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Characteristics of $ZnO–B_2O_3–SiO_2–CaO$ glass frits prepared by spray pyrolysis as inorganic binder for Cu electrode

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ABSTRACT

$ZnO–B_2O_3–SiO_2–CaO$ glass frits were directly prepared by high temperature spray pyrolysis for use in Cu electrodes. The frits prepared at temperatures above 1400 °C were spherical, amorphous, of fine size and dense structure. The mean particle size and geometric standard deviation of the frits prepared at 1400 °C were 0.87 μm and 1.37, respectively. The temperatures of glass transition, crystallization and melting were 454, 534 and 800 °C, respectively. The glass layer fired at 800 °C had a dense structure due to the material's complete melting, despite some crystals being observed by SEM. A copper electrode formed from copper paste with glass frits had a dense structure when fired at 800 °C. The specific resistances of electrodes formed from copper paste with and without glass frits were 2.5 and 8.5 μΩ cm, respectively.

1. Introduction

The development of small, high-capacity multilayer ceramic capacitors (MLCCs) forms part of the overall enhancement of electronic devices [1]. For this, both dielectric and inner electrode layers are required to be extremely thin. The termination electrode is also important in small, high-capacity MLCCs [1–3]. Copper terminations are usually formed from paste comprising copper powder, glass frits and organic binder. Thin terminations can be achieved through careful control of the copper powder and glass frits' properties, with each required to be fine [2].

Fine copper powders produced by physical and chemical methods have been applied in the electrodes of MLCCs [4–7]. The effects of the copper powder's morphology and mean particle size on the formation of Cu terminations have been well-studied [2]. Glass frits prepared by conventional melting have been used as inorganic binder for Cu terminations [2]. Glass flakes formed by quenching melted glass were ground by various milling processes to obtain the glass frits. The frits' mean size could be decreased to submicron by high-energy milling. However, milling did not allow tight control of the frits' morphologies and size. In addition, wet milling for fine sizes changed the frits' composition by leaching some of the glass's components into the milling solution. Lee et al. studied the effect of frits' mean size on the formation of end termination electrodes [2]. Smaller frits showed many merits over larger ones, such as better dispersion, improved corner coverage and surface roughness, and allowing low-temperature sintering.

Spray pyrolysis is a promising process, adapted for the fabrication of improved ceramic, and metal powders [8–11]. In previous studies, spray pyrolysis has been applied to the preparation of fine glass powders [12–19]. During spray pyrolysis each glass particle is formed from one droplet by complete melting and quenching process. Therefore, glass frits prepared by spray pyrolysis are relatively uniform in size and composition, spherical, fine-sized, and are less aggregated because of the microscale reactions within droplets. Glass frits prepared by spray pyrolysis had suitable characteristics for inorganic binders of Ag and Al electrodes [16–19]. However, glass frits with appropriate compositions for Cu electrodes prepared by spray pyrolysis have not been reported.

In this study, $ZnO–B_2O_3–SiO_2–CaO$ glass frits for Cu electrodes were directly prepared by high-temperature spray pyrolysis and investigated. The optimum spray pyrolysis conditions for the preparation of amorphous glass frits of fine size and dense structure were investigated. Fine Cu powders with spherical particles were prepared by spray pyrolysis and used as electrodes.

2. Experimental

The spray pyrolysis equipment used consisted of six ultrasonic spray generators that operated at 1.7 MHz, a 1000-mm-long tubular alumina reactor of 50-mm ID, and a bag filter. $ZnO–B_2O_3–SiO_2–CaO$ glass powders with small amounts of Na_2O and K_2O were directly prepared by spray pyrolysis. The preparation temperatures were changed from 1000 to 1400 °C. The flow rate of air used as the carrier gas was fixed to 20 L min^{-1}. The spray solutions were obtained by adding ZnO (Kanto, 99%), H_3BO_3 (Kanto, 99.5%), tetraethyl orthosilicate (TEOS, Aldrich, 98%), $Ca(NO_3)_2·4H_2O$ (Junsei, 98%), Na_2CO_3 (Aldrich, 99%), and K_2CO_3 (Junsei, 99%) to distilled water. The overall solution concentration of metal components composing the glass powders

