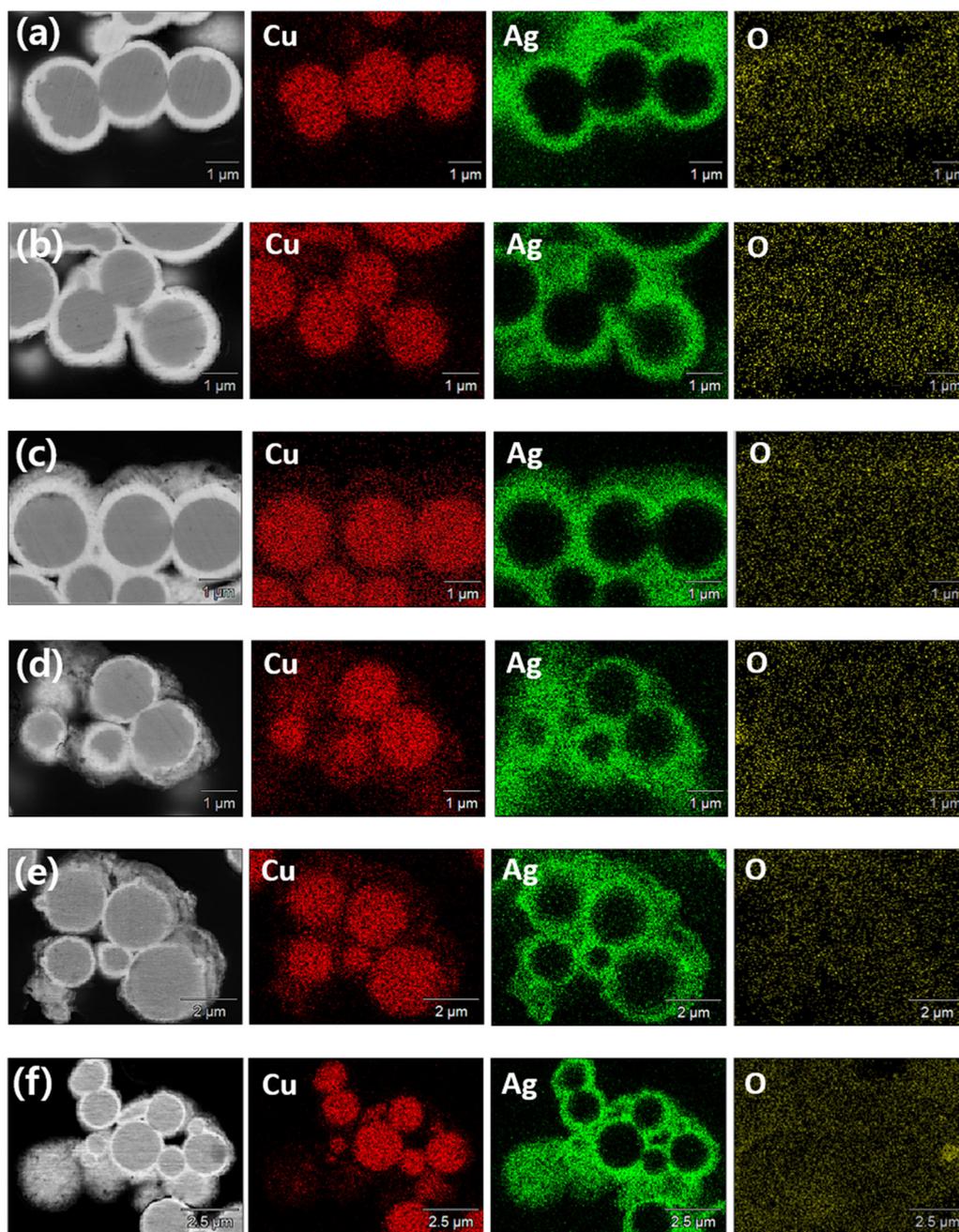


Fig. 5. Cross-sectional EDS mapping images of Cu@Ag particles during heat-treatment at 220 °C in air: (a) 0, (b) 2, (c) 4, (d) 6 (e) 8, and (f) 10 min.

