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Preparation and properties of borosilicate glass-coated Cu powder for internal electrode of multilayer ceramic device

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Abstract In this study, a process was proposed which allows a base metal electrode to be burnt-out in an oxidative atmosphere for fabrication of multilayer ceramic device. To protect Cu in an oxidative atmosphere, the Cu powder was coated with borosilicate glass via a sol-gel process. The oxidation resistance and shrinkage of the glass-coated Cu were investigated. When a 10% glass-coated Cu was heated up to 500°C under an oxidative atmosphere, the Cu could survive without formation of copper oxide. The oxidation of the Cu was observed when heating at temperatures above 700°C. This might be due to exposure of Cu to oxidative atmosphere related to softening behavior of glass. The glass-coated Cu exhibited a shrinkage behavior which follows the shrinkage behavior of glass in the low temperature range and the shrinkage of pure Cu in the high temperature range. To measure the electrical conductivity of the glass-coated Cu electrode, the Cu pastes were prepared and printed onto alumina substrate. The binder-burn-out process of the glass-coated Cu was carried out at 550°C under an air atmosphere, and was then sintered at 1000°C under a nitrogen atmosphere. The electrical conductivity of the Cu electrode measured was above 10^4 /Ωcm which means that it can be used as the internal electrode of a multilayer device.

Keywords Internal electrode · Copper powder · Glass coating · Sintering · Electrical conductivity

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1 Introduction

Multilayer ceramic devices (MCDs) are composed of dielectric layers, interleaved inner electrodes, and outer termination electrodes. The internal electrode of MCDs has changed from traditional noble metals and alloys, such as palladium or silver-palladium, to base metal electrode, such as copper and nickel [1–3]. However, there are two serious problems in use of base metal as an electrode material, which are a large sintering mismatch and oxidation of the base metal. The large sintering mismatch between electrode and ceramic layers was reduced by adding the small amount of ceramic powders into electrode. This has been widely used in the fabrication of MCDs despite the slight degradation of electrical conductivity in the electrode. In oxidation problem, base metal is easily oxidized under the oxidative atmosphere during co-firing. For this reason, the synthesis of defect-free MCDs under a reducing atmosphere has received considerable attention [4, 5].

The base metal particles react easily with oxygen in air even at room temperature and form an oxide phase on the surface, which has an undesirable effect on usage. To suppress the reaction of base metal with oxygen, the devices are cofired in a reducing atmosphere. During this co-firing, there are many vacancy-oxygen reactions and ionic exchange between the dielectric and metal. This requires several post processing including the formulations with the co-doping of acceptors and amphoteric cations, and the firing conditions and a second reoxidation step at low temperatures. The reoxidation step reduces the concentration of oxygen vacancies and aids optimization of the Schottky barriers at the grain boundaries. However, in such process a volumetric change occurs, resulting in cracking of the multilayer device. Consequently, in order to prevent the reaction between oxygen and base

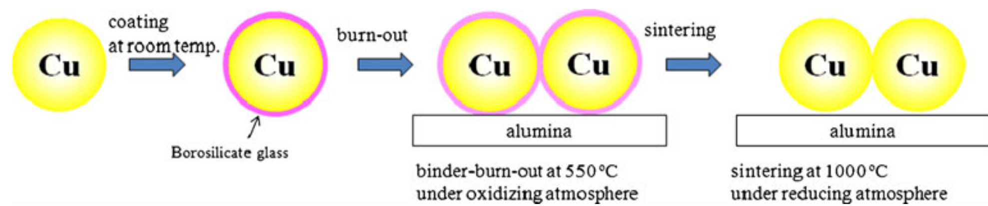


Fig. 1 Schematic illustration of binder burn-out and sintering of glass-coated Cu electrode printed on alumina substrate

metals, several techniques have been proposed including protective oxide layer coatings on the base metal powder by conventional sol-gel process and hydrothermal methods [3, 6–8]. A novel method was proposed [3] to improve the sintering and the oxidation resistances of Ni particles for the internal electrode of multilayer ceramic capacitors by the homogeneous coating of Ni powder with $BaTiO_3$ through the sol-gel method. The $BaTiO_3$ layer plays an important role in preventing the oxidation of Ni particles during sintering.

