



# Ethylene glycol-based Ag plating for the wet chemical fabrication of one micrometer Cu/Ag core/shell particles



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## ABSTRACT

With the aim of preparing an inexpensive metal filler that can be added to conductive adhesives used in fine-pitch electronic applications, a polyol solution was used to fabricate Ag-coated Cu (Cu@Ag) particles with a size on the order of one micron without the need for additional reagents. The continuity, uniformity, and thickness of the Ag shell were found to be strongly dependent on the plating conditions, particularly the reaction temperature. The Ag shell prepared at a peak temperature of 180 °C from a precursor with an initial Ag concentration of 15 wt.% was judged to be an optimum one. This same sample also showed an excellent oxidation initiation temperature of approximately 280 °C. It was inferred that the oxidation resistance of the Cu@Ag powder is largely determined by the continuity, uniformity and thickness of the Ag shell.

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## 1. Introduction

The low electrical resistivity and excellent resistance to oxidation of Ag particles relative to other metals has seen them extensively used as a filler material in various conductive pastes [1–5], but the high price of Ag has continued to be significant impediment to their industrial application in electronic materials. This has led to Cu being considered as an alternative to Ag, as it offers a similar resistivity but at a much lower cost; however, even at room temperature (RT) pure Cu is vulnerable to surface oxidation in air, and the severity of this oxidation only gets worse with increasing temperature [6–8]. To overcome this problem while still reducing material costs, the fabrication and application of Ag-coated Cu (Cu@Ag) powder has been suggested [8–10].

Another trend in conductive paste technology is an increase in demand for narrower print widths [11], thus creating an urgent need for smaller conductive particles. This study therefore explores the possibility of fabricating Cu@Ag particles at a micrometer-scale size with different Ag shell thicknesses using a polyol reduction method to plate Cu core particles with Ag; a method that eliminates the need to add reducing or complexing agents. The oxidation resistance of these Cu@Ag particles in air was then assessed in relation to the Ag shell thickness.

## 2. Experimental procedures

Core Cu particles of less than 1 μm in size were synthesized by means of a proprietary wet chemical method, immediately after which 3.987 g of the Cu particles obtained were immersed in 50 mL of ethylene glycol (EG, 99.0%, Dejung Chemical and Metals Co. Ltd.) without any pre-treatment being applied. This was followed by continuously plating Ag onto the core Cu particles using a polyol reduction method, which unlike conventional Ag plating process of dried Cu powders, is a simple method that eliminates the need for pre-treatment to remove the oxide layer on Cu.

The main Ag plating solution was fabricated in a separate vial by completely dissolving 0.186–0.553 M of silver nitrate (AgNO<sub>3</sub>, 99.8%, Dejung Chemical and Metals Co. Ltd.) precursor in 10 mL of EG by stirring at RT for 30 min; the amount of Ag in the final product being varied from 5 to 15 wt.%.

The Ag plating reaction was induced by adding the Ag plating solution dropwise into a solution containing core Cu particles at a rate of 3.3 mL min<sup>-1</sup> and stirring for 10 min. This was carried out in air under various temperatures, being maintained for 60 min at RT, or heated to 150 or 180 °C for 20 min to increase the effectiveness of plating. With the heated samples, the solution mixture was stirred for 40 min while cooling to RT. The resulting powders were then washed and solvent exchanged three times using methanol (99.9%, Duksan Pure Chemical Ltd.) by centrifugation for 5 min at 7000 rpm in order to eliminate any residual Ag ions and improve the ease of subsequent drying at RT using a vacuum chamber.

Scanning electron microscopy (SEM, VEGA 3 LMU, TESCAN Ltd.) was used to determine the morphology and size of the synthesized Cu and Cu@Ag powders, while X-ray diffraction (XRD, X'pert PRO-MPD, PANalytical) analysis was performed to confirm the extent of reduced Ag using Cu Kα radiation within a 2θ range of 20–80°. The amount of Ag plating was further confirmed through observation of epoxy-mounted and cross-sectioned powder samples.

Thermal analysis of the final samples was performed by thermogravimetric differential scanning calorimetry (TG–DSC, Q 600, TA Instruments) to measure the oxidation initiation temperature of each powder. For this, each powder was heated in air to 600 °C at a ramp rate of 10 °C min<sup>-1</sup>.