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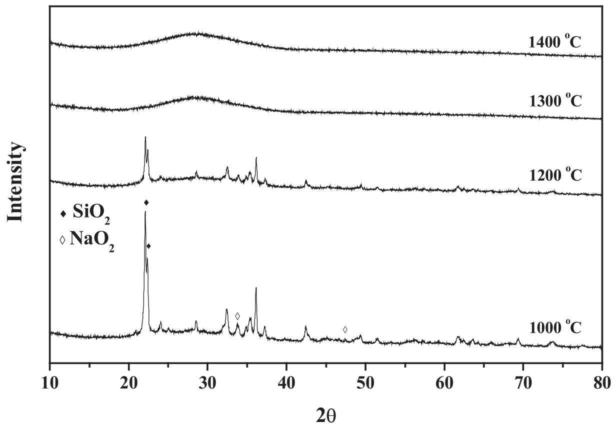


Fig. 1. XRD patterns of the powders prepared by spray pyrolysis at various temperatures.

was fixed at 0.5 M. Copper powders were directly prepared by spray pyrolysis from the cupric nitrate solution of 0.1 M at 800 °C. The flow rate of 10% H_2/N_2 mixed gas used as the carrier gas was fixed at 10 L min^{-1}.

Cu electrodes were fabricated by firing a printed layer formed by screen-printing using Cu paste containing Cu powders, glass frits and a resin binder. To obtain the paste, the Cu powders and glass frits prepared by spray pyrolysis were mixed with an organic vehicle consisting of ethyl cellulose, α-terpineol, and butyl carbitol acetate (BCA). The glass content was fixed at 3 wt% of Cu metal. Cu paste was screen-printed onto the alumina substrate. The printed alumina substrate was dried at 120 °C for 30 min. The screen-printed alumina substrates were fired at a temperature of 800 °C for 10 min at a heating rate of 7 °C/min.

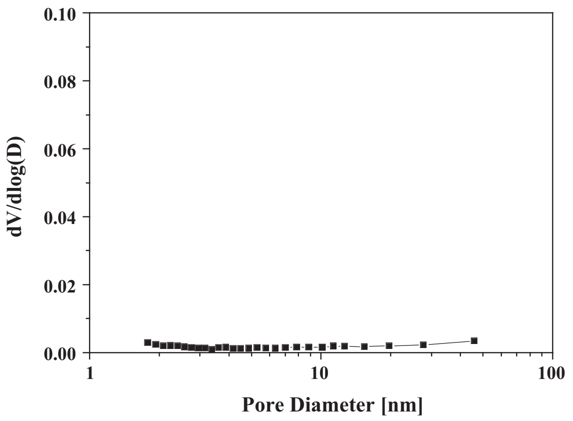
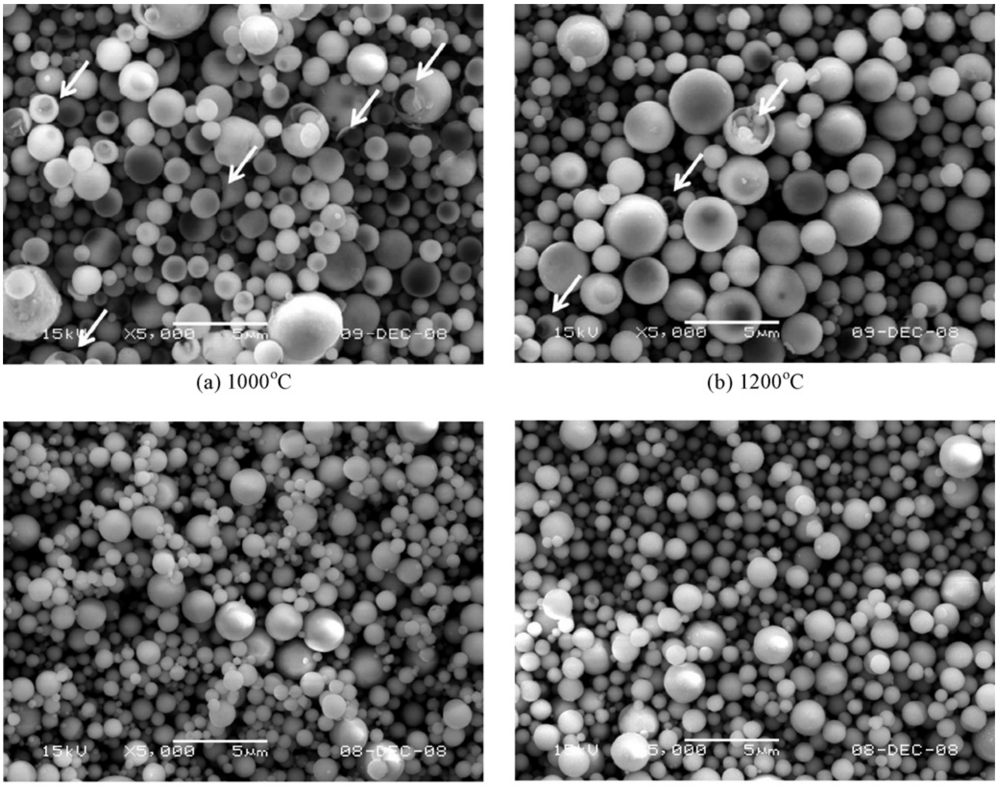


