

Preparation of spherical ultrafine copper powder via hydrogen reduction-densification of Mg(OH)₂-coated Cu₂O powder

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Abstract: A novel process was developed to produce spherical copper powder for multilayer ceramic capacitors (MLCC). Spherical ultrafine cuprous oxide (Cu₂O) powder was prepared by glucose reduction of Cu(OH)₂. The Cu₂O particles were coated by Mg(OH)₂ and reduced to metallic copper particles. At last, the copper particles were densified by high-temperature heat treatment. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), tap density, and thermogravimetry (TG). It is found that the shape and size distribution of the copper powder are determined by the Cu₂O powder and the copper particles do not agglomerate during high-temperature heat treatment because of the existence of Mg(OH)₂ coating. After densification at high temperature, the particle tap density increases from 3.30 to 4.18 g/cm³ and the initial oxidation temperature rises from 125 to 150°C.

Keywords: ceramic capacitors; multilayers; copper powder; hydrogen reduction; densification

1. Introduction

With the increase of precious metal price and the decrease of multilayer ceramic capacitor (MLCC) profits, base metal electrode multilayer ceramic capacitors (BME-MLCC) have become a more economical alternative to conventional precious metal electrode design [1]. Recently, an increasing interest has been found in synthesizing ultrafine base metal powder for MLCC [2-7]. Copper powder has recently attracted increasing attention because of its high electrical conductivity, relatively higher melting point, low electrochemical migration behavior, and low materials cost [8-9].

A number of synthetic methods have been developed for preparing copper particles, such as γ -radiolysis [10], microemulsion [11], sol-gel [12], electrolysis [13], vapor phase method [14], and liquid chemical reduction method [15-19]. Liquid chemical reduction is the most extensively used method because of its simplicity and low cost. However, the formation of Cu(I) compound happens simultaneously in the Cu(II) liquid reduction process, so it is difficult to control the nuclei formation and growth process of copper particles. Therefore, copper particles prepared by liquid chemical re-

duction method always are not uniform and with irregular morphology.

After a series of researches on liquid chemical reduction method [18-19], Hu *et al.* [20] tried the preparation of ultrafine copper powder via hydrogen reduction of cuprous oxide (Cu₂O) powder at a low temperature of 240°C. The results showed that the copper particles inherited the morphology and size distribution of Cu₂O, and spherical copper powder with a mean size of 1.25 μm was obtained. However, copper particles prepared by this process were porous and their tap density is low (2.1 g/cm³). These properties are not suitable for a conductive paste of MLCC. In this paper, a novel process, mainly including the Mg(OH)₂ coating of Cu₂O, hydrogen reduction, and densification of porous copper particles, has been developed. This process realized the densification of copper powder on the basis of preventing copper powder from sintering at high temperature.

2. Experimental

2.1. Preparation of Cu₂O powder

The procedure for the preparation of Mg(OH)₂-coated

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Cu₂O powder and the concentration of reagents is shown in Fig. 1. Firstly, 200 mL CuSO₄ solution and 200 mL NaOH solution were mixed slowly in a glass reactor at room temperature to prepare Cu(OH)₂ suspension. Secondly, the suspension and 200 mL glucose solution were heated up to 50°C, respectively, and the glucose solution was rapidly added into the reactor and kept at 50°C for 60 min to reduce Cu(OH)₂ into Cu₂O. After the Cu₂O suspension was prepared, 100 mL MgSO₄ solution was poured into the reactor, and then NaOH solution was dropped into the system to adjust the pH value to about 12.5. The coating reaction was kept for 30 min. The products were collected by centrifugation (3000 r/min), washed five times with distilled water and two times with ethanol, and dried at 65°C for 24 h. All the chemical reaction processes were under stirring (500 r/min).

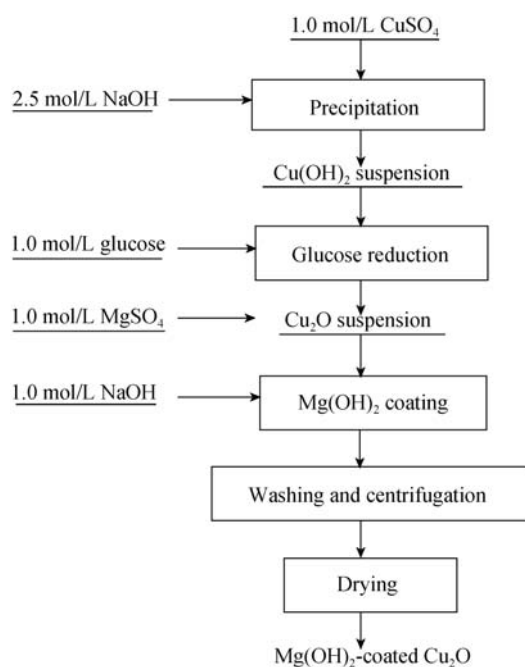


Fig. 1. Preparation process of Mg(OH)₂-coated Cu₂O powder.