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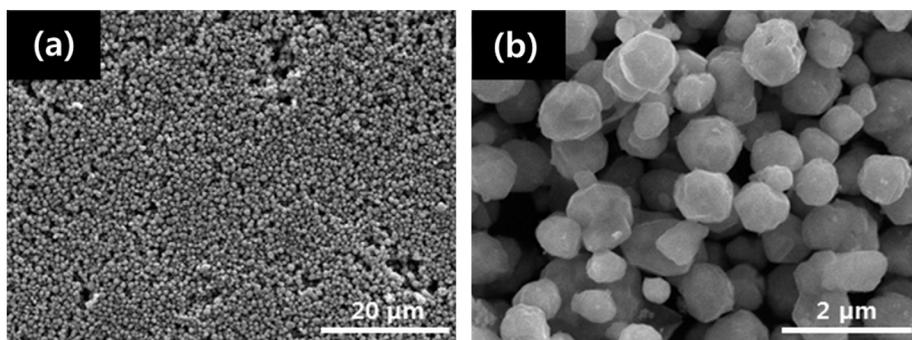


Fig. 1. Scanning electron microscopy (SEM) image of pure Cu particles synthesized using a proprietary wet chemical method.

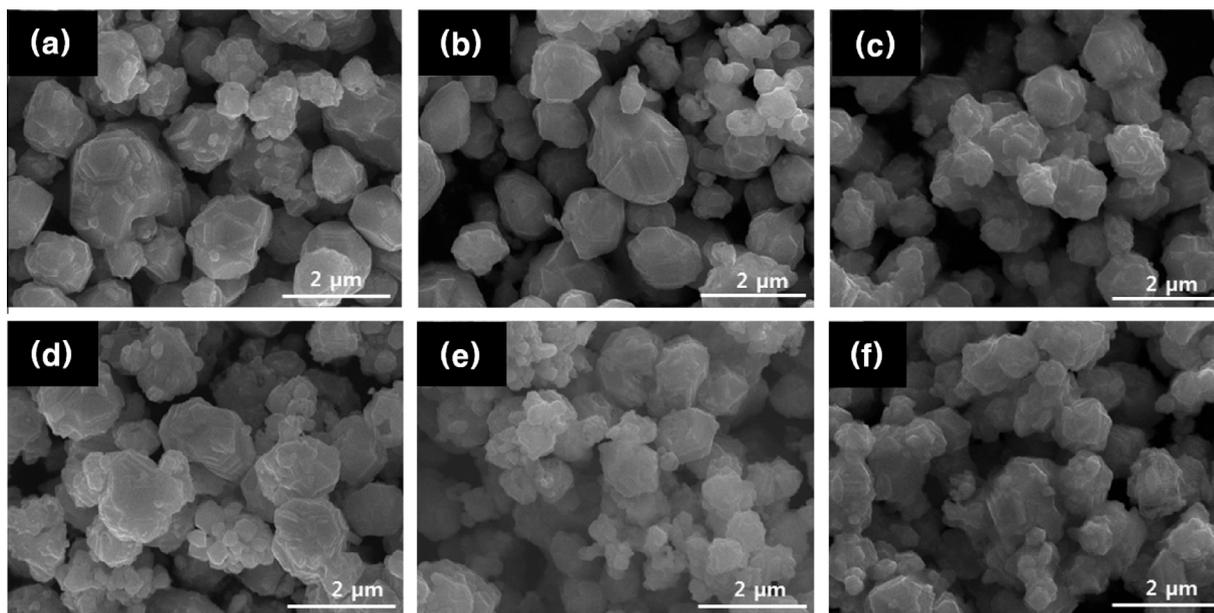


Fig. 2. SEM images of Ag-plated Cu powders produced using polyol solutions with different Ag contents and reaction temperatures: (a) 5 wt.%, RT; (b) 5 wt.%, 150 °C; (c) 5 wt.%, 180 °C; (d) 15 wt.%, RT; (e) 15 wt.%, 150 °C; and (f) 15 wt.%, 180 °C.