Fig. 3. Pore size distribution of the glass frits prepared by spray pyrolysis.

The crystal structures of the prepared Cu powders and glass frits were investigated by X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation (λ = 1.5418 Å). Measurement of the thermal properties of the prepared glass powders was performed on a thermo-analyzer (TG-DSC, Netzsch, STA409C, Germany) in the temperature range from 40 to 800 °C (10 °C/min). The morphological characteristics of the prepared Cu powders and glass frits were investigated by scanning electron microscopy (SEM, JEOL, JSM-6060). The sheet resistances of the Cu electrodes were measured using four point probe method (CMT-SR 1000N, Advanced Instrument Technology).

3. Results and discussion

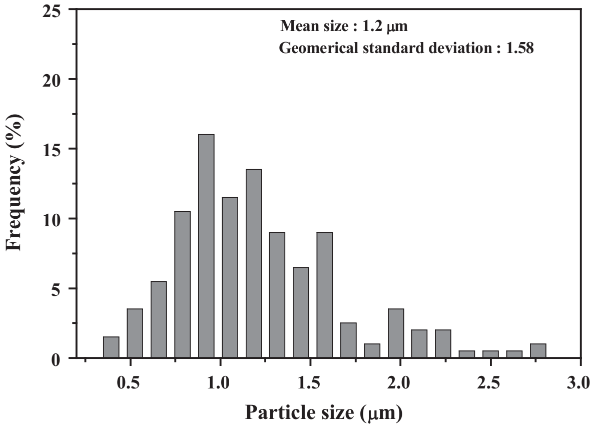
The formation of amorphous glass frits by spray pyrolysis is strongly affected by the preparation temperature, as each particle is formed from one droplet during a short residence inside the hot wall reactor. Complete melting of the glass components should occur for frits to form through melting and quenching. The morphologies of the glass frits prepared by spray pyrolysis were also affected by the preparation temperature; and conversely, the optimum preparation temperature for spherical, amorphous, dense frits was affected by the composition of the glass. Fig. 1 shows XRD patterns of ZnO–B_2O_3–SiO_2–CaO powders prepared by spray pyrol-



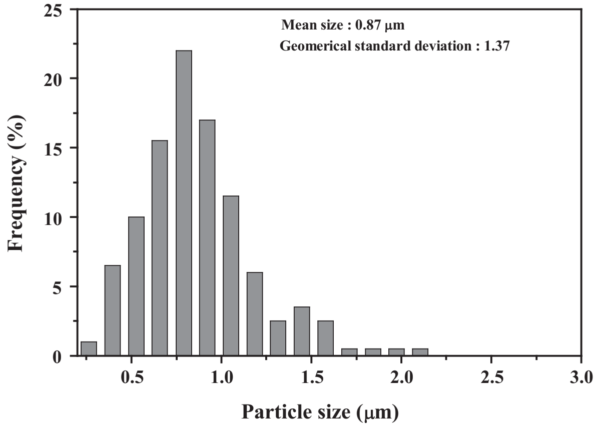
(a) 1000°C (b) 1200°C

(c) 1300°C (d) 1400°C

Fig. 2. SEM images of the powders prepared by spray pyrolysis at various temperatures.