For the preparation of uncoated Cu₂O powder, the procedure almost is the same as Fig. 1, except that the Mg(OH)₂ coating stage was omitted.

2.2. Hydrogen reduction of Cu₂O powder

About 5 g uncoated Cu₂O powder or coated Cu₂O powder was spread evenly in a porcelain boat, put into a tubular electric furnace, and reduced by H₂ at 175°C for 1.5 h.

2.3. Densification of copper powder

After the hydrogen reduction was finished, the copper powder was densified by keeping the furnace temperature at

300, 400, and 500°C for 1 h, respectively. The densified copper powder was cooled to room temperature under the atmosphere of H₂. When the precursor was the coated Cu₂O powder, the coating layer was dissolved by dilute sulfuric acid, washed by pure water until the pH value of the waste washing water was up to about 5, and then washed twice by ethanol. Finally, the copper powder was dried at 65°C under vacuum.

In the experiment, the flow rate of hydrogen was 300 mL/min and the rate of temperature increase was 7°C/min.

2.4. Characterization of the powder

X-ray diffraction (XRD) of the powder was carried out using a Rigaku D/Max 2550 X-ray diffractometer with Cu K_α radiation ($\lambda=0.15418$ nm). The morphology and size of the Cu₂O particles were investigated by scanning electron microscopy (SEM, JSEM-6360LV, Japan). Transmission electron microscopy (TEM) images were taken with a Hitachi Model-800 TEM using an accelerating voltage of 200 kV. The tap density of the Cu powder was determined by a JZ-1-type powder tap density spectrometer (Chengdu Jingxin Co., Ltd., China). The Mettler Toledo TGA SDTA851 was used for thermogravimetry (TG; air atmosphere, gas velocity 100 mL/min, the rate of temperature rise was 10°C/min, and the temperature range was 30-500°C).

3. Results and discussion

3.1. Characterization of uncoated and Mg(OH)₂-coated Cu₂O particles

SEM micrographs of Cu₂O particles before and after Mg(OH)₂ coating are shown in Figs. 2(a) and 2(b), respectively. It can be seen that both the uncoated Cu₂O particles and Mg(OH)₂-coated Cu₂O particles are spherical and with good dispersibility.

TEM micrographs of Cu₂O particles before and after Mg(OH)₂ coating are shown in Figs. 3(a) and 3(b), respectively. It can be seen that the surface of Cu₂O particles before coating is smooth, but there is a membranous layer after coating. It can be explained by virtue of Mg(OH)₂ coating.

Fig. 4 shows the XRD patterns of the uncoated Cu₂O particles and Mg(OH)₂-coated Cu₂O particles. XRD patterns of both the uncoated Cu₂O particles and Mg(OH)₂-coated Cu₂O particles are identical with the standard XRD pattern of Cu₂O crystals, and no diffraction peak of Mg(OH)₂ is found. It is probably because that the amount of the coated Mg(OH)₂ is below the detective limit of XRD or Mg(OH)₂

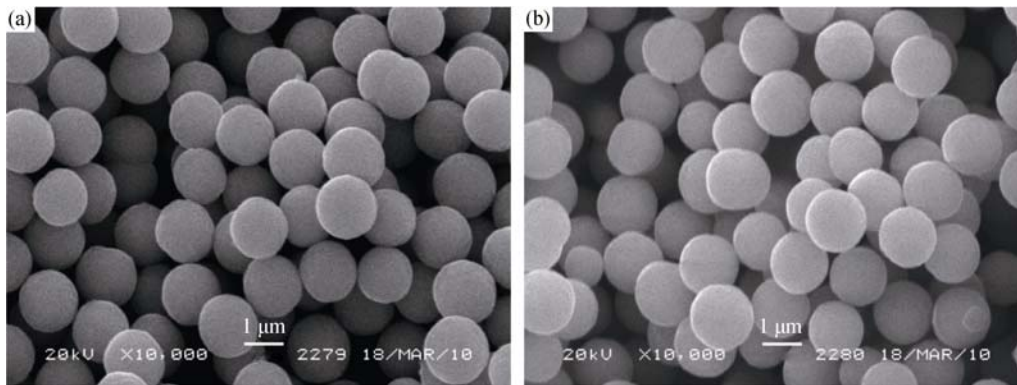


Fig. 2. SEM images of Cu_2O particles: (a) uncoated Cu_2O ; (b) coated Cu_2O .

