

Preparation and oxidation behaviour of cobalt-coated copper powder

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Spherical copper (Cu) particles with an average particle size of $\sim 2 \mu\text{m}$ were coated with cobalt (Co) via electroless plating in an acid bath to prepare Co-coated Cu particles. The prepared particles maintained the initial core-shell structure even under heating up to 350°C in air. However, as the temperature exceeded 350°C , oxide phases of the Co_3O_4 , CuO, and Cu_2O phases were formed with microstructural change. Immediately after the oxidation of the Co shell, out-diffusion of the Cu core through the relatively porous cobalt oxide shell and copper oxidation occurred, thereby forming the outermost copper oxide shell. At 400°C , the copper oxide shell grew and the destruction of the cobalt oxide shell oxidised the edge region of an initial copper core. At the highest temperature of 600°C , a hole was formed at the centre of a particle due to excess out-diffusion of Cu.

1. Introduction: There is increasing interest in the fabrication of core-shell particles for various applications because of their unique electrical, optical, magnetic, catalytic, and mechanical characteristics [1–3]. With identical reasons, Co-coated Cu particles can be applied to various engineering fields, although substantial research results are lacking. For example, the magnetic shell/electric core structure can be treated as a novel material for the magnetoelectric effect which can be enhanced by coupling between the magnetic and electric properties by the large interfacial area [4–6]. In the application, Co-coated Cu particles may be novel building blocks. Furthermore, cobalt-copper oxides have been studied for applications as a catalyst in the oxygen evolutions reaction, a Fischer-Tropsch process, synthesis of syngas-based alcohol, and a thermoelectric material [7–21]. In either material, the oxidation property of a Co-coated Cu particle as a function of temperature is crucial to the antioxidation of the magnetoelectric material or formation of cobalt-copper oxides by heating in air. Therefore, in this Letter, Co-coated Cu particles were fabricated and the oxidation behaviour of the particles was studied during heating in air. The cobalt coating was performed using a powerful reducing agent of dimethylamine borane (DMAB) [22].

2. Experimental study: In the fabrication of Co-coated Cu particles using electroless plating, spherical Cu powder (99.64%, $d_{50} = 2\text{--}2.5 \mu\text{m}$, JOIN M) was first pretreated by mixing 2 g of the powder with 20 ml of a 1.74 M sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99.0%, Samchun Pure Chemicals Co. Ltd.) aqueous solution and stirring for 10 min. The powder was then rinsed in distilled water four times. Two different types of cobalt precursors were used: cobalt sulphate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 98.0%, Duksan Pure Chemicals Co. Ltd.) for an alkaline bath and cobalt chloride ($\text{CoCl}_2 \cdot 7\text{H}_2\text{O}$, $\geq 97.0\%$, Samchun Pure Chemicals Co. Ltd.) for an acid bath. The alkaline bath was prepared by dissolving 3 g of cobalt sulphate, 8 g of sodium citrate, 9 g of ammonium chloride (NH_4Cl , Susin Chemicals, 98.0%), and 0.4 g of DMAB ($\text{BH}_3\text{NH}(\text{CH}_3)_2$, 97.0%, Alfa Aesar) in 100 ml of distilled water. The citrate was added as an organic radical to function as buffer, exaltant, and/or chelate. After heating the solution to 80°C , 2 g of pretreated spherical Cu was added to the solution, and adjusted to pH 9 using ammonium hydroxide (NH_4OH , Yakuri Chemicals Co. Ltd., 28.0%). To allow adequate plating, the mixture was maintained at 80°C for 15 min. After the reaction, the prepared powder was collected by centrifugation,

the supernatant was decanted, and the powder sediment was rinsed with distilled water. The procedures were performed in triplicate. The powder was dried in a vacuum chamber after a final wash using methyl alcohol (CH_3OH , 99.0%, Samchun Pure Chemicals Co. Ltd.). For acid bath plating, a bath was prepared by dissolving 2.5 g of cobalt chloride, 0.4 g of sodium succinate ($\text{C}_4\text{H}_4\text{Na}_2\text{O}_4$, $\geq 98.0\%$, Sigma Aldrich), and 0.4 g of DMAB in 100 ml of distilled water. In the bath, the succinate was used as an organic radical. After heating the solution to 70°C , 2 g of pretreated spherical Cu was added to the solution, and the solution was adjusted to a pH of 5 using sulphuric acid (H_2SO_4 , 95.0%, Samchun Pure Chemicals Co. Ltd.). The reaction proceeded for 15 min at 70°C , and the final powder was prepared using the described procedure.