(a) 1000°C



(b) 1400°C

Fig. 4. Size distributions of the powders prepared by spray pyrolysis at various temperatures.

ysis at various temperatures. The powders prepared below 1200 °C had crystal peaks of SiO_2, NaO_2, etc. However, the powders prepared above 1300 °C showed broad peaks at *ca.* 28°, characteristic of glasses.

Fig. 2 shows the morphologies of powders prepared at various temperatures. Those prepared below 1200 °C had spherical, hollow particles. The powders did not melt below 1200 °C and exhibited the crystal structures shown in Fig. 1. The glass frits prepared above 1300 °C were fine, spherical and dense. Fig. 3 shows the pore size distribution of the glass frits analyzed by the Barrett–Joyner–Halenda (BJH) method. Dense glass frits comprising particles with a small pore volume of $4 \times 10^{-9}\,m^3\,g^{-1}$ were prepared by spray pyrolysis at 1400 °C. The BET surface area of the glass frits was $2.0\,m^2\,g^{-1}$.

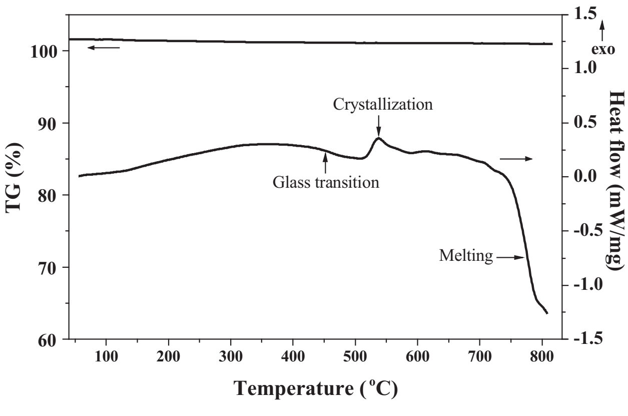
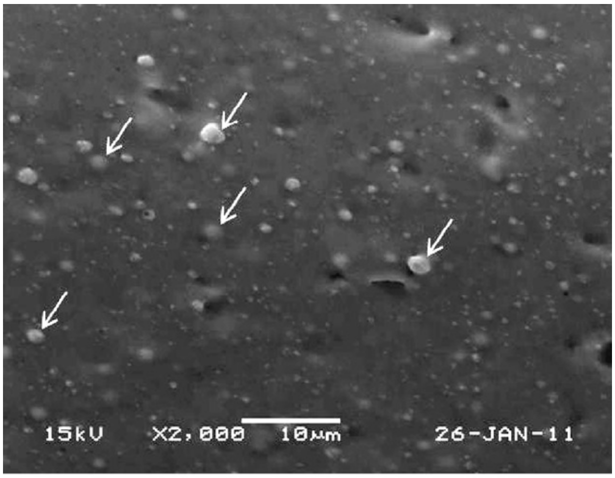
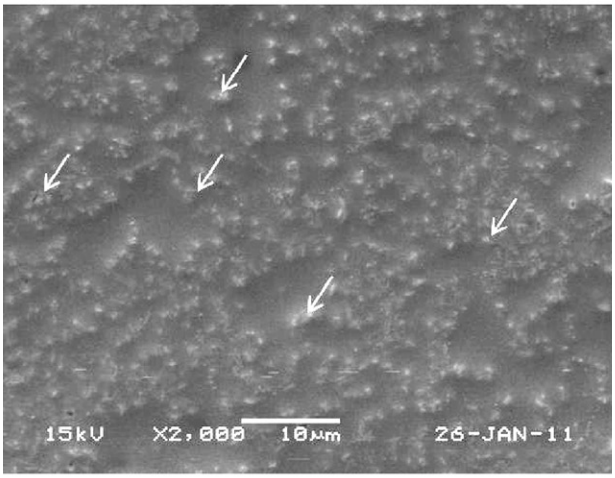