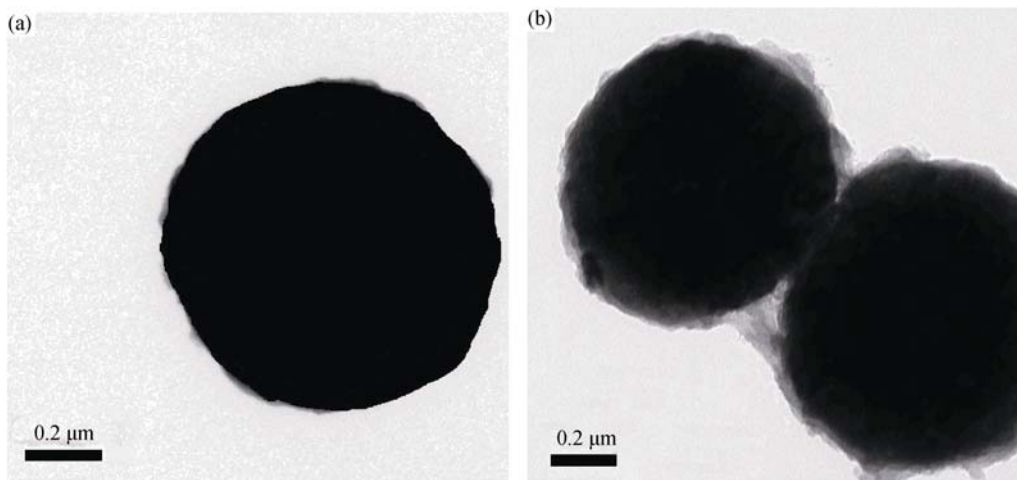


Fig. 3. TEM images of Cu_2O particles: (a) uncoated Cu_2O ; (b) coated Cu_2O .

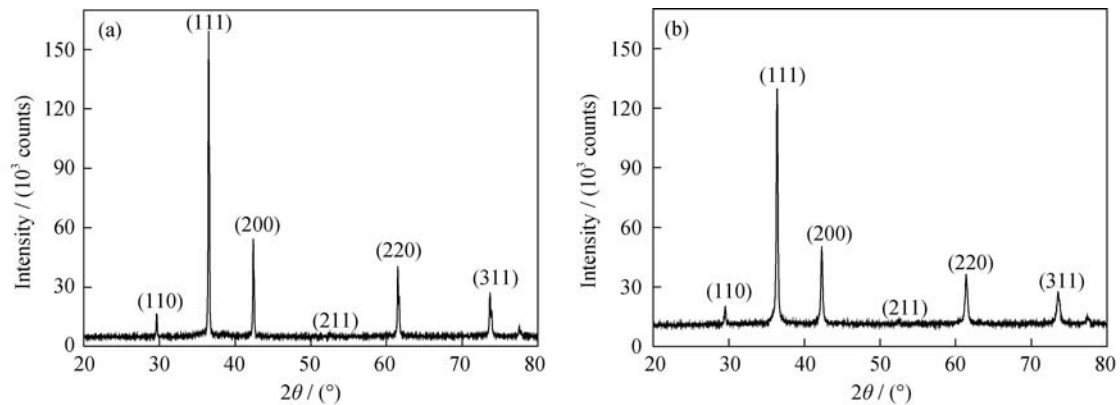


Fig. 4. XRD patterns of Cu_2O particles: (a) uncoated Cu_2O ; (b) coated Cu_2O .

exists in an amorphous form. Comparing Fig. 4(b) with Fig. 4(a), the diffraction peak intensity becomes much weaker after $\text{Mg}(\text{OH})_2$ coating. It can be explained as an effect of $\text{Mg}(\text{OH})_2$ coating.

