

Preparation of copper-plated graphite powder, and the sintering behavior of its composite with copper

Pyo-Hyun Uk, Tae-Joo Chung and Hyukjae Lee*

Materials Research Center for Energy and Green Technology Andong National University Andong, Gyeongbuk 36729, Korea

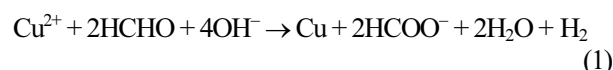
To reduce the inhomogeneity from density difference in copper-graphite composite, which is a material system for DC-motor brushes, copper is deposited on graphite surface via electroless plating, and then the copper-plated graphite mixed with pure copper powders is pressed and sintered to produce a final compact. Here, we identified the optimum electroless plating condition for a large amount of copper deposition, and used it to prepare composite powders with pure copper. We compared the sintering behavior of the copper-plated graphite/copper composite powder with that of pure graphite/copper composite powder. The results show that the copper-plated graphite/copper composite significantly enhanced the sinterability of the composite powder, along with the homogeneity of the sintered compact.

Key words: DC-motor brush, Electroless plating, Copper, Graphite, Sintering, Composites.

Introduction

The DC-motor brush is a component that conducts current between a commutator and an external electrical circuit. Since the brushes have sliding contact with the rotating commutator, the friction between them induces heat, sparking, and wear of both surfaces, which eventually deteriorate the performance and life of the DC-motor. One of the attempts to skirt these effects is to manufacture a brush made from a mixture of copper and softer carbon [1, 2]. The ratio of copper to carbon in the brush can be changed for a specific application. For high current applications, brushes with higher copper content are normally used, where softer carbon acts as a solid lubricant. However, the density difference between copper and carbon causes local inhomogeneity during mixing, leading to a lack of sinterability, performance degradation, and shortened life [2]. Coating of copper on carbon powder can mollify this inhomogeneity, by reducing the density difference between the two composite powders, i.e., copper and carbon.

Although there are various means for copper coating on carbon, a simple method is electroless plating, which uses a reducing agent to chemically deposit ions on the target surface [3, 4]. The reaction in an aqueous solution for electroless plating of copper with formaldehyde as a reducing agent is:



Electroless plating of copper on carbon has been performed for many applications in the past, such as active material for Li-ion batteries [5-7], copper coating on carbon nanotubes [8-10], and composite materials [11, 12]. For these purposes, the amount of copper does not need to be large, because the plated copper is only expected to offer unique functionality to the carbon. On the other hand, to reduce the density difference, a higher content of copper in the copper-plated carbon powder would be preferable, i.e., more than 80 vol% of copper. In this study, we prepared copper-coated graphite powders via electroless plating, and investigated their sintering behavior. We did so to understand how various plating conditions changed the amount of plated copper, and to identify the plating conditions that result in the highest copper content in copper-plated graphite powders. Further, we compared the sintering behavior of the copper/copper-plated graphite composite with copper/graphite composite, to determine if the copper plating on graphite could improve the homogeneity in the sintered compact.

Experimental Procedure

Cu@C (Carbon-plated graphite) powder was prepared by an electroless plating. Before plating, a two-step sensitization and activation pretreatment was performed. The heat-cleaned graphite powder (Hyundai Coma) was added into a sensitization solution prepared by dissolving SnCl_2 (5 g/L) and HCl (37 wt%, 7 mL/L) in distilled water under ultrasonication. After 10 min of

*Corresponding author:
Tel : +82-54-820-6272
Fax: +82-54-820-6211
E-mail: hlee@anu.ac.kr

sensitization, the graphite powder was washed with water, and then added into a solution containing PdCl_2 (0.2 g/L) and HCl (37 wt%, 5 ml/L) under sonication for 10 min. The pretreated graphite was then washed thoroughly, and subsequently put into the plating solution (200 ml), which was prepared by mixing formaldehyde (6 ml/200 ml), EDTA (12 g/200 ml), and CuSO_4 (4, 8, 12, 16, 20, 24 g/200 ml). During electroless plating, NaOH was also periodically added into the solution to adjust the pH. After 1 to 3 hrs of plating, the powder was filtered and washed with distilled water, and then vacuum dried at 80 °C for 24 hrs.

The composite powder for sintering was prepared by ball milling of unplated or Cu@C powders with pure copper powder in ethanol for 12 hrs. It was then first uniaxially pressed in a cylindrical mold at 30 MPa, and then isostatically cold pressed at 150 MPa. The resulting green compact was sintered in a vacuum furnace at 900 or 1,000 °C for 1 hr with 5 °C/min heating rate under N_2 (90 vol%)/ H_2 (10 vol%) gas atmosphere. After cooling, the sintered compact was subsequently re-sintered at 900 °C for 1 hr under flowing argon to achieve higher densities.

