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Preparation of micron-sized flake copper powder for base-metal-electrode multi-layer ceramic capacitor

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ARTICLE INFO

Article history:
Received 29 June 2006
Received in revised form
2 March 2008
Accepted 16 March 2008

Keywords:
Micron-sized copper powders
Flake powders
Chemical reduction
Ball milling
BME-MLCCs
Thick films

ABSTRACT

The preparation of flake micron-sized copper powders with the chemical–mechanical method was investigated. Reaction of $[Cu(NH_3)_4]^{2+}$ complex with hydrazine hydrate at 85 °C produced monodispersed fine spherical copper powders, which were used as precursor to synthesize flake copper powders by the ball milling process. The flake copper powders having an excellent dispersibility and a uniform size of 9 ± 2 μm could be achieved. Thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) of the flake copper were investigated with thermal analyzer. The results showed that the oxidizing temperature increased with a decreasing specific area. The flake copper powder particles were employed as functional conductive materials in copper thick film paste for base-metal-electrode multi-layer ceramic capacitors (BME-MLCCs). Excellent connection between internal and terminal electrode and even distribution of glass in copper thick film can be observed by polarized light photograph. The dense thick films were also found by scanning electron microscopy (SEM) analysis, and the high densification of the fired films could be attributed to the "framework" effects.

1. Introduction

Thick film technology was widely used for versatile application. The steady growth of thick film technology has been due to the continual growth of new microelectronic circuit needs and the ability to develop materials to accommodate them. Amongst the various conductive materials, copper has been established as an important choice because of high electrical conductivity, relatively higher melting point, excellent solderability, low electrochemical migration behavior and low materials cost (Wu et al., 2007; Wu, 2007a).

The fired-on type base-metal-based pastes were successfully used in base-metal-electrode multi-layer ceramic capacitors (BME-MLCCs) as demonstrated (Im et al., 2006). In copper-based conductive paste, it is necessary to employ flake copper powders as a supplement to spherical particles for optimizing rheological behavior of paste and improving electrical conductivity of thick film. Either spherical or flake particles, the parameters, such as particle size, shape and distribution, of copper particles are of utmost importance, which have direct bearing on the printing process and, in turn, the microstructure and electrical properties of the resulting films (Rane et al., 2003; Lin and Wang, 1996). For conductive paste application, it is required to use micron-sized non-agglomerated metallic powders (Deshpande et al., 2005; Wu, 2007b). Generally speaking, flake copper powders could be prepared with the two-stage method. Firstly, precursor copper particles were produced by electrolytic method (Xue et al., 2006), pyrolysis (Rosenband and Gany, 2004), atomized process (Karibyan et al., 1981) or chemical-reduction method (Wu,

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doi:10.1016/j.jmatprotec.2008.03.010

2007a; Sinha and Sharma, 2002). Secondly, the spherical copper particles are processed by a high energy ball mill. Precursor particles are extruded by ball milling media, and the flake particles could be achieved.

In the paper, we reported a chemical–mechanical method for the formation of the flake copper particles, which could meet the requirement of copper thick film paste. The behaviors and microstructures of BME-MLCCs made by as-synthesized flake particles were also studied by scanning electron microscopy (SEM) and polarized light photograph.

2. Experimental

2.1. Synthesis of spherical copper powders

All chemicals of reagent grade quality were used without further purification. 1500 ml solution containing 400 g $CuSO4{\cdot}5H_2O$, 200 g NH_4Cl and 900 ml $NH_3{\cdot}H_2O$ was added during 60 min to a stirred hydrazine hydrate ($N_2H_4{\cdot}H_2O$) solution. The temperature was kept at 70 °C. The solution was heated to 85 °C for 1 h to reduce copper ion in the solution to metallic copper.

2.2. Preparation of flake copper powders

Above-mentioned spherical copper powders, ZrO_2 ball milling media and dispersing agent, i.e. sodium dodecyl sulfate, were mixed in a container fixed on a planet-type grinding mill rotating at a rate of 250 rpm for 8–12 h, so that the precursor particles were processed to flake copper particles. The flake copper powders were recovered from the solution, washed and dried under vacuum.