3.2. Effects of $\text{Mg}(\text{OH})_2$ coating on preventing copper particles from sintering

SEM micrographs of copper particles prepared from the

uncoated Cu_2O particles and $\text{Mg}(\text{OH})_2$ -coated Cu_2O particles are shown in Figs. 5(a) and 5(b), respectively. The products from the uncoated Cu_2O aggregated evidently, while the products from the coated Cu_2O kept the spherical morphology and good dispersibility. The results show that the $\text{Mg}(\text{OH})_2$ coating is effective for avoiding the sintering of copper particles at high temperature.

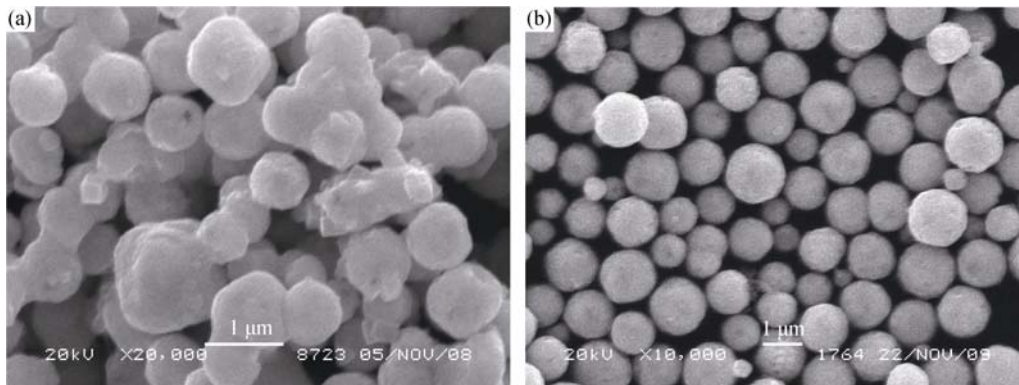


Fig. 5. SEM images of copper particles prepared via hydrogen reduction-densification from different precursors: (a) from uncoated Cu₂O; (b) from coated Cu₂O.

3.3. Effects of densification on performances of copper powder

In order to investigate the effect of densification, the properties of copper powder with and without densification after hydrogen reduction were compared.

3.3.1. Surface character and tap density of copper powder

SEM micrographs of copper powder before and after densification are shown in Figs. 6(a) and 6(b), respectively. The particle surfaces are coarse and porous before densification and become smooth after densification. It means that

pores form when H₂O vaporizes from the particles. The results also show that high-temperature treatment at 500°C is effective for the densification of porous copper particles. At the same time, the tap density of the copper powder increases from 3.30 to 4.18 g/cm³ by virtue of high-temperature treatment.

3.3.2. Crystallinity of copper powder

XRD patterns of copper powder before and after densification are shown in Fig. 7. The diffraction peaks appear at 43.22°, 50.36°, and 74.05° on the XRD patterns of the two

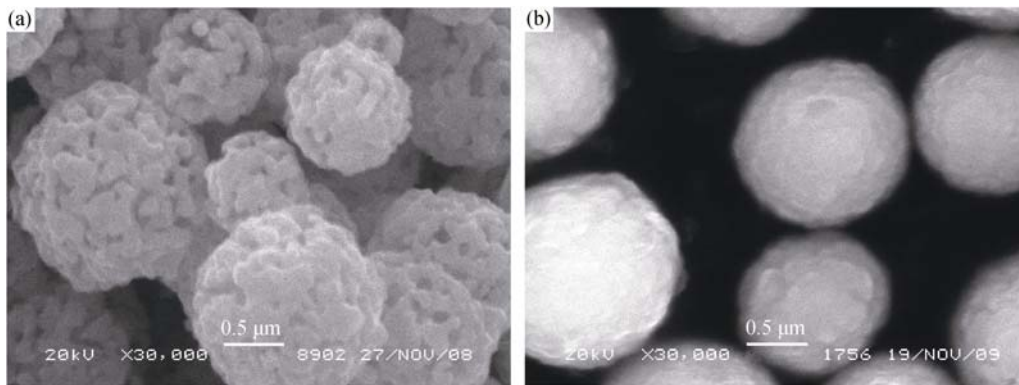


Fig. 6. SEM images of copper particles: (a) before densification; (b) after densification.