amount of the Cu was eluted into ions during the Ag coating process via the galvanic displacement reaction [24]. The Ag content measured by ICP-AES was 38.04 wt%, slightly lower than that amount of Ag added, which indicates that the Ag amount was not completely coated on the Cu. The thickness of the Ag shells in the Cu@Ag particles is in the range 250–400 nm and the core-shell structure of the Cu@Ag particles is clearly observed with peaks of Ag and Cu at the edge and center of the particle, respectively.

The TG-DSC results of the Cu and Cu@Ag particles with thick Ag shells are shown in Fig. 2. During dynamic heating to 240 °C in air at the heating rate of 10 °C/min (Fig. 2(a)), the initial weight of the Cu and Cu@Ag particles is slightly decreased by 0.03 and 0.04 wt%, respectively, because of elimination of the residues remaining on the particles. For the Cu particles, the weight is increased from 148 °C by the oxidation of Cu, and the total weight gain at 240 °C is 1.4 wt%. Meanwhile, the oxidation initiation temperature of the Cu@Ag particles is delayed

to 220 °C and the weight gain at 240 °C is only 0.2 wt% because of the thick and dense Ag shell. The TG-DSC results of the Cu@Ag particles during isothermal heating at 220 °C in air are shown in Fig. 2(b). The weight is decreased by 0.08 wt% as the temperature approaches 220 °C at the rapid heating rate of 20 °C/min. Then the Cu@Ag particles are oxidized after ~12 min, with increases in weight. Therefore, it is considered that the dewetting of the Cu@Ag particles with thick Ag shells occurs within 12 min during heating at 220 °C in air.

Fig. 3 presents the SEM images of the Cu@Ag particles during heating at 220 °C for 10 min in air; the insets are surface images obtained at high magnification of the corresponding particles. Before heating, the surface of the thick Ag shell comprised grains of 100–140 nm in size. The surface morphology of the Cu@Ag particles begins changing within 2 min of heat-treatment; the distinct grain boundaries of the Ag shell become vague and the surface roughness is decreased, yielding a smooth surface. After 4 min, the Ag shell is