Although several investigations have shown that the resistance to the oxidation and sintering of Ni powder was greatly improved by coating the surface with $BaTiO_3$, the nanometer thick surface coating of $BaTiO_3$ is easily prone to breaking during the formulation of the paste and subsequent screen-printing. Consequently, the coating processes are less effective in co-firing processes at oxidative atmosphere. Instead, special isolation and passivation techniques for the metal powders are required for co-firing of electrode paste at oxidative atmosphere. As a solution to the isolation of a base metal from oxidative atmosphere, this study proposed the use of a submicron-sized base metal powder with a coating of glass prepared by a sol-gel process. Conventionally, conducting metal, glass frit and inorganic vehicle are prepared to fabricate conductor paste. In this case, instead of using the glass frit for the paste, the glass was coated on the surface of the metal particles. The base metal powder is protected from oxidation during the co-firing under an oxidative atmosphere. The schematic illustration of our proposed cofiring of glass-coated Cu is shown in Fig. 1.

In this study, we propose a novel method to improve the oxidation resistances of Cu particles for internal electrode of MLDs by the homogeneous coating of Cu powder with borosilicate glass using a sol-gel method. The glass layer plays an important role in preventing both contacting and oxidation of Cu particles during binder-burn-out and sintering. The Cu powder was coated with borosilicate glass via the sol-gel process. The oxidation resistance and shrinkage behavior of the glass-coated Cu were examined. The shrinkage characteristics of the electrodes were described. The pastes consisting of the glass-coated powder and other conventional organic vehicles were prepared to evaluate their electrical conductivity.

Table 1 Organic materials for glass preparation

$Si(OC_2H_5)_4$ (ml)	$B(OCH_3)_3$ (ml)	H_2O (ml)	C_2H_5OH (ml)
153.7	25.6	53.2	10.0

2 Experimental setup

$Si(OC_2H_5)_4$ $B(OCH_3)_3$, H_2O, CH_3OH were used as the starting materials. Table 1 shows the quantities of materials used to prepare the gels [9, 10]. $Si(OC_2H_5)_4$ was initially hydrolyzed with a mixed solution of 40% ethanol and 60% water (0.15 mol/liter HCl solution). Then, the solution was stirred at 70°C for 15 h. Second hydrolysis process was performed by mixing of the solution with tributhyl borate. The solution was then mixed with Cu powders (Alfar Aesar Co. 41205). The final solutions were condensed by drying them at 90°C for 12 h. The sol-gel solution chosen was

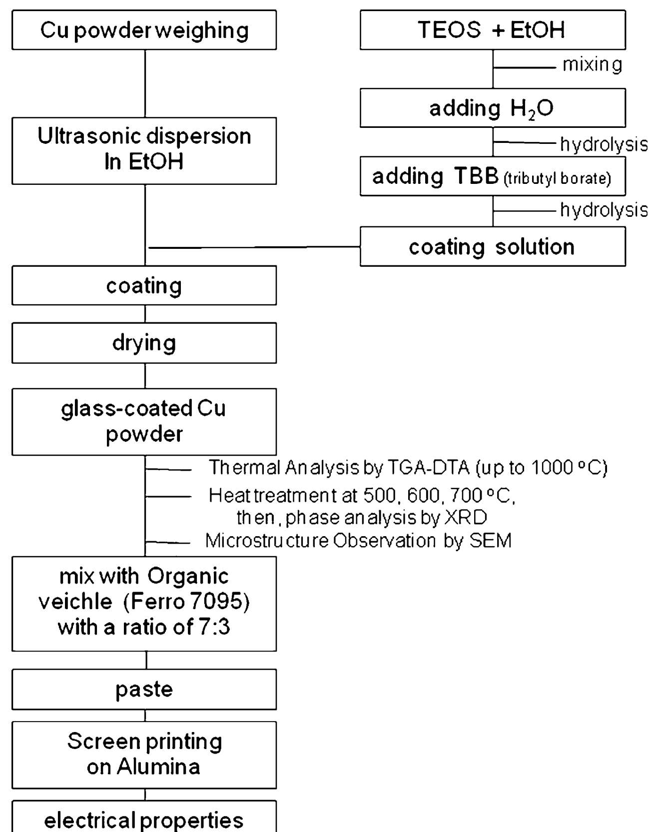


Fig. 2 Experimental procedure of SiO_2-B_2O_3 glass and the glass-coated Cu powder fabrication by a sol-gel route