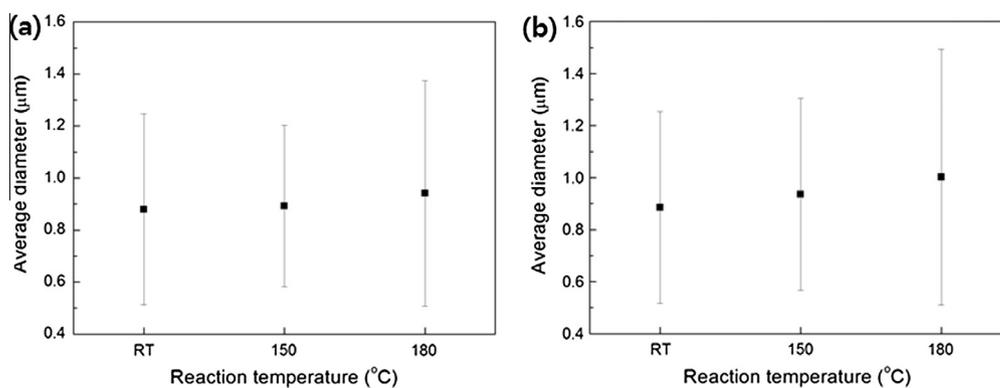
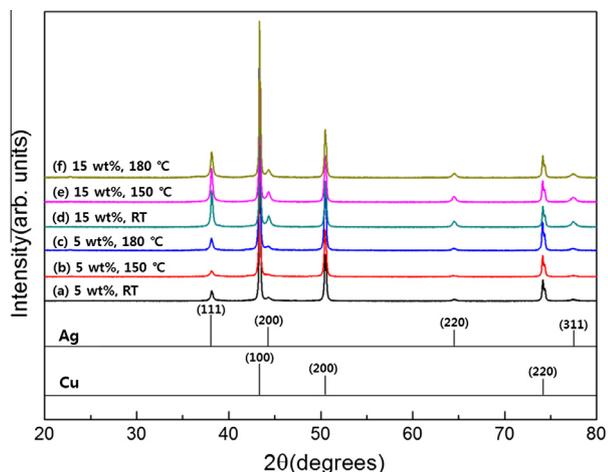


Fig. 3. Average diameter of Ag-plated Cu particles as a function of reaction temperature with polyol solutions containing (a) 5 and (b) 15 wt.% Ag.

### 3. Results and discussion

The Cu core particles had an average diameter of 0.705 μm with a standard deviation of  $\pm 0.177$  and a slight non-uniformity in particle size, as shown in Fig. 1. However, their surface was smooth

and very little agglomeration between particles was observed. In contrast, as shown in Fig. 2, the Cu@Ag particles were far more irregular in terms of both size and shape. Furthermore, not only was the surface of the Cu@Ag particles rough and angular, but increasing the Ag content and temperature induced a greater