2.3. Fabrication of thick films for BME-MLCC

The thick film pastes were formulated having the composition of as-prepared copper powders as the functional material, $ZnO–SiO_2–B_2O_3$ glass frit as the permanent binder, a mixture of ethyl cellulose and solvent, i.e. ethylene glycol acetate, as a vehicle. The weight ratio of the composition was kept at 65:10:25. The pastes were rolled several times by a three-roll mill and coated on the termination of MLCC chip, whose specification was 0805Y5V, and dried, then, copper end terminations were fired at the peak temperature of 910 °C for 10 min in a nitrogen atmosphere, with a controlled level of oxygen.

2.4. Characterization

The behaviors of powder particles and microstructure of copper thick films were directly observed with the scanning electron microscopy on a XL30δDX-4i (Philips). The crystal structure was characterized by X-ray diffraction (Philips). Thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) were carried out at scanning rates of 10 °C/min in a flowing air atmosphere (Q600, SDT, TA Inc., USA). The purity of powder was determined with inductively coupled plasma spectrometer (ICPS) (PE Optima 3000). The specific areas of powder particles were measured by SA3100 (Beckman Coulter) with Brunauer–Emmett–Teller (BET) method.

The BME-MLCCs were fixed with resin and processed with grinding and polishing machine, and then the connection of internal–terminal electrode and distribution of glass in termination were analyzed with the polarized light microscope (Olympus BX51M). Electrical conductivity of the thick films was measured by the four-point probe method. The bulk resistivity of copper thick film was calculated according to the following equation:

$$\rho = \frac{RS}{L} \quad (1)$$

where R is the resistance measured with four-point technology, S is the area of cross-section of thick film estimated by SEM analysis and L is the length. The adhesion strength of electrode was determined with FDV-50 force apparatus (Wagner Instruments, USA). Resistance behavior of termination of BME-MLCCs to soldering was tested by immerging termination of MLCCs in solder at 260 ± 5 °C for 5 s.

3. Results and discussion

3.1. Synthesis of spherical and flake copper powders

In this work, spherical copper particles were obtained by reaction of $[Cu(NH_3)_4]^{2+}$ complex with hydrazine hydrate in ammonia chloride solution. In this process, the following chemical reaction occurred:

$$Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4{}^{2+} \quad (2)$$

$$2[Cu(NH_3)_4]^{2+} + N_2H_4 \rightarrow 2Cu + N_2 + 4NH_3 + 4NH_4{}^{+} \quad (3)$$

In aqueous ammonia media, ammonia reacts with Cu^{2+} according to Eq. (2) and $[Cu(NH_3)_4]^{2+}$ complex was reduced to obtain fine copper powder as seen in Eq. (3). It was obvious that Eq. (3) occurred in basic solution. If pH value was low, reaction could not occur smoothly. Ammonia chloride/aqueous ammonia buffer was employed to keep constant pH values at 8–8.5, in where the dispersability of powder particles increased.

It was very important to choose appropriate dispersion agent for preparing fine metallic particles with chemical-reduction method. Dispersion agent could effectively control particle size and dispersability according to electrostatic repulsion effect, space hindrance effect and interfacial tension effect. We could distinctly find out that the micron-sized monodispersed non-agglomerated single spherical copper particles have been synthesized when sodium tartrate was employed as an inorganic dispersing agent. In an optimal condition, as-synthesized particles have an excellent dispersability and uniform single particle size of 3.5 ± 0.5 μm by SEM analysis as given in Fig. 1a.

By ball milling precursor spherical copper powders, the thin flake copper particles with a uniform size of 9 ± 2 μm were formed as shown in Fig. 1b. The powder particles have a uniform size, less specific area and suitable ratio of diameter–thickness. By size distribution analysis, one could see that the powder particles have an excellent dispersabil-