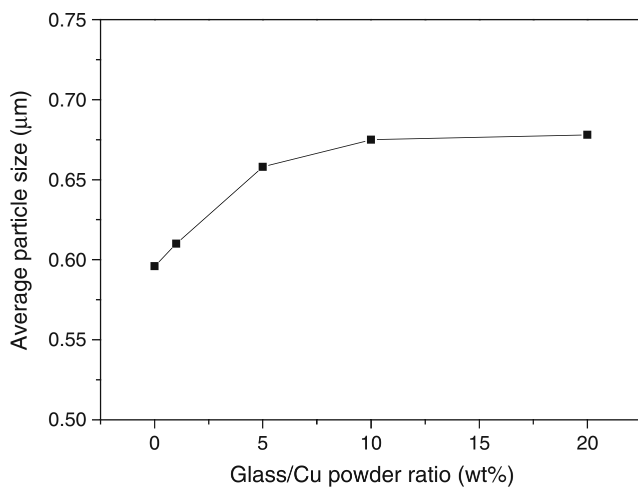
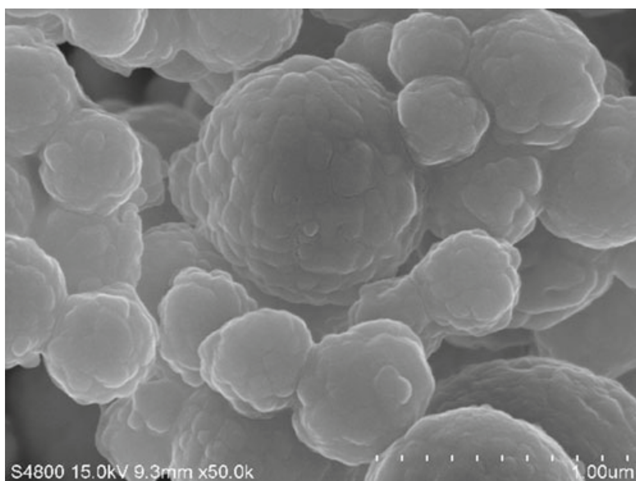
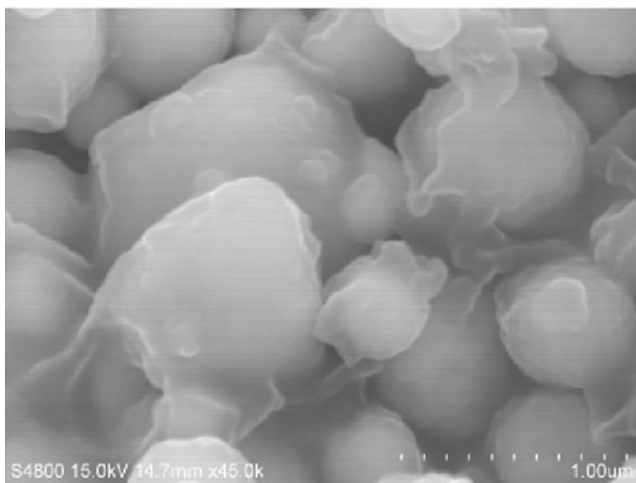


Fig. 3 Average particle size for glass-coated Cu powder as a function of glass/Cu ratio



(a) As-received Cu powder



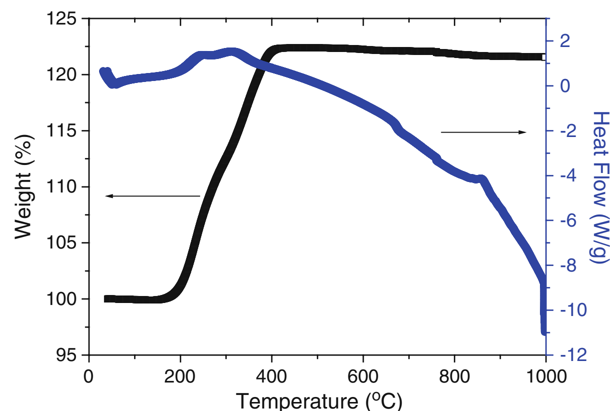
(b) 10% SiO_2:B_2O_3-based glass-coated Cu powders

