Effects of Copper Powder Shape on Sintering Behavior of Termination in MLCC

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Abstract
One of the main trends in the development of multilayer ceramic capacitors (MLCCs) is to achieve a higher volumetric capacitance density. As for termination, it needs to be thin enough with a sufficiently dense microstructure to meet the overall chip size as well as to guarantee a reliable chip performance. The technical development of termination, however, can be made based upon a better understanding of the microstructural evolution of the termination during sintering process. In the present study, the effects of material characteristics of the copper paste, particularly shape of copper powder, on the sintering behavior of termination were investigated. The microstructural investigations of the terminations formed using spherical and flaky copper powders revealed that the paste with spherical powders experienced a microstructural evolution at lower temperatures on sintering compared to that with flaky powders conforming well to the liquid phase sintering behavior. It is considered that the larger number of contact points of the spherical powders leaded to earlier forming the powder-to-powder connection even before the glass frit formed a liquid phase. In addition, the termination from the spherical powders had less coverage at the corner area than that from flaky powders. The *in-situ* observation of the termination on heating showed that the flaky powders would form a connection, in which the dragging effect of glass is weakened, and leave the empty spaces not covered by the Cu powders smaller.

Introduction
In recent years, a need for multilayer ceramic capacitors (MLCCs) of a higher volumetric capacitance density driven by the technological development of overall electronic devices puts rather strict limitations on the dimensions of chips. To achieve this goal, both of dielectric and inner electrode layers are required to be extremely thin, and the similar thickness issue is also of importance for termination, particularly in case of small sized MLCCs such as 1005 or 0603 (in millimeters). The reduction of termination thickness can give room for chip dimensions as well as overlap area of inner electrode so that help in achieving high capacitance.

For base-metal electrode (BME) MLCCs, copper termination is usually employed and made from the paste which consists of copper, glass frits and binders as basic components. As the termination needs to be thinner, sintering conditions of the termination becomes more complicated and the understanding of sintering behavior is of significance in achieving a thin termination hermetically sealing the chip body [1,2]. The sintering behavior of the termination is basically governed by metallic copper and glass frits, and the organic binders contained in the paste help in forming the shape of termination and are eliminated during the early stage of sintering.

The present study was aimed at understanding the effects of material characteristics of the copper paste on the sintering behavior of termination. Particularly, the shape of copper powders in the starting paste was selected as a principal element to study, so the pastes using different types of copper powders were used to form the termination on MLCC chips. The microstructure of the sintered termination was investigated mainly using a scanning electron microscope (SEM). For a more detailed analysis, an *in-situ* investigation in an environmental scanning electron microscope (ESEM) equipped with a heating stage was attempted.

Experimental procedure

Two types of termination pastes were used to investigate the differences in sintering behavior. Paste A consisted of spherical Cu powders while paste B employed flaky Cu powders. As shown in Table I, the amounts of glass frits and binder vehicles were 10 wt% and 8 wt% with respect to Cu content. Although the compositions of glass frits for both pastes were not fully disclosed, their softening temperatures were not much different according to the paste manufacturers.

Table I. Compositions of termination pastes

		Paste A	Paste B
Copper	Powder	Spherical (SSA* ~ 0.8 m^2/g)	Flaky (SSA* ~ 0.4 m^2/g)
	Content	69±2 wt%	
Glass frit	Content**	10 wt%	
Binder	Content**	8 wt%	