The appearance of the as-prepared particles was observed using a field emission scanning electron microscope (FE-SEM, model, JSM-7500F, JEOL Ltd.), and the line profiles of the elements in the cross-sectional images were measured by using energy dispersive spectroscopy (EDS, INCA Energy, Oxford). Phases in the Co-coated Cu particles as a function of temperature were identified using an X-ray diffractometer (XRD, D/MAX 2200V/PC, Rigaku). The oxidation behaviour of powder with respect to temperature was surveyed by using thermogravimetric-differential scanning calorimetry (TG-DSC, Q600, TA Instrument, KBSI PH407 Pusan). The microstructural change of a particle with respect to temperature was examined using a field emission electron probe micro-analyser (FE-EPMA, JXA-8530F, JEOL Ltd.).

3. Results and discussion: Fig. 1 shows the SEM images of the Co-coated Cu particles prepared using different bath types. When the particles were prepared in an alkaline bath (Fig. 1a), the formation and uniformity of the coating could not be confirmed. Moreover, tiny or small-sized Co particles were also observed, indicating that this bath type was not suitable for the formation of cobalt coatings on Cu particles. However, the sample prepared in an acid bath (Fig. 1b) exhibited a distinct surface morphology. The surface was rough and comprised of a bumpy morphology of cobalt. Unlike the condition using sodium hypophosphite [23], formation of the tiny or small-sized Co particles by homogeneous nucleation and growth might be accelerated under a powerful reducing condition using the DMAB reductant. Suppression of the homogeneous nucleation by decreasing the reduction rate of Co chelate ions with a higher pH, such as pH 11, seems to be essential for effective Ag coating in the alkaline bath

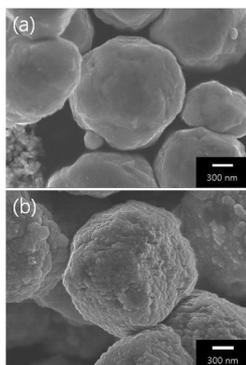


Fig. 1 SEM images of copper particles coated with cobalt in
a Alkaline bath
b Acid bath

incorporating DMAB [24]. The pH condition is also important in the acid bath. It has been reported that the pH 5 in the acid bath incorporating DMAB is proper, not inducing change in plating rate during the Co plating [22].

Fig. 2 shows the SEM images and EDS line profiles of Co-coated Cu particles prepared in alkaline and acid baths. In the alkaline bath (Fig. 2*a*), trace amounts of Co were detected in the particle region. However, the intensity at the edge of the particle was not significantly higher than that in the core of the particle, which was suggestive of incomplete cobalt coating. However, the Co-coated Cu particle in the acid bath (Fig. 2*b*) exhibited a significantly high intensity of cobalt at the edge of the particle, confirming the formation of an effective cobalt coating on the surface of the Cu particle. Hence, Co-coated Cu particles prepared in an acid bath were used to evaluate the oxidation characteristics of the core-shell particle. The reduction of cobalt was estimated using

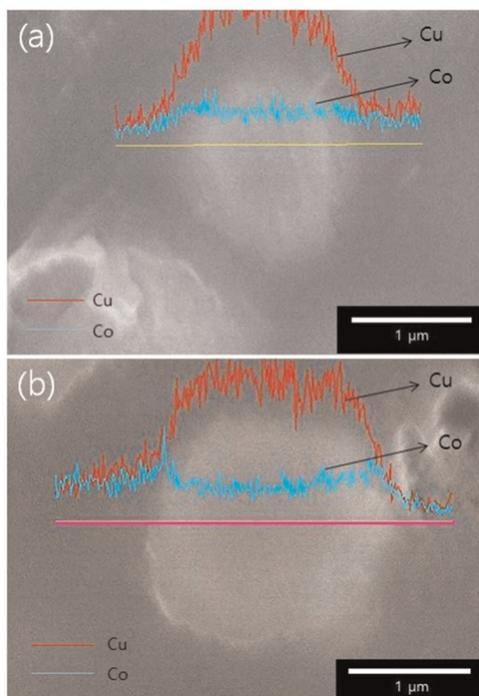


Fig. 2 SEM images and EDS line profiles of Co-coated Cu particles prepared in
a Alkaline bath
b Acid bath

the following reaction:

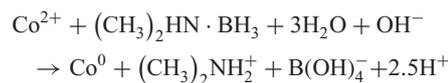


Fig. 3 presents the high-temperature XRD patterns of Co-coated Cu powder prepared in an acid bath as a function of temperature. Although Co and Cu were almost indistinguishable because their main peaks were observed at similar degrees, their patterns were almost identical between room temperature and 350°C. However, the Co₃O₄, CuO, and Cu₂O phases were detected when the temperature reached 400°C. This result thus indicates that the oxidation of this core-shell particle occurs between 350 and 400°C, and the oxidation of copper simultaneously takes place upon cobalt oxidation. Moreover, the intensity of the Co₃O₄ phase slightly decreased and the novel Co₂O₃ phase appeared when the temperature exceeded 450°C. Since then, the intensity of the CuO phase increased and the intensities of the other phases were similarly retained with increasing temperature up to 600°C. The TG-DSC result of the Co-coated Cu powder is shown in Fig. 4. At temperatures exceeding 350°C, the weight of Co-coated Cu powder abruptly increased with the formation of a big exothermic peak,

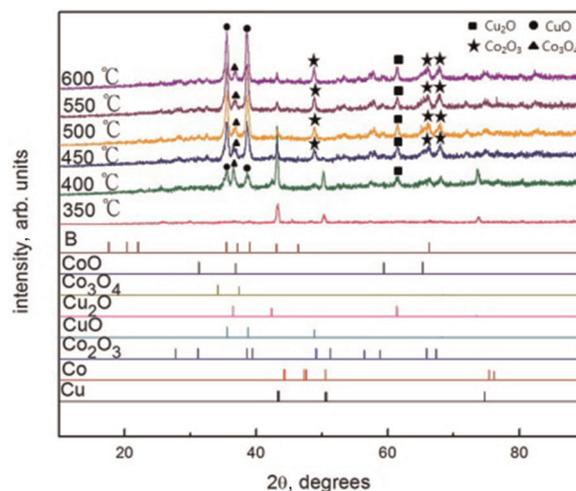


Fig. 3 High-temperature XRD patterns of Co-coated Cu powder as a function of temperature

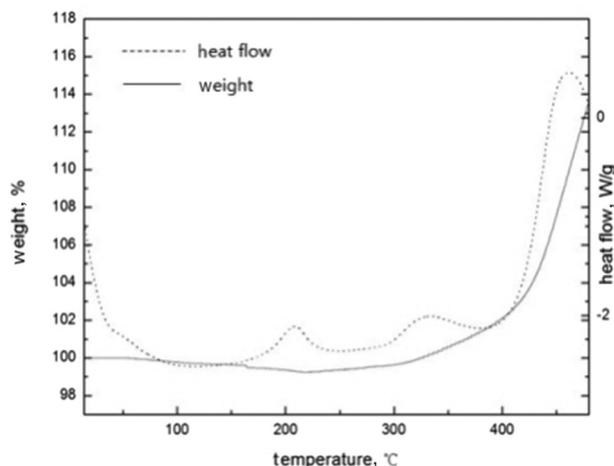


Fig. 4 TG-DSC result of Co-coated Cu powder

confirming that the core-shell powder oxidises around that temperature.