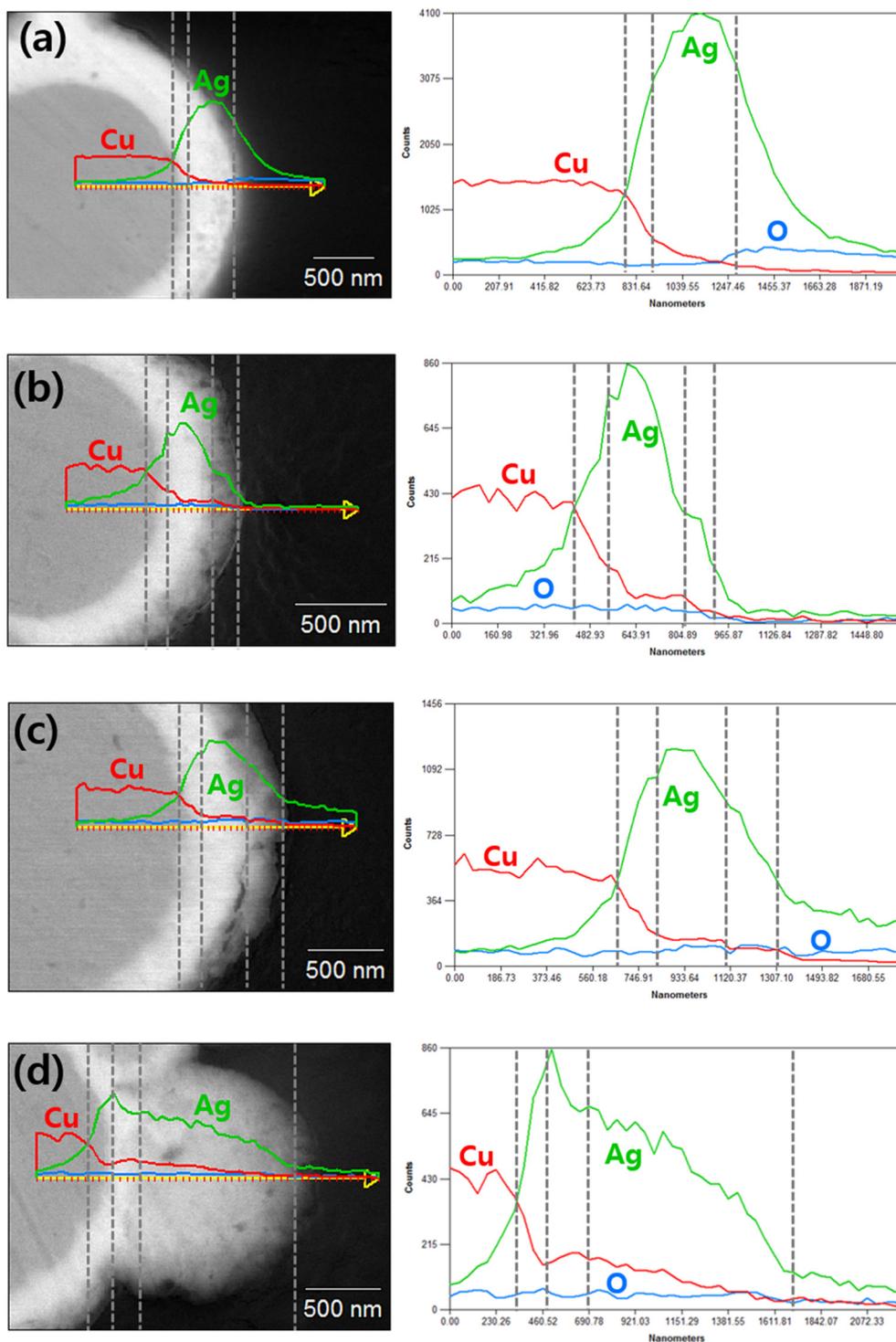


Fig. 6. Cross-sectional BSE images and EDS line profiles of Cu@Ag particles during heat-treatment at 220 °C in air: (a) 0, (b) 4, (c) 6, and (d) 10 min.

Table 1

Diffusion coefficients and distances of Ag and Cu during heat-treatment at 220 °C for 10 min.

Matrix material	Diffusing material	Activation energy for diffusion [26] (kJ/mol)	Material constant [26] (mm ² /s)	Diffusion coefficient (mm ² /s)	Diffusion distance (nm)
Ag	Ag	192.464	89.125	3.607×10^{-19}	0.015
Cu	Cu	103.763	6.026×10^{-3}	6.104×10^{-14}	6.052
Cu	Ag	148.950	1.175	1.94×10^{-16}	0.341
	Cu	194.556	17.783	4.32×10^{-20}	0.006

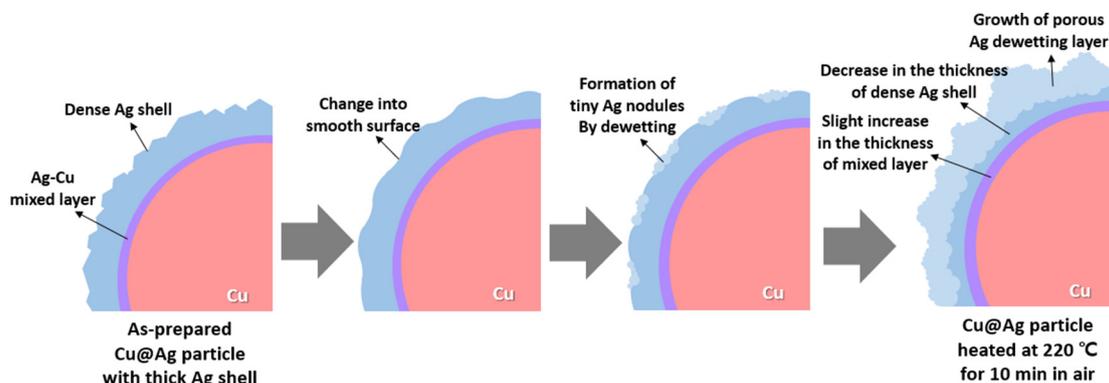


Fig. 7. Schematics showing the dewetting behavior of the thick Ag shell in Cu@Ag particle during heat-treatment at 220 °C for 10 min in air.