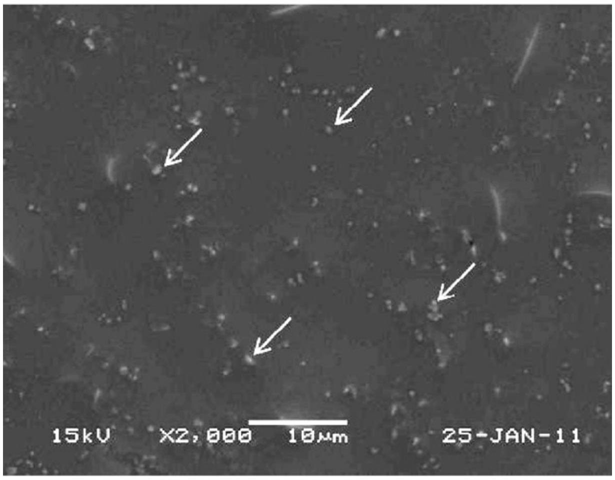
Fig. 5. TG-DSC curves of the glass frits prepared by spray pyrolysis.



(a) 600°C



(b) 700°C



(c) 800°C

Fig. 6. SEM images of the surfaces of the glass layers fired at various temperatures.

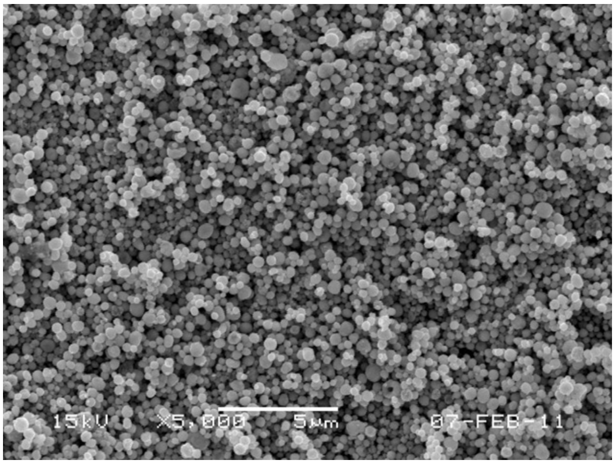


Fig. 7. SEM image of the copper powders prepared by spray pyrolysis.

The frits' mean sizes were determined from the SEM images by sampling at least 500 particles in each sample. Fig. 4 shows particle size distributions of the powders prepared at 1000 and 1400 °C. The mean size and geometric standard deviation of the particles prepared at 1000 °C were 1.2 μm and 1.58, respectively compared with 0.87 μm and 1.37, respectively, for the frits prepared at 1400 °C. Complete melting of the powder resulted in finer frits with a narrower size distribution.

Fig. 5 shows TG-DSC curves of the glass powder prepared at 1400 °C. Weight loss did not occur below 800 °C, as complete decomposition of the precursor metal salts occurred during preparation at 1400 °C. The frits' glass transition (T_g) was observed at 454 °C in the DSC curve. The small exothermic crystallization peak (T_c), where molecules obtained enough freedom of motion to arrange spontaneously into crystals, was observed at 534 °C. The frits melted (T_m) at 800 °C.

The frits' melting was also investigated. Frits prepared at 1400 °C were mixed with an organic vehicle consisting of ethyl cellulose, α-terpineol, and butyl carbitol acetate (BCA). The glass paste was screen-printed onto Si substrates, which were dried at 120 °C for 30 min and fired at between 600 and 800 °C for 10 min at a heating rate of 7 °C/min. Fig. 6 shows SEM images of the surfaces of the glass layers fired at various temperatures. Partial melting was observed at 600 °C, where some of the frits maintained their spherical shapes (arrows in Fig. 6(a)). Complete melting of the frits occurred at 700 °C, with no remaining spherical frits observable. Partial crystallization of the glass layer occurred at 700 °C (arrows in Fig. 6(b)). The glass layer fired at 800 °C had a dense structure due to complete melting, despite some crystals being observable in the SEM image. The melting of the glass frits in Fig. 6 corroborates the DSC results of Fig. 5.