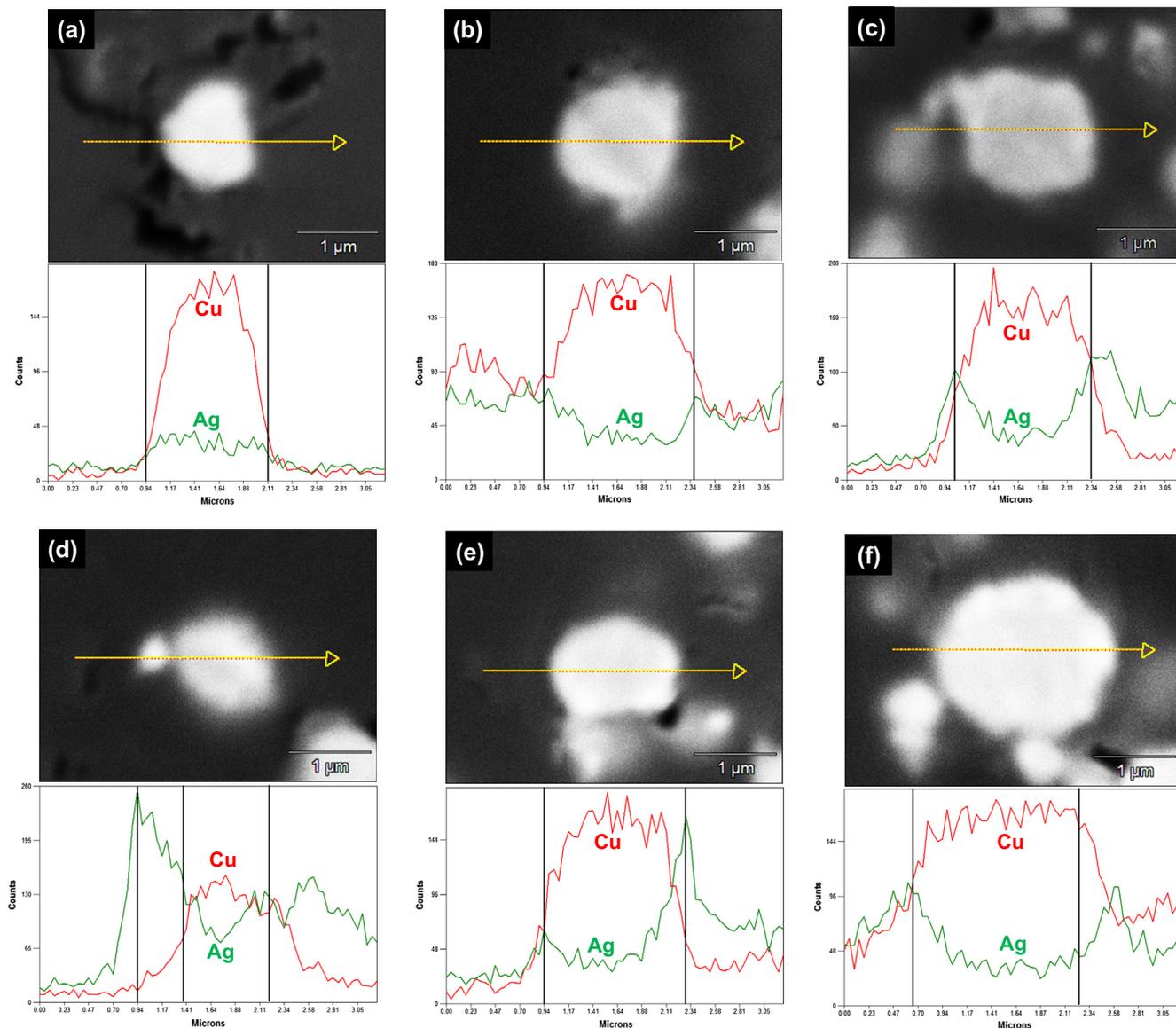


**Fig. 4.** X-ray diffraction (XRD) patterns of Ag-plated Cu powders with different Ag contents and reaction temperatures.

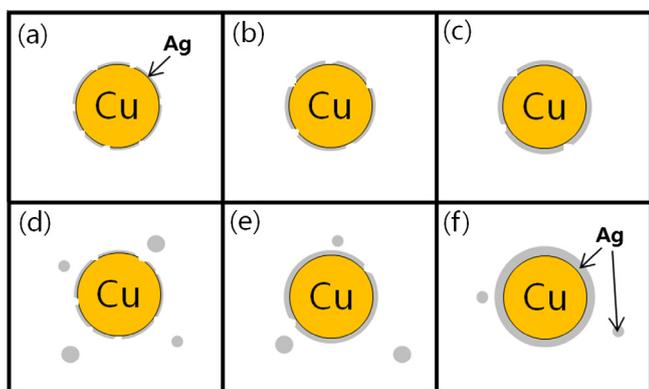
agglomeration of particles. As such, the most agglomerated particles were observed in sample produced with a 15 wt.% Ag polyol solution and a peak temperature of 180 °C.

The average diameter of the Cu@Ag particles as a function of reaction temperature is shown in Fig. 3 for polyol solutions with different initial Ag contents. This reveals that the average diameter increases with both initial Ag content and temperature, but is more sensitive to the latter. The average diameters in Fig. 2(a)–(f) were 0.882 ( $\pm 0.361$ ), 0.892 ( $\pm 0.369$ ), 0.941 ( $\pm 0.311$ ), 0.885 ( $\pm 0.370$ ), 0.936 ( $\pm 0.434$ ), and 1.002 ( $\pm 0.492$ )  $\mu\text{m}$ , respectively. Thus, when compared to the average diameter of a core Cu particle, all samples showed an increase in average diameter that can be considered to be roughly double the actual Ag shell thickness. For example, the Ag shell thickness of the sample shown in Fig. 2(f) can be judged to be roughly around 0.149  $\mu\text{m}$ . Considering the agglomeration of particles, however, actual Ag shell thickness seems to be thinner than 0.149  $\mu\text{m}$ .