dewetted, which induces the formation of tiny Ag nodules of around 20 nm along the grain boundaries, indicating a high surface energy per unit area. As the heat-treatment time is increased, the small Ag nodules formed at the grain boundaries grow and become agglomerated to form larger Ag nodules of ~60 nm, which finally cover the entire surface of the Cu@Ag particles. In addition, necking between the Cu@Ag particles begins forming from 4 min onward because of the high sintering ability of the small Ag nodules formed on the surfaces. Eventually, aggregation between the particles becomes more obvious after heat-treatment at 220 °C for 10 min. These results indicate that the thick Ag shell is dewetted from around 4 min at this temperature and that the Cu@Ag particles are promptly sintered by forming Ag nodules with high surface energies through the dewetting.

To identify the phases in the Cu@Ag particles upon heat-treatment, XRD results before and after heating at 220 °C are shown in Fig. 4. Only pure Cu and Ag peaks are found, regardless of the heat-treatment, and thus it is confirmed that the Cu@Ag particles are not clearly oxidized, even after heating at 220 °C for 10 min in air, because of the thick and dense Ag shell. Meanwhile, the intensity of the Ag (111) peak is increased after the heat-treatment. This seems to arise from the enhancement in the crystallinity of the Ag shell [17].

Fig. 5 shows the cross-sectional EDS mapping images of the Cu@Ag particles during heating at 220 °C in air. For the initial Cu@Ag particles, the Ag and Cu are located in the outer shell and inner core, respectively, demonstrating the high concentrations of Ag and Cu elements in these regions. As the time of heat-treatment increases, it is observed that the edge of the thick Ag shell becomes spread outward, indicating the formation of a dewetting layer having many Ag nodules, as shown in Fig. 3. Interestingly, the EDS mapping images show that the cross-section of Ag shell contains both Ag and diffused Cu during Ag dewetting. The diffusion during dewetting is accompanied by the outward diffusion of Cu from the inner core, as well as that of Ag at the surface [17,25]. However, even when the outward diffusion of Cu occurs, no obvious increase of the oxygen concentration is observed during the heat-treatment because of the thick Ag shell, which is consistent with the result of non-oxidized particles after heating, as indicated in Fig. 4.

To precisely analyze the compositional variation in the thick Ag shell, magnified cross-sectional BSE images and line profiles of the Cu@Ag particle are shown in Fig. 6. The thick Ag shell of the initial Cu@Ag particles contains a mixed Ag-Cu layer and a dense Ag layer. The mixed Ag-Cu layer (124.8 nm) at the interface between the Cu core and Ag shell presents decreasing Cu and increasing Ag concentrations with increasing distance from the interface. The dense Ag layer of 364.0 nm thickness exhibits a high concentration of Ag in the profile and a distinctly bright shell in the BSE image. From 4 min after heating, a relatively low-density Ag dewetting layer is additionally observed at the outer region of the dense Ag shell. The thickness of the dewetting layer is increased to 102.64, 207.73, and 1007.39 nm, respectively, as Ag dewetting occurs continuously at the heat-treatment times of 4, 6,

and 10 min. From the high content of Cu observed in the lengthened Ag dewetting layer of Fig. 6(d), it is anticipated that the oxidation of Cu by reaction with oxygen in air may proceed rapidly with additional increases in heating time, especially at the regions non-covered with the dewetted Ag nodules. On the other hand, because the dense Ag layer in the initial shell is consumed by formation of the dewetting layer, the dense layer of 346.0 nm in initial thickness is decreased to 271.69, 268.41, and 204.36 nm with increasing time. Moreover, the Cu and Ag are diffused into each other at the interface, and the Ag-Cu layer of 124.8 nm in initial thickness is increased to 130.81, 158.71, and 166.94 nm with increasing time.