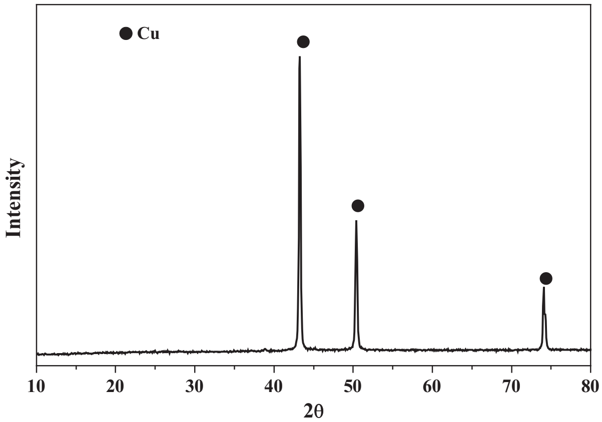
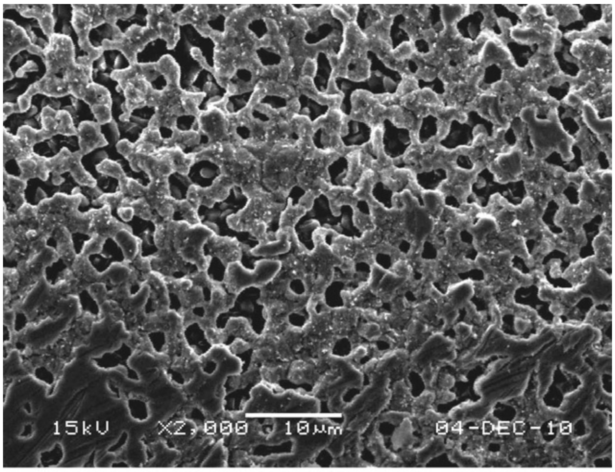
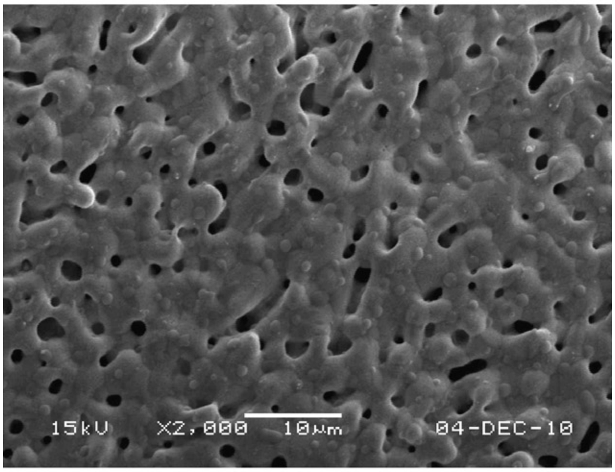


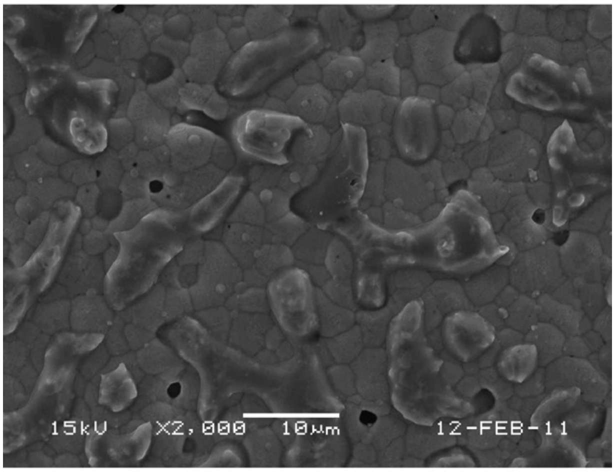
Fig. 8. XRD pattern of the copper powders prepared by spray pyrolysis.