Fig. 4 Scanning electron images of as-received and glass-coated Cu powders

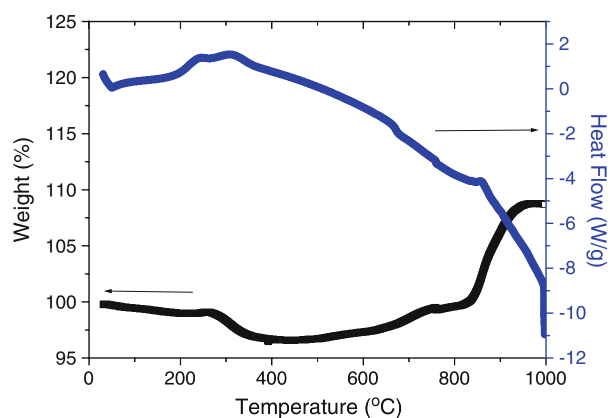
SiO_2:B_2O_3=3:2. The ratio of silicate to borate was chosen to obtain melting point near 1000°C and a glass softening point at about 680°C. The relative ratios of glass/Cu were in the range 2–20 wt%.

The coating of glass to the surface of Cu powders, the experimental procedure regarding analysis of the glass-coated powders and their paste preparation are shown in

(a) As-received Cu



(b) 10% glass-coated Cu



(c) SiO_2-B_2O_3 glass

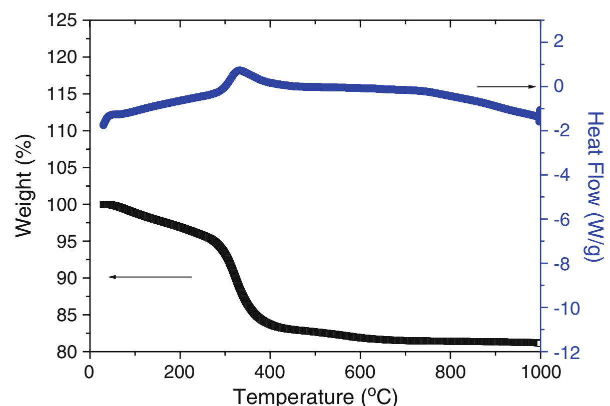


Fig. 5 TGA and DTA of SiO_2-B_2O_3 glass, as-received and glass-coated Cu powder

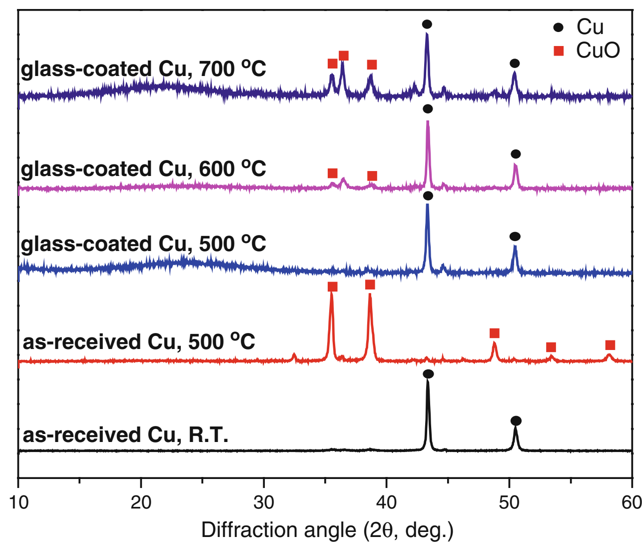


Fig. 6 X-ray diffraction patterns of as-received and glass-coated Cu powders heat-treated at 500°C, 600°C, and 700°C

Fig. 2. The powder morphology was observed by a scanning electron microscope (JEOL JEM2010, at an accelerating voltage of 15 kV). The thermal gravimetric analysis (TGA) and differential thermal analysis (DTA, SDT Q600 TA instruments) were performed in air for the powder specimens to evaluate the oxidation resistance. After the powders were heat-treated at 500°C, 600°C, and 700°C under an air flow, the crystal structures of the powders were identified with a powder X-ray diffractometer (XRD, 200 Philips Co.). The compacts were then fabricated by pressing the powders in a hand–press (Carver Co. model C). The sintering characteristics of the compacts were measured in nitrogen atmosphere at a heating rate of 5°C/min using a thermomechanical analyzer (TMA Q400, TA Instruments).