The compositional and microstructural properties of composite powders and sintered compacts were characterized by X-ray spectroscopy (EDX) attached to the scanning electron microscope (VEGA II, TESCAN) and X-ray diffraction (Ultima IV, Rigaku) with $\text{Cu K}\alpha$ ($\lambda = 1.54059 \text{ \AA}$) target. Thermogravimetry analysis (TGA) was also performed on several specimens to verify the measured carbon content by EDX. The density of sintered compact was obtained by the conventional Method of Archimedes.

Results and Discussion

To investigate how the Cu content varies with different plating conditions, EDX analysis was performed on Cu@C powders after electroless plating, and Fig. 1 shows the results. Fig. 1(a) shows the variation of Cu content in the Cu@C powder with different amounts of Cu_2SO_4 in the plating solution. Unsurprisingly, a larger amount of Cu_2SO_4 in the solution led to higher copper content in Cu@C powder; however, more than 16 g/200 ml of Cu_2SO_4 did not increase the copper content further. In fact, the copper contents from 20 g/200 ml and 24 g/200 ml Cu_2SO_4 in plating solution were lower than that from 16 g/200 ml of Cu_2SO_4 . This saturated copper content in Cu@C powder suggests that when the plating solution contains 16 g/200 ml of Cu_2SO_4 , the surface of graphite might be fully covered by copper, so that further Cu ions cannot be plated on the graphite surface, even though more Cu ions are added into the solution. Figs. 1(b) and 1(c) show the changes of copper content with different plating time and solution pH, respectively. The longer plating time led to higher copper content; however, after 2 hrs, the

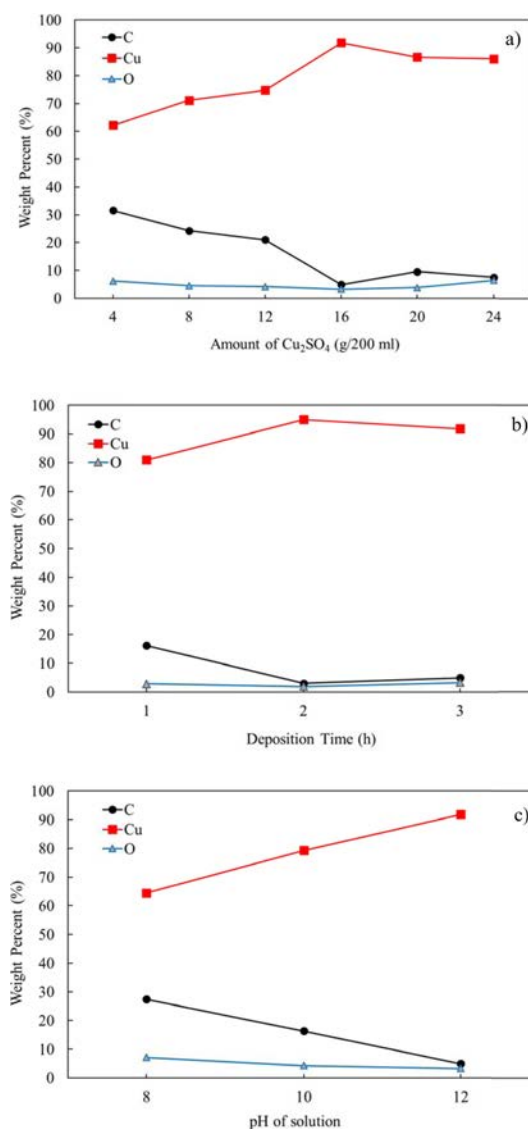


Fig. 1. (a) Copper contents in Cu@C powder as a function of the amount of Cu_2SO_4 in 200 ml plating solution (pH = 12 and plating time = 2 hrs), (b) Change of Copper contents in Cu@C powder with the plating time (the amount of Cu_2SO_4 in 200 ml plating solution = 16 g and pH = 12), and (c) Copper contents in Cu@C powder with the pH of plating solution (the amount of Cu_2SO_4 in 200 ml plating solution = 16 g, and plating time = 2 hrs).