In the XRD patterns of the Cu@Ag powders polyol-plated with different Ag contents and reaction temperatures given in Fig. 4, it is apparent that those samples plated with a 15 wt.% Ag solution exhibit more clear Ag-phase peaks than those plated with 5 wt.%

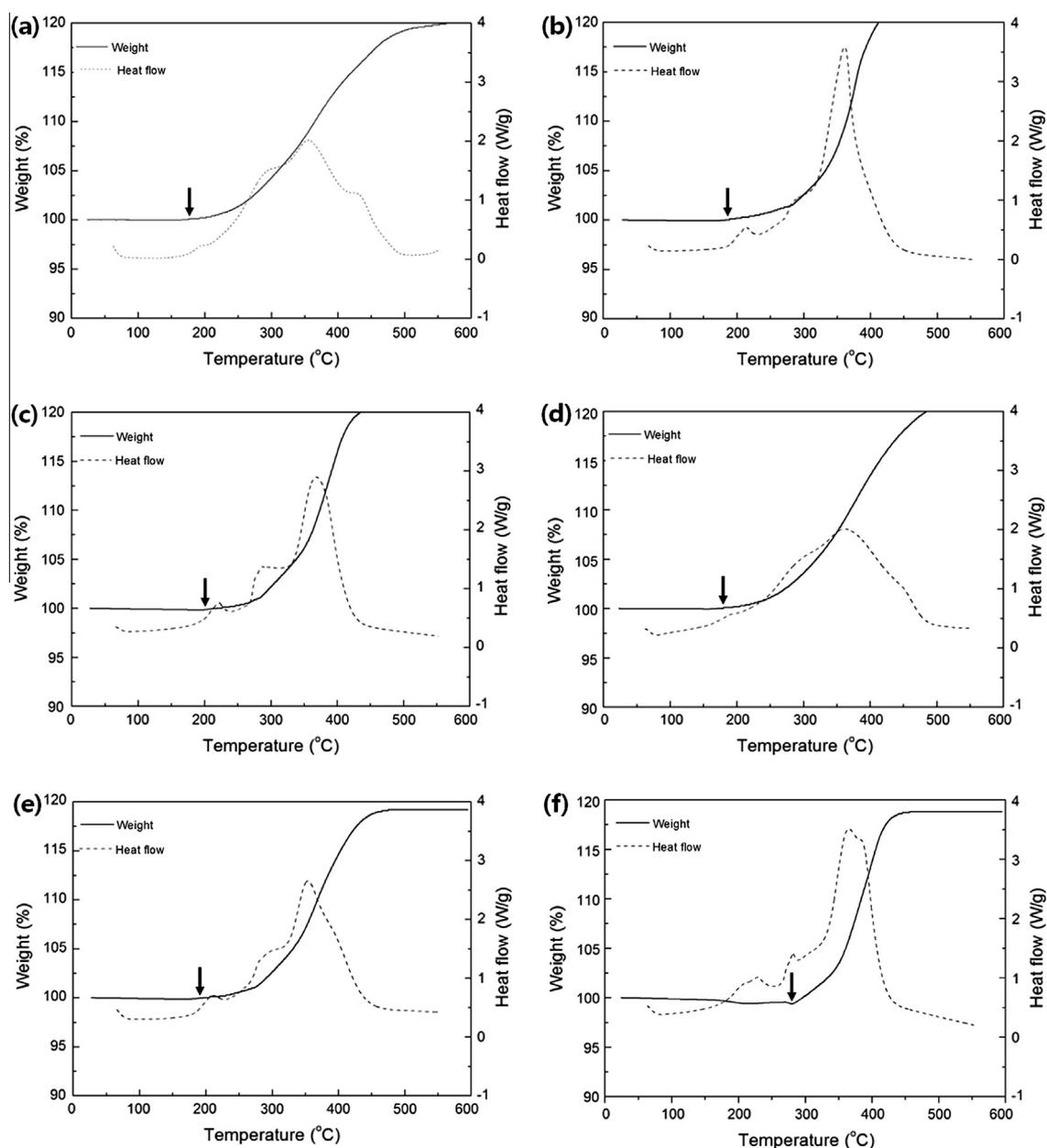


**Fig. 5.** Cross-sectional backscattered electron images and energy dispersive spectroscopy (EDS) profiles of Ag-plated Cu particles produced using polyol solutions with different Ag contents and reaction temperatures: (a) 5 wt.% Ag, RT; (b) 5 wt.% Ag, 150 °C; (c) 5 wt.% Ag, 180 °C; (d) 15 wt.% Ag, RT; (e) 15 wt.% Ag, 150 °C; and (f) 15 wt.% Ag, 180 °C.