Paste was fabricated by mixing the coated Cu power with a commercial organic vehicle (ferro 7095). The paste was screen-printed onto alumina substrate, and then burn out at 550°C for 1 h under air atmosphere followed by sintering at 1000°C under nitrogen atmosphere. Their electric conductivity was measured by a four probe method.

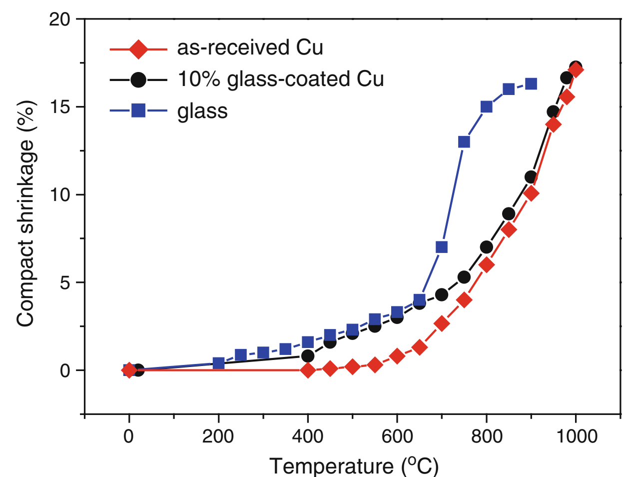
3 Results and discussion

3.1 Glass-coated Cu powders

Figure 3 shows the average size of the particle of coated powder as a function of the glass/Cu ratio. The average size increases with increasing the ratio up to 10%, and then is, to a measurable extent, constant at higher ratios. This result indicates that the coating of glass on Cu powder is effective at the ratio of 10%. Figure 4 shows the microstructures of glass-coated Cu powders. Cu has smooth surfaces and a spherical shape. As shown in Fig. 4, the glass is coated onto Cu particles. The thickness of the glass layer on the Cu partcles is approximately 0.02–0.05 μm. As the coating becomes saturated at 10% glass addition, the oxidation resistance and other characteristics were observed on a specimen with 10% added glass.

3.2 Oxidation and sintering behaviors of glass-Cu

Typical results of TGA and DTA measurements on glass-coated powders are shown in Fig. 5. For comparsion, as-received Cu powder and glass were also analyzed by keeping them heated up to 1000°C. All tests were performed at air atmosphere. In the curve of as-received Cu, the weight gains were observed at 200°C, which



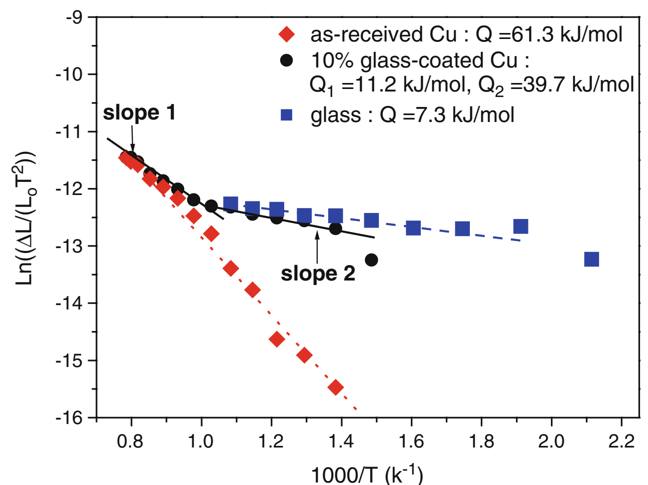


Fig. 7 Shrinkage and kinetic behaviour of as-received and glass-coated copper electrode specimen