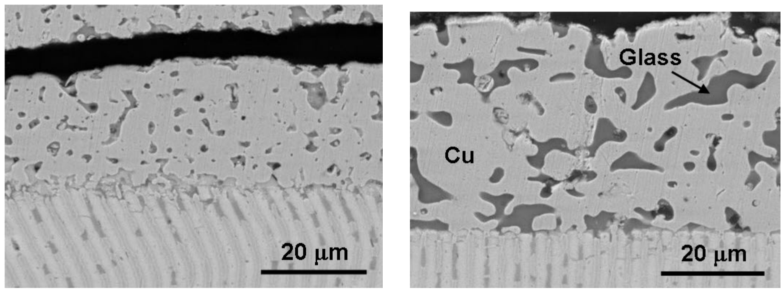
* SSA: specific surface area

** Content of glass frit and binder is with respect to copper.

MLCC chips of 1005 size were dipped into the pastes to form terminations and then fired at 855^{o}C in a nitrogen atmosphere. After sintering, the microstructure of the termination was investigated using SEM (Tescan, Vega II LSH) as well as ESEM (FEI, Quanta 200 FEG).

Results and discussion

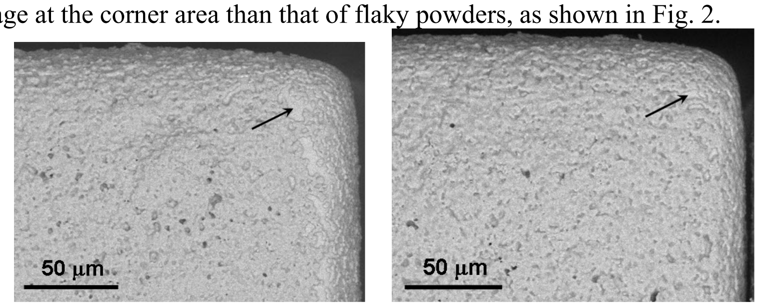
Terminations which were formed using pastes A and B were sintered at 855^{o}C in a nitrogen atmosphere. Fig. 1 shows scanning electron micrographs of the cross sections of terminations.



(a) (b)

Fig. 1. Scanning electron micrographs of the cross sections of terminations; (a) from paste A, (b) from paste B.

Although both terminations were shown to be fully densified after sintering, the distribution of glass phase was somewhat different. Since the flaky powders are not packed so tightly as the spherical ones, the spaces between the powders which the liquid glass phase needs to fill out would be larger in case of the flaky powders. In addition to this cross sectional feature, the plan view SEM images showed that the termination made of the spherical powders had less coverage at the corner area than that of flaky powders, as shown in Fig. 2.



(a) (b)

Fig. 2. Scanning electron micrographs of the plan views of terminations; (a) from paste A, (b) from paste B. The arrow indicates the area where the ceramic body is not covered with termination.

The overall microstructures of the sintered terminations indicated that the two cases, i.e., spherical and flaky powders, had differences in sintering behavior, and to address this issue, the microstructural evolution of the termination was investigated on the chips which were quenched out at individual temperatures during the sintering. Fig. 3 shows the change of microstructure of the termination formed using flaky Cu powders. Compared to the microstructure at 630^{o}C, the glass frits seemed to be softened to form a liquid phase at 719^{o}C and the Cu powders were rearranged to contact to adjacent ones. On further compaction, the densification in the termination started at 770^{o}C and was completed at 804^{o}C. The termination microstructure at 804^{o}C and that of the final sintered one shown in Fig. 1(b) are not much different in terms of densification.