Fig. 5 shows the EPMA images and element line profiles of Co-coated Cu particles at different temperatures. At 350°C, the core-shell structure that was comprised of Cu and Co remained intact. However, the core-shell structure was destroyed by the diffusion of Cu out of the Co shell once the temperature approached 400°C. Moreover, the oxygen profile observed at 400°C indicated that the out-diffused Cu was also oxidised with the oxidation of the Co shell and the edge of the core Cu. XRD analysis indicated that the oxide phases could be indexed as Co_3O_4 , CuO , and Cu_2O (Fig. 3). The core-shell structure was finally transferred into the microstructure depicted in Fig. 5c. The intensity of the out-diffused Cu increased and the intensity of Cu in the centre of the core Cu particle apparently decreased by the out-diffusion. In addition, oxygen was detected in the core of the particle as well as at the edge of the particle. The diffusion of Co inward was also observed in the broader profile of Co. These results suggest the following three phenomena: the amount of the outermost layer (comprised of copper oxide) increased, the Cu core was nearly oxidised with decreasing Cu content at the centre point, and the oxidation of the Co shell intensified concurrently with the inner-diffusion of Co.

Fig. 6 shows the EPMA element mapping images of Co-coated Cu particles at different temperatures. At 350°C, the core-shell structure remained intact and no distinct signs of Co shell oxidation were observed. On the other hand, at 400°C, a novel Cu-based shell

formed and grew around the Co-based shell, and both the Cu-based and Co-based shells were oxidised. These findings indicated that the out-diffusion of Cu through the cobalt oxide shell results in oxidation because the affinity with oxygen is higher with Cu than with Co [25]. The cobalt oxide shell was transformed into an uneven shape with the destruction of the full covering structure. In terms of the core Cu, its edge region was also oxidised, although the core region remained at a non-oxidation state. The edge oxidation was analysed based on the penetration of oxygen across the porous cobalt oxide as well as the rapid rate of diffusion of oxygen. The inner region of the edge copper oxide was thus designated as the Cu_2O phase. When the temperature reached 600°C, the outermost copper oxide shell grew further and the cobalt oxide phase was distributed across several points of the initial core Cu region by inner-diffusion. Although the copper oxide phase was also detected in the interior of the main habitat of the cobalt oxide phase, Cu was not observed at the centre point of the core particle, thereby indicating the formation of a hole at that point. The hole was created from the depletion of copper by excess out-diffusion. It has been previously reported that the hollow structure forms within particles of the Cu core-noble metal shell during Cu oxidation [26].

The proposed oxidation behaviour of a Co-coated Cu particle is summarised in Fig. 7. At temperatures exceeding 350°C, the Co shell is oxidised, and the inner Cu out-diffuses through the porous cobalt oxide shell and is oxidised, thereby forming the outermost copper oxide shell. With increasing temperature, the