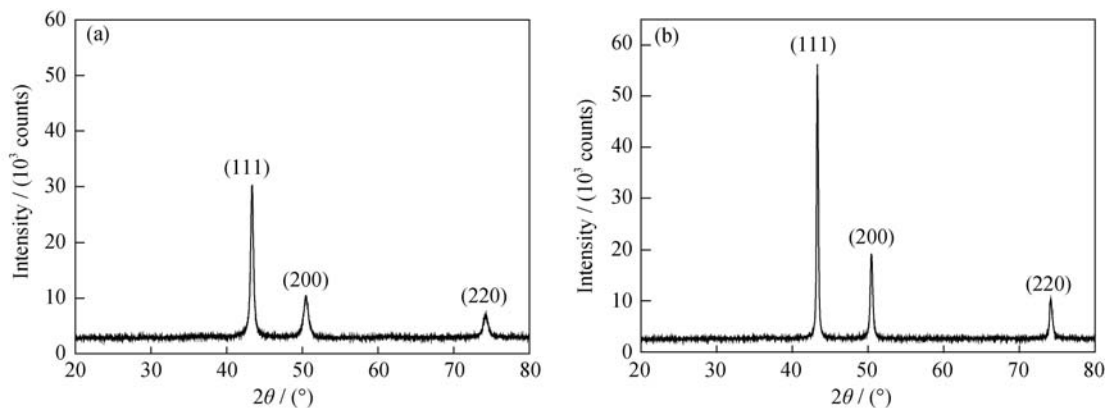


Fig. 7. XRD patterns of copper powder: (a) before densification; (b) after densification.

products and correspond to the (111), (200), and (220) faces of Cu on the standard XRD pattern. Thus, the two products are all pure copper powder. The diffraction peak of copper powder after densification at 500°C is much stronger, which means that the crystallinity of the product after densification is more mature. This is due to the formation of more regular crystal structure in the copper particles that resulted from the movement of copper atoms during densification.

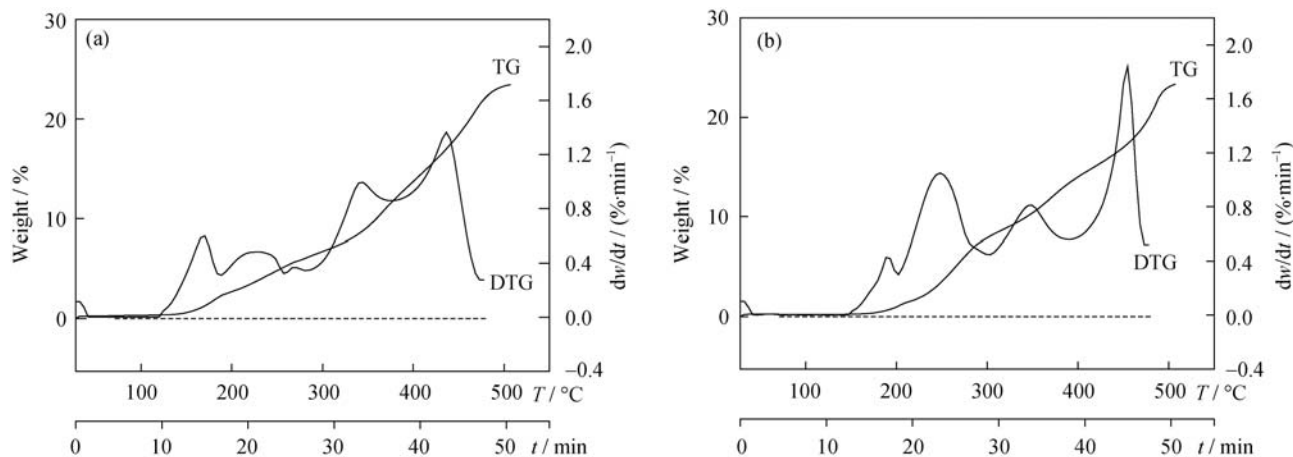


Fig. 8. Thermal analyses of copper powder: (a) before densification; (b) after densification.

4. Conclusions

(1) Ultrafine copper powder prepared via hydrogen reduction of Cu_2O inherits the morphology of the precursor. Thus, the morphology of the copper powder can be conducted through controlling the Cu_2O powder.

(2) The $\text{Mg}(\text{OH})_2$ coating of Cu_2O particles can effectively prevent Cu_2O particles from aggregation at high temperature, and the densification of copper particles by high-temperature heat treatment is feasible.

(3) Through densification at high temperature, the tap density of the copper powder increases from 3.30 to 4.18 g/cm^3 and the initial oxidation temperature rises from 125 to 150°C.

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