copper content did not change much with plating time. The reason for this would be either the Cu ions in the solution were exhausted, or the graphite surface was fully plated after 2 hrs of plating. Considering that further Cu ions cannot increase the copper content in Fig. 1(a), it can be speculated that 2 hrs of plating time is enough to fully plate Cu on graphite surface. Since the pH of the solution normally relates closely to the potential of the solution, the copper content of Cu@C powder should depend strongly on the solution pH. Fig. 1(c) shows that, as expected, the copper content increases more than 10 wt% with the change of solution pH from 10 to 12. Based on these results, the optimal condition to achieve the highest copper content

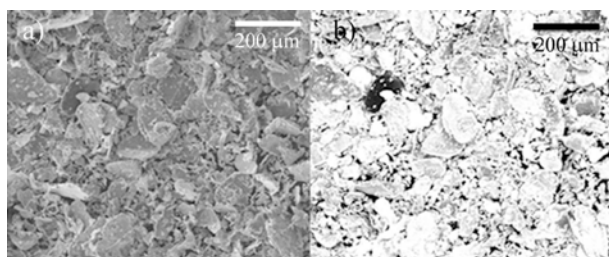


Fig. 2. SEM imagery of Cu@C powders prepared by the standard plating condition (16 g/200 ml of Cu_2SO_4 , pH = 12, and plating time = 2 hrs); (a) SE mode and (b) BSE mode.

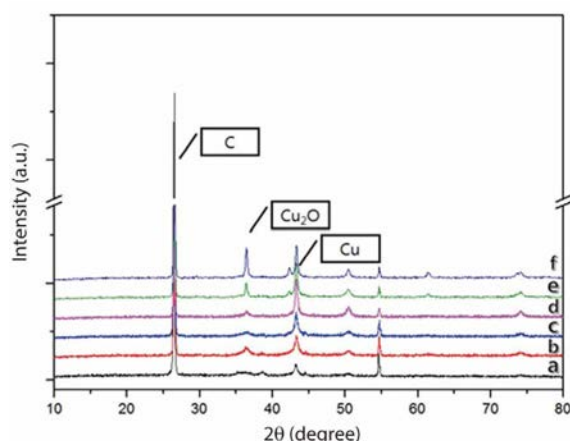


Fig. 3. XRD patterns of Cu@C powders prepared from different contents of Cu_2SO_4 : (a) 4, (b) 8, (c) 12, (d) 16, (e) 20, and (f) 24 g/200 ml.

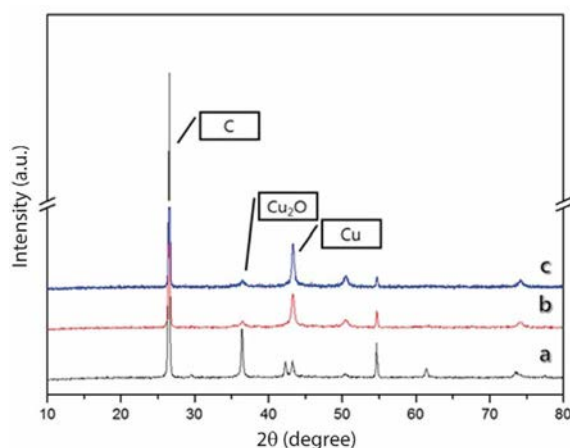


Fig. 4. XRD patterns of Cu@C powders prepared from various solution pH: pH = (a) 8, (b) 10, and (c) 12.

would be 16 g of Cu_2SO_4 in 200 ml plating solution (pH = 12) with 2 hrs plating time, which was thus set in this study as the standard plating condition to prepare Cu@C powders for sintering.

Fig. 2 shows SEM imagery of the Cu@C powder prepared using the standard plating condition. The plate-like graphite morphology can be seen in the SE mode SEM image (Fig. 2(a)). Meanwhile, Cu@C powders appear very bright in the BSE mode image

Table 1. Specifications of the starting powder mixtures.

Copper/graphite powders		
Copper: graphite (wt%)	Cu (vol%)	C (vol%)
90 : 10	68.1	31.9
92.5 : 7.5	74.5	25.5
95 : 5	81.8	18.2
97.5 : 2.5	90.2	9.8

Copper/Cu@C powders		
Copper: Cu@C (wt%)	Cu (vol%)	C (vol%)
70 : 30	65.1	34.9
80 : 20	74.5	25.5
90 : 10	85.9	14.1

(Fig. 2(b)) because of the plated copper atoms, which are much heavier than carbon, on the surface of graphite. However, a few dark particles are also present in Fig. 2(b). This incomplete copper plating might be from the agglomeration of graphite particles during electroless plating.