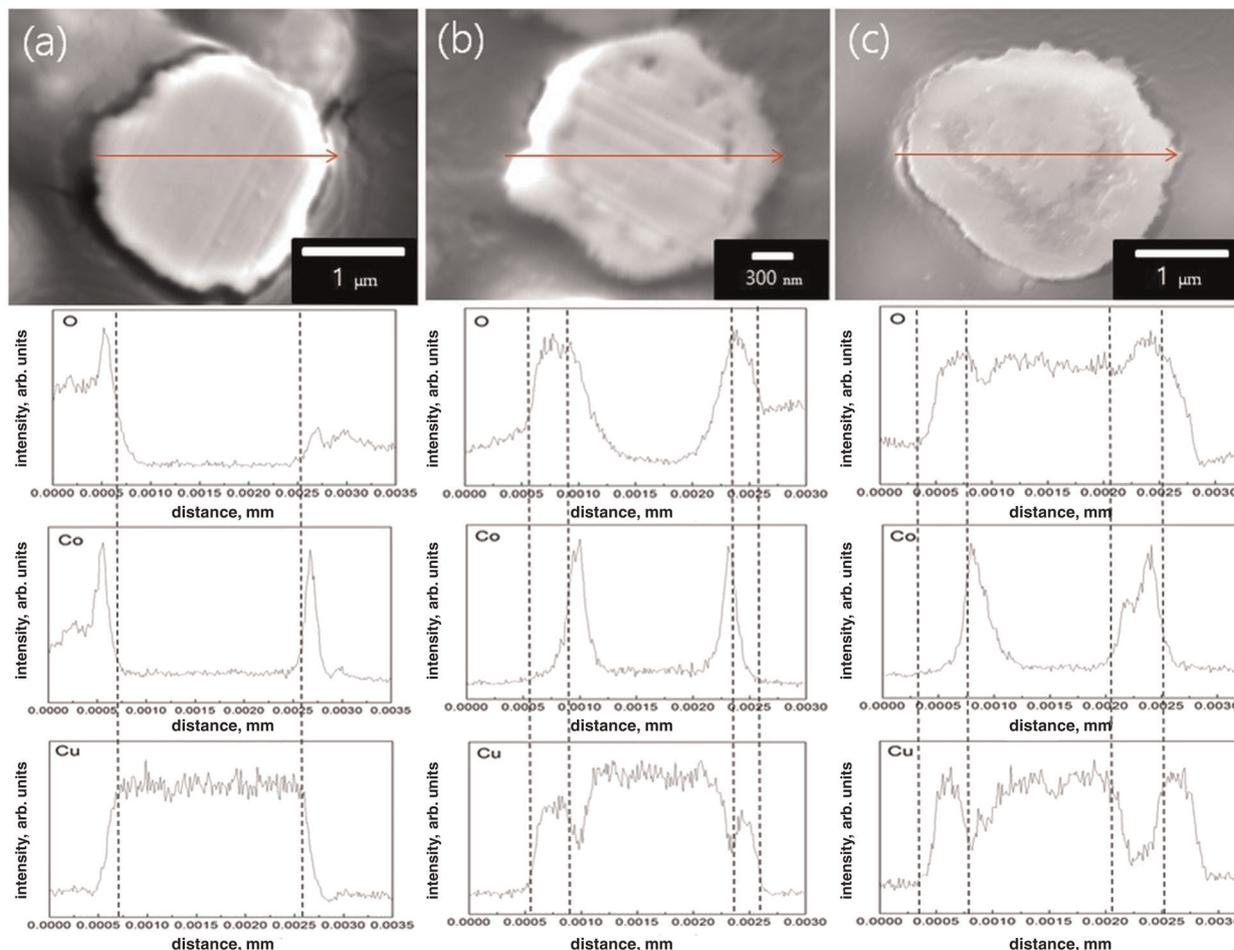


Fig. 5 EPMA images and element line profiles of Co-coated Cu particles at different temperatures
a 350°C
b 400°C
c 600°C