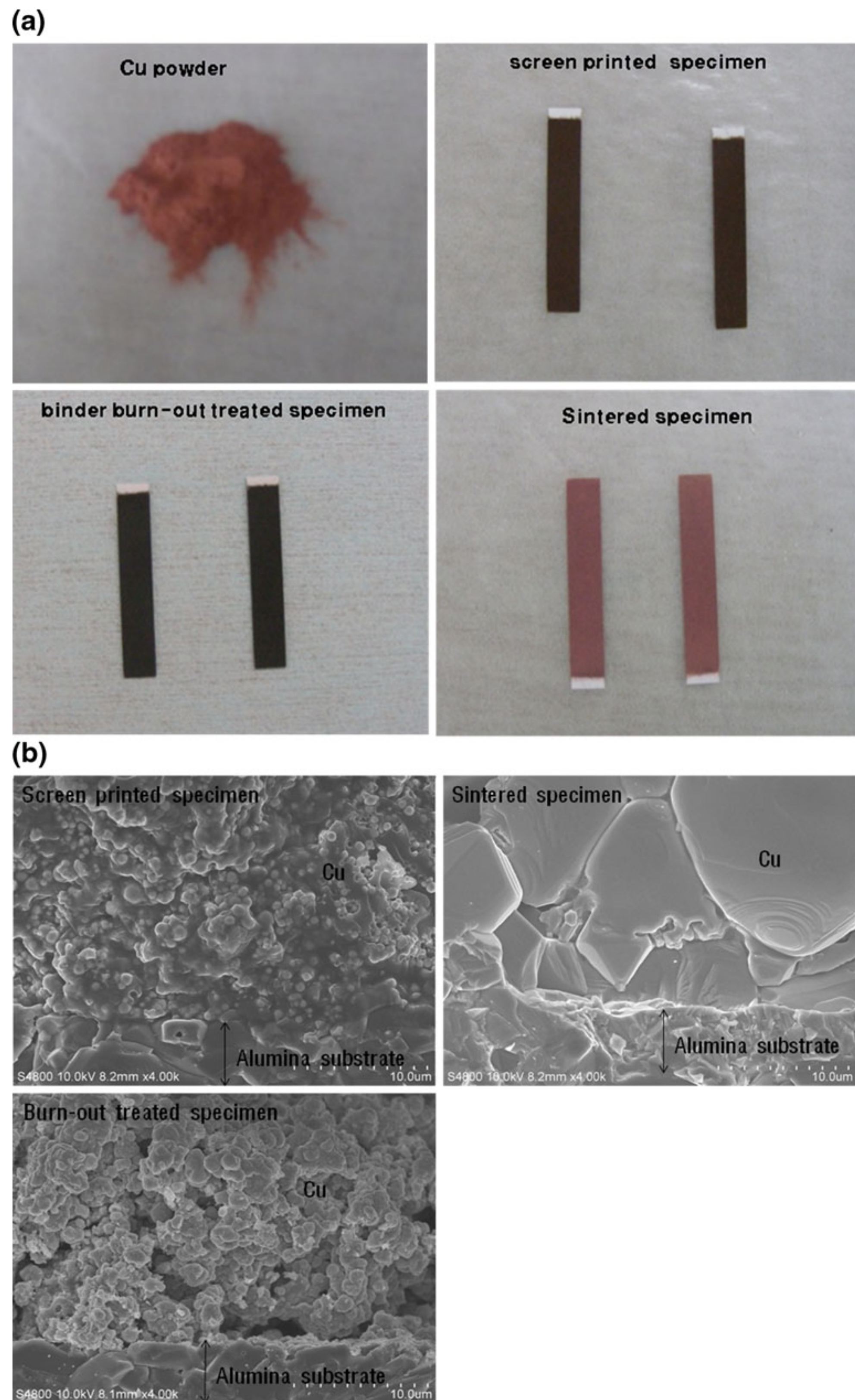


Fig. 8 Overview images showing (**a**) Cu powder, printed Cu paste on alumina, binder-burn-out treated and sintered Cu electrode, and (**b**) scanning electron micrographes showing cross section of printed specimen, binder burn-out treated and sintered Cu eletrodes

indicates that the Cu particles react with oxygen, resulting in the formation of copper oxide. On the other hand, weight loss starts to 200°C and finishes at 400°C for the 10% glass-coated Cu powder. The same weight loss was also observed in as-recevied glass case as shown in Fig. 5(c). The weight loss may be due to the evaporation of inorganic

residuals formed during the sol-gel process. The weight remains constant in the glass-coated Cu powder up to temperatures above 600°C. At temperatures above 600°C, the coated Cu powder experiences weight gain, which is indicative of oxidation of the Cu powder. The oxidation reaction of Cu may be retarded by the presence of the protective glass layer on the powders. This possiblity can be shown in phase identification of XRD experiments.