**Fig. 6.** Schematic diagrams depicting the preparation of Ag-plated Cu particles using polyol solutions with different initial Ag contents and reaction temperatures: (a) 5 wt.% Ag, RT; (b) 5 wt.% Ag, 150 °C; (c) 5 wt.% Ag, 180 °C; (d) 15 wt.% Ag, RT; (e) 15 wt.% Ag, 150 °C; and (f) 15 wt.% Ag, 180 °C.

Ag solution. This indicates that many large Ag ions were reduced, but the increase in reaction temperature had only minimal effect. On first impression, this would not seem to correspond well to the results shown in Figs. 2 and 3; however, it should be noted that the XRD data represents all traces of Ag, regardless of whether it is formed as a shell on the core Cu particle or as a separate, detached particle. Thus, the XRD results do not in fact confirm the efficacy of Ag plating, as they do not show whether a shell was formed or not. For instance, the shell created in the sample (Fig. 2(c)) prepared with a 5 wt.% Ag content at a peak temperature of 180 °C was thicker than that of the sample (Fig. 2(d)) prepared with a 15 wt.% solution at RT, as shown in Fig. 3; yet despite this, the total amount of reduced Ag in the latter was higher than that of the former, as shown in Fig. 4. It is therefore inferred that the large number of Ag atoms reduced in the sample shown in Fig. 2(d) do not participate in the plating structure, but are in fact consumed to form particles detached from the Cu core.



**Fig. 7.** Thermogravimetric differential scanning calorimetry (TG-DSC) curves of Cu@Ag powders prepared from polyol solutions with different initial Ag contents and reaction temperatures: (a) 5 wt.% Ag, RT; (b) 5 wt.% Ag, 150 °C; (c) 5 wt.% Ag, 180 °C; (d) 15 wt.% Ag, RT; (e) 15 wt.% Ag, 150 °C; and (f) 15 wt.% Ag, 180 °C.

Fig. 5 shows cross-sectional backscattered electron images and energy dispersive spectroscopy (EDS) profiles of Cu@Ag particles prepared with different plating conditions. It is apparent from this that while the sample (Fig. 5(a)) prepared with a 5 wt.% Ag content at RT shows a trace distribution of Ag on the particle in profile, an Ag layer was clearly formed on the 5 wt.% sample (Fig. 5(c)) prepared at a peak temperature of 180 °C despite the presence of irregular Ag nodules. The high Ag counts measured at the edge of the particle clearly indicate the formation of an Ag coating layer. 5 wt.% sample (Fig. 5(b)) prepared at 150 °C indicated tendency between RT and 180 °C. The increase in temperature was judged to be responsible for enhancing the shell thickness and plating uniformity, and thus even a high Ag content at RT would be ineffective in enhancing these properties. The reaction temperature may also directly affect the variation in the Gibbs free energy difference ( $\Delta G_{\text{red}}$ ) during reduction synthesis [12], in that a higher reaction temperature should lower  $\Delta G_{\text{red}}$  to a more negative value.

Meanwhile, all samples prepared from a solution with 15 wt.% Ag contained fine particles of pure Ag that were detached from the main Cu@Ag particles. Note that the Ag and Cu profiles of the fine particles in Fig. 5(d) are extremely high and low, respectively; and thus it is inferred that a high Ag concentration in the plating solution induces homogeneous nucleation and growth of Ag. The concentration of Ag atoms that are rapidly reduced by high temperature increases steeply over a critical supersaturation level [13], which may allow homogeneous nucleation (i.e., the formation of fine, pure Ag particles) in addition to the heterogeneous nucleation of the Ag plating. Nevertheless, the image and profile results in Fig. 5(d)–(f) indicate that a thicker and more uniform Ag shell is obtained with a 15 wt.% solution than with a 5 wt.% solution at the same temperature. Furthermore, a sample (Fig. 5(e)) prepared from a 15 wt.% Ag solution at 150 °C exhibits an asymmetric distribution of Ag (Fig. 5(f)), whereas increasing the temperature to 180 °C produces a symmetric distribution characteristic of a more uniform and continuous Ag shell. Schematic diagrams showing this difference between particles prepared with different initial Ag contents and reaction temperatures are given in Fig. 6.