(a) No glass

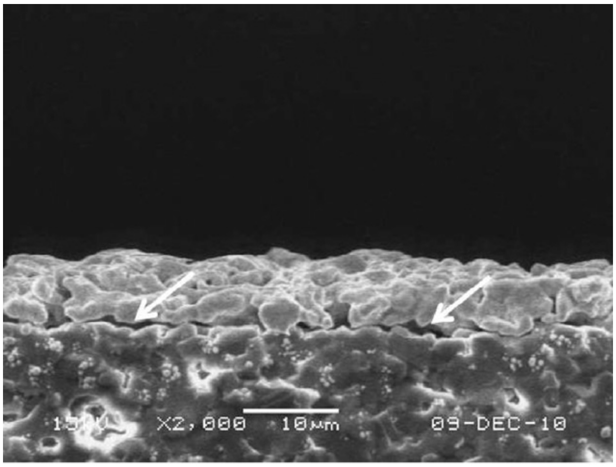


(b) 3 wt% glass

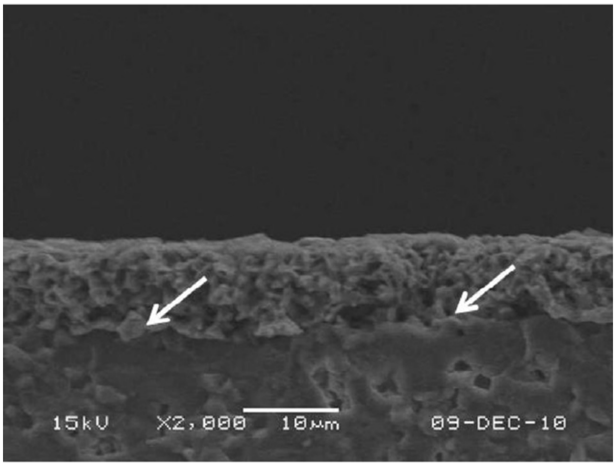


(c) 8 wt% glass

Fig. 9. SEM images of the surfaces of the Cu electrodes formed from the copper paste with and without glass frits.



(a) No glass



(b) 8 wt% glass

Fig. 10. SEM images of the cross-sections of the Cu electrodes formed from the copper pastes with and without glass frits.

The morphologies and crystal structure of the copper powders prepared by spray pyrolysis are shown in Figs. 7 and 8. The powders had pure Cu crystal structure. The particles were spherical and not aggregated because each particle was formed from a single droplet in the gas-phase reaction. The mean particle size of the Cu powder measured from the SEM image was 0.37 µm. The effects of $ZnO–B_2O_3–SiO_2–CaO$ glass frits as an inorganic additive on the sintering of copper electrodes was investigated. The glass was added to the copper paste at 3 and 8 wt% of the copper powder. Fig. 9 shows SEM images of copper electrodes formed from copper pastes with and without glass frits when fired at 800 °C. The electrode formed with frits had a denser structure than that formed without. Fig. 10 shows the SEM images of the cross-sections of the Cu electrodes formed from the copper pastes with and without glass frits. The Cu electrode formed from the paste with glass frits had good adhesion property to the alumina substrate due to the glass frits. On the other hand, the Cu electrode formed from the paste without glass frits had poor adhesion property to the substrate as shown by arrows in Fig. 10(a).

The specific resistance of Cu electrode without frits was 8.5 µΩ cm. However, the specific resistances of the Cu electrodes with 3 and 8 wt% frits were 2.5 and 5.9 µΩ cm, respectively. The glass frits improved the sintering characteristics of the copper electrode, allowing the formation of an electrode with a dense structure and low specific resistance when fired at 800 °C.

4. Conclusions

$ZnO–B_2O_3–SiO_2–CaO$ glass frits prepared by spray pyrolysis were investigated for use as an inorganic binder in Cu electrodes. Glass frits were spherical, dense and amorphous when prepared by spray pyrolysis at 1400 °C. Spray pyrolysis formed each glass particle from a single droplet of spray solution. The fine-sized glass frits improved the sintering characteristics of the copper electrode, resulting in an electrode with a dense structure and low specific resistance when fired at 800 °C.

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