The XRDs of the Cu powder are shown in Fig. 6. Figures 6(a) and (b) are for as-received and 500°C-heated Cu powders, respectively. For Cu specimen heated at 500°C, the peaks representing CuO are shown in Fig. 6 (b). This indicates that Cu could be fully oxidated upon heating at even 500°C. On the other hand , as shown in Fig. 4(d), there are no peaks of CuO for 500°C-heated Cu powder with glass-coating. However, when the heat-treatment temperrature is above 700°C, the Cu peaks shrank and less CuO was present, becase the glass softens near 700°C. When the sample was heated above 700°C, the glass softens and the Cu can be exposed to oxidative atmosphere. This results in the formation of copper oxide. Similar behavior has been reported in many investigations of metallization with conductor paste [11–15]. When the condcutor paste is heat-treated at temperatures above the glass softening point, the glass frit experiences wetting on the substrate and then penetrates inside the conductor. The glass has a pillar structure at the interface between substate and conductor [11–14]. In a similar manner, on heating at temperatures above softening point, the Cu particle was expected to transform into CuO.

Figure 7 shows the linear shrinkage profiles of the as-received and 10%-coated Cu compacts, respectively, and the profile for the only glass case. There are three important aspects of the sintering process which need to be considered when investigating the sintering behavior of the electrodes and the glass. These are (i) the original sintering temperature, (ii) the initial and final sintering temperatures, (iii) the total shrinkage of the material during sintering. The densification of the as-received Cu compact takes place at temperatures from 600 to 1000°C, while the glass densifies at 400–800°C. There is also a shrinkage mismatch between the two materials, which results in the formation of interfacial stresses and warping deformations [12]. If the SiO_2-B_2O_3 glass is coated on the Cu powder, however, it can be seen that the sintering behavior of the electrode is modified. The densification of the glass-added electrodes starts at 400°C, which is same point as only glass case. Then it finishes at same temperature as the Cu compact does. The specimen containing 10% glass exhibited shrinkage in the wider temperature range (400–1000°C) than the pure glass and as-received Cu specimen. A closer investigation of Fig. 7(a) makes it clear that the shrinkage of the glass-coated electrodes follows behavior of pure glass at initial stage. Then, at final stage, the glass-coated electrodes exhibited the similar shrinkage as that of as-received Cu specimen. It is apparent from this that the shrinkage profile of the glass-coated Cu powder was affected by the densification of pure glass at low temperature like 400–600°C. When the heating temperature is higher than 700°C, glass-softening-point, the glass starts to soften and then separates with Cu powders. Then Cu particle densifies at high temperature being 1000°C.

The densification mechanism and kinetics were determined on the basis of Kingery's analysis [15] for a ceramic–metal–glass composite. The shrinkage results obtained in Fig. 6(a) were analyzed with a reference to the following equation [15].

$$\ln[\mathrm{T}d(\Delta \mathrm{L}/\mathrm{L}_0)/d\mathrm{T}] = \ln(1/n\mathrm{K}1/n) - 1/n\ln\alpha - \mathrm{Q}/(n\mathrm{RT}) \quad (1)$$

where $\Delta L/L_0$ is the fractional shrinkage, T the absolute temperature, n the exponent, K the heating rate, Q the apparent activation energy of sintering and R the gas constant. The n values for these substances are known to be in the range of 1.1–1.3 [10]. Given these, the apparent activation energy of densification for the glass-enriched electrodes can be determined by re-plotting the data from Fig. 7(a) in the form ln [T $d(\Delta L/L_0)/dT$] versus 1/T. The results are shown in Fig. 7(b). Straight lines were fitted to the data sets, and their slopes were used to determine the apparent activation energies (Q). The activation energies for glass and as-received Cu are 7.3 kJ/mol and 61.3 kJ/mol, respectively. The glass-coated Cu shows two activation energies, Q_1=11.2 kJ/mol at low temperature regime and Q_2=39.7 kJ/mol at high temperature regime, which are obtained from slope 1 and 2 in the figure. The value of activation energy increased with increasing temperature for the 10% glass-enriched electrode specimen. This increase in