In the TG–DSC curves of the Cu@Ag powders prepared with different plating conditions shown in Fig. 7, the oxidation initiation temperature was determined as the point at which both the TG and DSC curves first started to increase (as marked by an arrow). This temperature varied greatly in the 176–281 °C range due to a strong dependence on the plating conditions, with the oxidation initiation temperature in Fig. 6(a)–(f) being 176, 189, 200, 180, 206, and 281 °C, respectively. The formation of Ag agglomerates on the surface of Cu through Ag dewetting during air heating at temperatures near 200 °C has been recently reported as being the result of unstable interfacial energy, which induces oxidation of the exposed pure Cu [9,14]. Given this, it is plausible that the homogeneous and thick Ag shell fabricated in this study may delay this dewetting phenomenon through Ag diffusion. It should also be noted that although the oxidation temperature increased with both initial Ag content and reaction temperature, it was much more sensitive to the increase in reaction temperature. Consequently, the increase in oxidation temperature correlated very well to the average diameter (or Ag shell thickness) of the Cu@Ag particles, as shown in Fig. 3. This means the Cu@Ag sample with the

thickest shell (Fig. 6(f)) also has an excellent oxidation initiation temperature of approximately 280 °C; and when compared to the sample shown in Fig. 6(c) that was prepared at an identical temperature (200 °C), clearly has a greatly enhanced resistance to the onset of corrosion (by around 80 °C). Ultimately, this means that provided the Ag shell is uniform, the corrosion resistance is predominantly determined by the Ag shell thickness.

#### 4. Conclusions

Fine Cu@Ag particles with a size in the order of one micron were fabricated through polyol-plating with different initial Ag contents and reaction temperatures. When compared to pure Cu particles, the average diameter of these Cu@Ag particles increased with Ag content and reaction temperature, indicating that the formation of the Ag shell is strongly dependent on the plating conditions. Significantly, the increase in diameter was more sensitive to reaction temperature than Ag content, with the shell thickness of a sample prepared with a 15 wt.% Ag solution at a peak temperature of 180 °C determined to be around 0.149 nm. The oxidation initiation temperature of the Cu@Ag powders was also largely determined by the plating conditions, in that the corrosion resistance corresponds well with the average diameter of the Cu@Ag particles. However, the excellent oxidation initiation temperature demonstrated by a sample prepared from a 15 wt.% Ag solution at a peak temperature of 180 °C confirms that it is in fact the Ag shell thickness that determines the corrosion resistance.

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#### References

- [1] J. Zhao, D. Zhang, J. Zhao, J. Solid State Chem. 184 (2011) 2339.
- [2] B.K. Park, D. Kim, S. Jeong, J. Moon, J.S. Kim, Thin Solid Films 515 (2007) 7706.
- [3] H.T. Hai, J.G. Ahn, D.J. Kim, J.R. Lee, H.S. Chung, C.O. Kim, Surf. Coat. Technol. 201 (2006) 3788.
- [4] L. Ye, Z. Lai, J. Liu, IEEE Trans. Electron. Pack. Manuf. 22 (1999) 299.
- [5] N.A. Luechinger, E.K. Athanassiou, W.J. Stark, Nanotechnology 19 (2008) 445201.
- [6] W. Li, M. Chen, J. Wei, W. Li, C. You, J. Nanopart. Res. 15 (2013) 1949.
- [7] Y.H. Kim, D.K. Lee, B.G. Jo, J.H. Jeong, Y.S. Kang, Colloids Surf. A 284 (2006) 364.
- [8] X. Xu, X. Luo, H. Zhuang, W. Li, B. Zhang, Mater. Lett. 57 (2003) 3987.
- [9] M. Grouchko, A. Kamyshny, S. Magdassi, J. Mater. Chem. 19 (2009) 3057.
- [10] A. Muzikansky, P. Nanikashvili, J. Grinblat, D. Zitoun, J. Phys. Chem. C 117 (2013) 3093.
- [11] D. Erath, A. Filipovic, M. Retzlaff, A.K. Goetz, F. Clement, D. Biro, R. Preu, Sol. Energy Mater. Sol. Cells 94 (2010) 57.
- [12] D. Larcher, R. Patrice, J. Solid State Chem. 154 (2000) 405.
- [13] B.K. Park, S. Jeong, D. Kim, J. Moon, S. Lim, J.S. Kim, J. Colloid Interface Sci. 311 (2007) 417.
- [14] H.T. Hai, H. Takamura, J. Koike, J. Alloys Comp. 564 (2013) 71.