The XRD patterns in Figs. 3 and 4 show the presence of Cu_2O phase from all Cu@C powders prepared in this study. Overall the plating solution with higher concentration of Cu_2SO_4 or pH results in higher Cu_2O peak intensities; however, no appreciable difference in XRD patterns could be found with different plating time (not shown here). This Cu_2O phase would naturally form from the reaction of copper and oxygen in the solution/air, and hence it is difficult to remove during electroless plating. As will be shown later, the Cu_2O phase can be removed during sintering.

For sintering, Cu@C powders, prepared by the standard plating condition, were first ball milled with pure copper powders in ethanol, to prepare homogeneous copper-Cu@C powder mixture. Because the desired copper content for manufacturing the DC-motor brush is more than 80 vol%, more copper than Cu@C should be needed for the starting powder. Moreover, the added copper can greatly enhance the sinterability. Another powder mixture of copper and graphite was also prepared by ball milling for comparison. Table 1 shows the weight percent of each powder in mixtures, and the resulting volume percent of copper and graphite.

Sintering was performed in N_2/H_2 (9 : 1) atmosphere to remove the Cu_2O phase, which presents in Cu@C powders. Fig. 5 shows that this resulted in no Cu_2O phase in the XRD pattern of sintered compact. Fig. 6 shows surface SEM imagery of sintered compacts, where the plated copper on graphite surface can be seen in Figs. 6(b) and 6(d).

The comparative sinterability of two powder mixtures, copper/graphite and copper/Cu@C mixtures, is determined in terms of relative density after sintering.

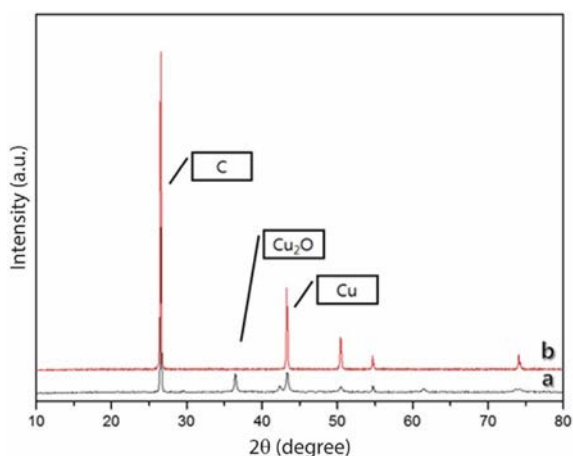


Fig. 5. XRD patterns of Cu@C compacts (a) before, and (b) after sintering at 900 °C for 1 hr under H₂/N₂ gas atmosphere.

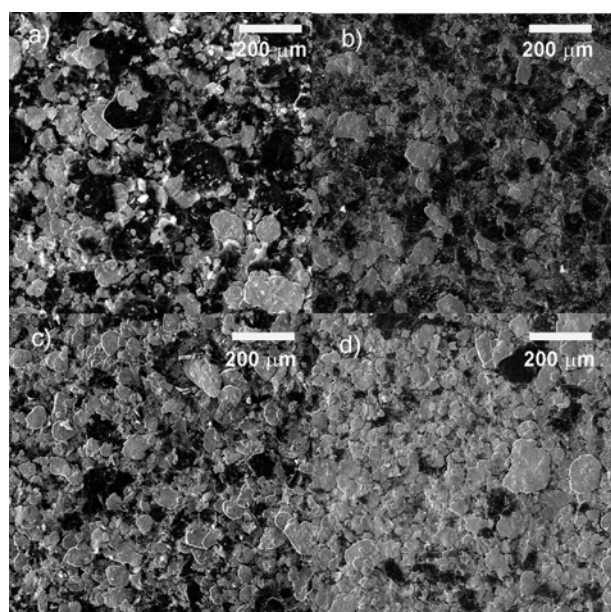


Fig. 6. SEM imagery of compacts sintered at 900 °C. (a) Copper/graphite mixture (wt% ratio = 90 : 10), (b) copper/graphite mixture (wt% ratio = 97.5 : 2.5), (c) copper/Cu@C mixture (wt% ratio = 70 : 30), and (d) copper/Cu@C mixture (wt% ratio = 90 : 10).