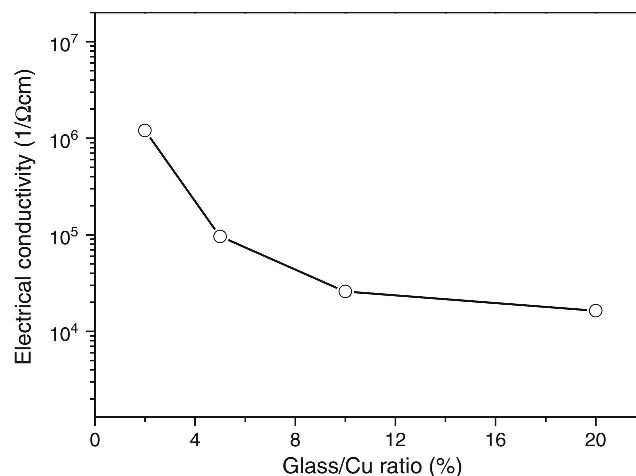


Fig. 9 Electrical conductivities of Cu electrode as a function of glass/Cu ratio

the activation energy indicates that the densification which occurs during sintering changes from a process which relies on glass diffusion in low temperature regime to one which is controlled by the rate of Cu solid state diffusion in high temperature regime. As a consequence, the shrinkage of the electrode becomes much more complicated than the shrinkage which occurs during sintering of the pure Cu electrodes.

3.3 Cu paste and microstructure and electric property of Cu eletrode

Figure 8 shows images and scanning electron micrographes showing microstructure of Cu powder, printed Cu paste on alumina, binder burn-out and sintered Cu electrode. As shown in Fig. 8(a), the sintered Cu electrode shows the typical reddish-brown color which is almost identical to that of Cu powder. This reddish-brown Cu electrode indicates that the glass-coated Cu powder can survive even when exposed to air atmosphere. In addition, the microstructures of screen-printed Cu, binder burn-out and sintered Cu electrode were presented in the Fig. 8(b). The screen printed Cu and binder burn-out treated Cu specimen shows small grain agglomeraltes on alumina. In the sintered specimen, considerable large grains were observed on the alumina substate.

Figure 9 shows a plot of electrical conductivity versus the amount of glass additive in the electrodes. A small amount of the glass (here, up to 10%) did not make any measurable difference to the electric conductivity of the electrode. The fact that the electrical conductivity was constant, regardless of the addition of glass to the electrodes, may be related to the microstructure of the glass melting and distribution in Cu electrode matrix.

MCDs are stacks of functional ceramic/metal electrode which experience a process of binder-burn-out for a long time, followed by co-sintering. When a base metal such as Cu is used as the electrode, the entire process of cofiring should be in a reducing atmospere and speial consideration should be taken to control the partial pressure. Instead of the conventional metal paste consisting of Cu powders and glass frit, the specially treated Cu could be protected from an oxdiative atmopshere as proposed in this study. It was seen that the Cu remains survive without any reaction with oxygen when heating up to glass softening point where the glass exists in a stable shape With this concept, the glass-coated Cu particle can withstand heat-treatment at 500–600°C, which is suitable for the binder-burn-out process. However, at temperatures above glass softening point Cu could easily be transformed into copper oxide. There are still points to be improved thorough further study, although the advantages of glass addition to the Cu powders were described in this study. If the matrix ceramics are substance with high vapor pressure, the Cu may have a possibility of reaction with oxygen dissolved from the ceramics during high temperature sintering. The irregular shaped powders was formed when taking a look at the shape of the glass-coated cu powders in Fig. 2, and thus the powders has an negative impact to post-processing such as powder mixing and sliding in handing electrode materials. In addition, the addition of 10% glass in the Cu powders is still too much for replacement of a conventional glass frit, viewing the content of frit is less than 5 wt % in commercial electrode pastes.

4 Conclusion

To improve the oxygen resistance of Cu electrode during the binder burn-out process, the borosilicate glass-coated Cu powder was prepared by a sol-gel process and its properties were analyzed.

The average particle size increased from 0.596 μm to 0.7 μm as the glass/Cu ratio was increased up to 10 wt %. The glass–coated Cu powder can be heat treated at 500–600°C under air atmosphere, which is suitable for the binder burn-out process. The addition of glass to Cu powder allows this material to be sintered over a wider range of temperatures than for as-received Cu and glass alone. The initial sintering temperatures were shifted to a lower temperature range than is the typical for the as-received Cu powder electrode case. The sintered electrode has an electrical conductivity of more than $10^4/\Omega$ cm, which can be applied for electrode material in MCDs. In this study we have shown the possibility of a Cu electrode.

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