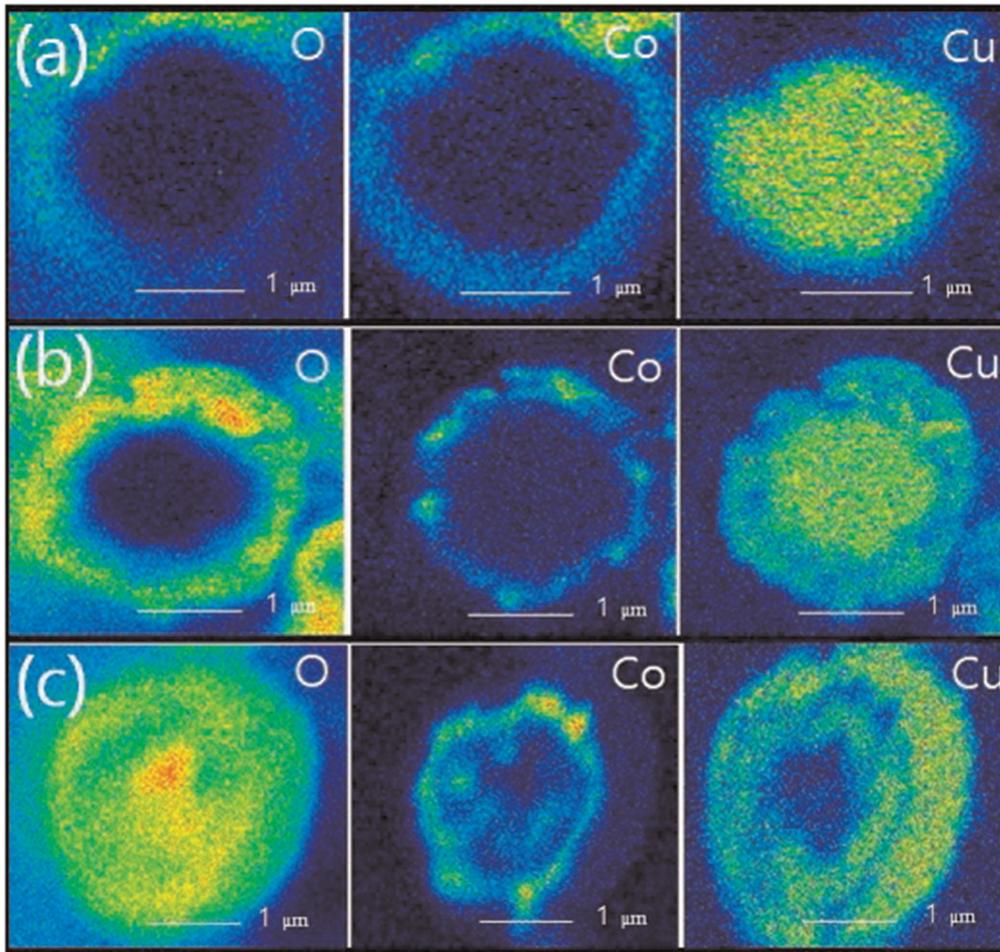


Fig. 6 EPMA element mapping images of Co-coated Cu particles at different temperatures
 a 350°C
 b 400°C
 c 600°C

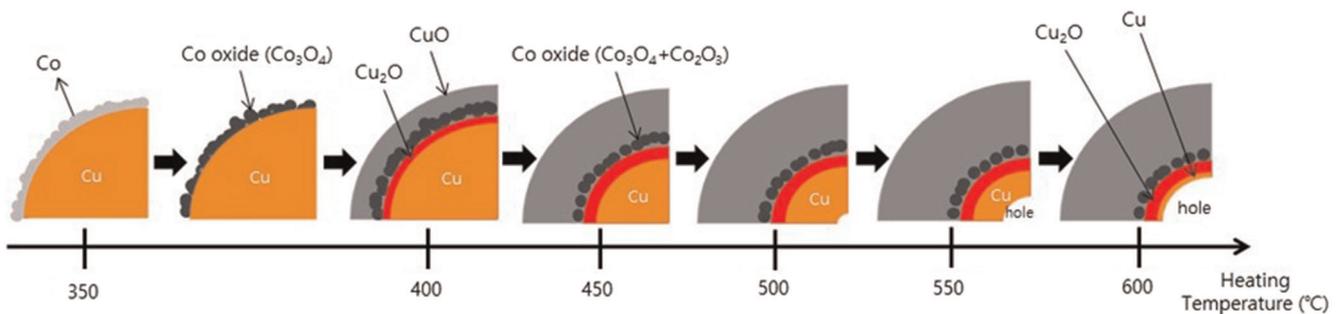


Fig. 7 Schematics depicting the oxidation behaviour of a Co-coated Cu particle

outermost copper oxide shell grows and the cobalt oxide shell is destroyed. Once cobalt oxide develops a more porous structure, Co atoms diffuse into the interior of the particles. The edge region of the initial core Cu is oxidised simultaneously with the destruction of cobalt oxide. The oxidation amount in the initial core Cu increases and the Cu is eventually converted into a nearly complete oxide phase with increasing temperature. Finally, a hole is formed at the centre point of the core Cu due to excessive Cu out-diffusion. These oxidation procedures suggest that a Co-coated Cu particle can be induced into complete oxide phases by heating in air.

4. Conclusion: When fabricating Co-coated Cu particles, a Co shell was successfully formed using an acid bath. The prepared Co-coated Cu particle shows an intact core-shell structure despite heating at 350°C. At temperatures exceeding 350°C, oxide phases of Co_3O_4 , CuO, and Cu_2O were formed. Some portions of the Co_3O_4 phase were transformed into the Co_2O_3 phase at 450°C. EPMA analysis elucidated the mechanism underlying the oxidation of a Co-coated Cu particle. Immediately after the oxidation of the Co shell at a temperature approaching 400°C, out-diffusion of the core Cu through an apparently porous cobalt oxide shell and copper oxidation occurred, resulting in the

formation of the outermost copper oxide shell. Further increases in temperature resulted in the growth of the outermost copper oxide shell, and the destruction of cobalt oxide shell enhanced the oxidation of the edge region of the initial core Cu. The formation of a hole at the centre point of core Cu was attributed to excess Cu out-diffusion.

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