Fig. 7 shows that the sintered densities of both copper/graphite and copper/Cu@C mixtures after the first sintering are not that high, such that the maximum densities for copper/graphite and copper/Cu@C compacts are ~80 and 86%, respectively, which were achieved with the highest copper content, because the sinterability of copper is much better than graphite at these temperatures. Nevertheless, it should be noted that copper/Cu@C compacts show higher sintered densities than copper/graphite compacts with comparable total copper content, due to the copper-copper contacts between copper and Cu@C particles. Further, while the difference in sintering temperature does not influence the relative density for copper/graphite compact, it does enhance the sintered

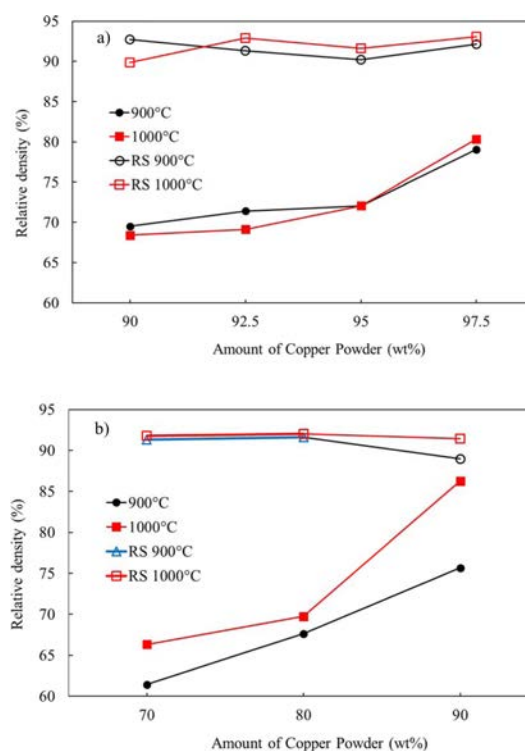


Fig. 7. Relative density of (a) copper/graphite mixture and (b) copper/Cu@C mixture sintered at 900 and 1,000 °C. RS indicates the relative density of re-sintered compact at 900 °C for 1 hr after the first sintering at the respective temperatures.

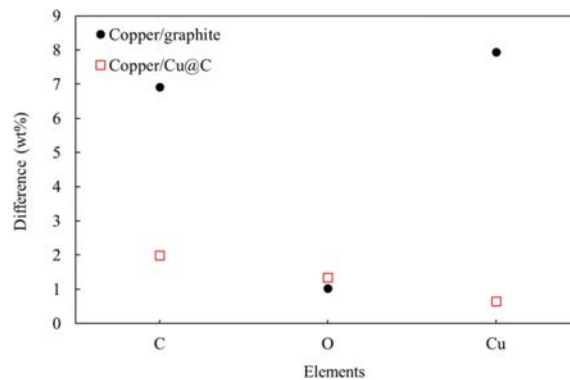


Fig. 8. The difference in composition between the top and bottom of the compact sintered at 900 °C, and then re-sintered. The copper/graphite compact was made of 95 wt% of copper and 5 wt% of graphite, while the copper/Cu@C compact has 90 wt% of copper with 10 wt% of Cu@C.

density for copper/Cu@C compact at the higher sintering temperature, which also suggests a better sinterability of copper/Cu@C mixture. To improve the sintered density to the level of commercial use, re-sintering was required to be performed at 900 °C for 1 hr in Ar atmosphere. Fig. 7 shows that the re-sintering results in more than 90% of relative density for almost all specimens.

Cu@C powder was prepared to alleviate the density difference between graphite and copper, and thus maintain homogeneous composition throughout the

sintered compact. To investigate the compositional homogeneity, the EDS analysis was performed on the top and bottom surfaces of the sintered compact, and Fig. 8 shows the results. Clearly, the copper/Cu@C compact has much less density difference than copper/graphite compact, as the maximum compositional difference for the copper/Cu@C compact is about 2 wt% of C; whereas, that for the copper/graphite compact is about 8 wt% of Cu. Therefore, the use of copper-plated graphite, instead of pure graphite powders, in the starting powder can effectively reduce the compositional inhomogeneity of copper/graphite sintered compact. Since electroless plating is widely used in industry, we expect that the simple coating method studied in this study can be quickly applied to the commercial production of DC-motor brushes.

Conclusions

In this study, copper is plated on the graphite surface via electroless plating to alleviate the inhomogeneity in copper/graphite composites, and a mixture of Cu-plated graphite and pure copper powders is used as the starting powder for manufacturing sintered composites. From the course of this study, the following conclusions are drawn:

1. A maximum 81 wt% of copper can be uniformly deposited on graphite powder via electroless plating, after sensitization/activation processes.
2. Cu₂O phase that exists in copper-plated graphite powders can be removed by sintering under N₂/H₂ atmosphere.
3. The plated copper can enhance the sinterability of copper/copper-plated graphite composites, but re-sintering is required to achieve more than 90% of sintered density.
4. As compared to copper/graphite composites,

copper/copper-plated graphite composites show better compositional homogeneity in sintered compact, due to the lesser difference in density between copper and copper-plated graphite.

Acknowledgments

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