The diffusivity of Ag and Cu can be determined based on the Arrhenius law for expressing the relation between temperature and diffusion rate by the following equation: $D = A \cdot \exp\left[-\frac{Q}{RT}\right]$, where D is the diffusion coefficient, A is the material constant, Q is the activation energy for diffusion, R is the universal gas constant (8.314 J/K·mol), and T is the heating temperature. The activation energy for diffusion and the material constants of Ag and Cu as the matrix materials are shown in Table 1 [26]. Additionally, the diffusion distance of Cu and Ag can be calculated by the following equation: $d \approx \sqrt{Dt}$, where d is the diffusion distance and t is the heating time.

The diffusion coefficient and distance calculated using the above equations during heat-treatment at 220 °C for 10 min are shown in Table 1. The diffusivity of Cu in the Ag matrix is much higher than that in the Cu matrix because of the low activation energy, and the diffusion distance estimated during heat-treatment is approximately 6 nm. Meanwhile, the diffusivity of Ag in the Cu matrix is also higher than that in the Ag matrix, although the diffusion distance of Ag was much less than 1 nm. Thus, the thickness increase of the Ag-Cu layer at the interface of the Cu core/Ag shell is observed to be ~seven times higher than the calculated diffusion distance. Therefore, the outward diffusion of Cu seems to be strikingly accelerated by the high interfacial energy from the large lattice mismatch of Cu and Ag [17,19,20].

Fig. 7 illustrates the dewetting behavior of the thick Ag shell in a Cu@Ag particle during heating at 220 °C for 10 min in air. The initial Cu@Ag particle with a thick Ag shell has the mixed Ag-Cu layer and a dense Ag layer. During heat-treatment, the surface of the Ag shell becomes smooth, and then Ag and Cu diffuse simultaneously. The tiny Ag nodules are preferentially formed in the grain boundaries of the Ag shell as a dewetting phenomenon, and the entire surface is eventually covered with numerous Ag nodules forming the dewetting layer. Thus, the thickness of the dewetting layer, the different low-density structure, greatly increases in the outer region of the initial Ag layer with increased heating time. Concurrently, the thickness of the mixed Ag-Cu layer increases by inter-diffusion at the interface of the Cu core/Ag shell, whereas the dense Ag layer becomes thin. Thus, although the dewetting phenomenon in the thick Ag shell of the Cu@Ag particles proceeds consistently for 10 min of heat-treatment, the remaining Ag shell protects the Cu core from oxidation even after heating at 220 °C

for 10 min in air. These results suggest that the Cu@Ag particles with thick Ag shells possess better properties and performance about anti-oxidation and void filling ability than those with thin Ag shells as a sinter-bonding material for the chip bonding.

4. Conclusions

The dewetting behavior of average 2- μm -diameter Cu@Ag particles with 250–400-nm-thick Ag shells was studied during heating at 220 °C for 10 min in air. As the heating time was increased, the Cu@Ag particles with thick Ag shells became highly sintered by forming numerous Ag nodules covering the entire surfaces of the particles. During the dewetting phenomenon, the thickness of the dewetting layer and the Ag-Cu mixed layer were increased, while that of the remaining dense Ag layer decreased. Because the diffusion of Cu and Ag were accelerated by the instability of the Cu/Ag interface, the measured thickness of the mixed layer was larger than the sum of the diffusion distances calculated for Cu and Ag. Although the dewetting of the thick Ag shell proceeded persistently in the outer region of the Ag shell for 10 min of heat-treatment, the Cu@Ag particle was not oxidized because the remainder of the dense Ag layer even after the heating.

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