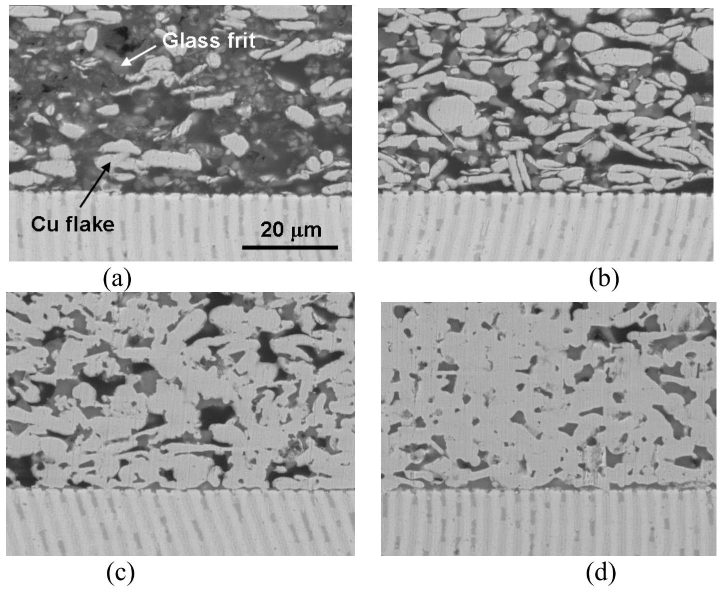


Fig. 3. Microstructural evolution of the termination formed using flaky Cu powders during sintering; (a) 630^{o}C, (b) 719^{o}C, (c) 770^{o}C, (d) 804^{o}C.

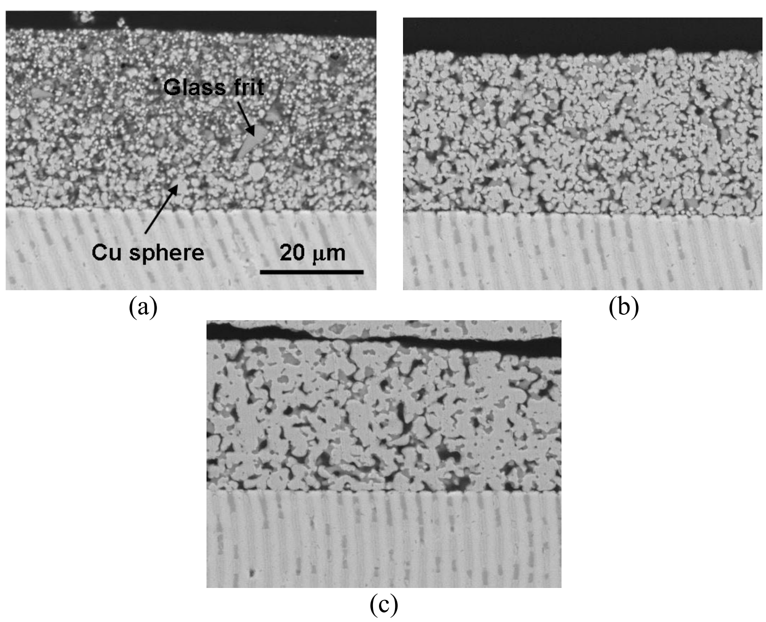
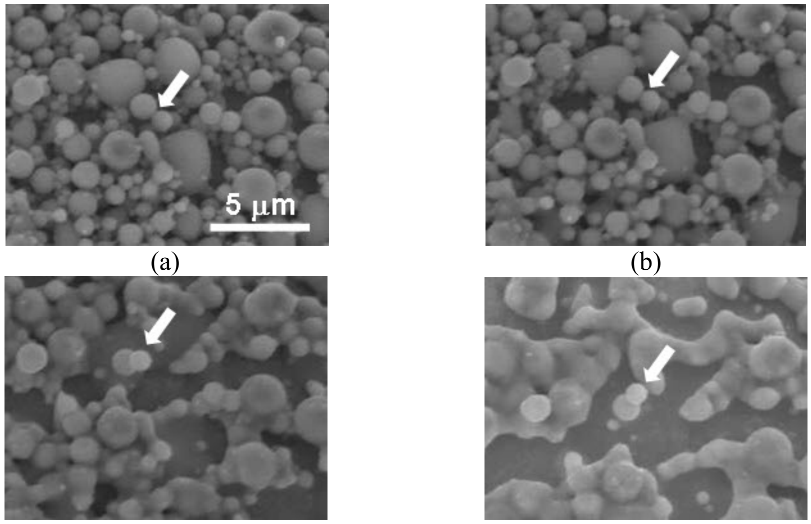


Fig. 4. Microstructural evolution of the termination formed using spherical Cu powders during sintering; (a) 529^{o}C, (b) 672^{o}C, (c) 770^{o}C.

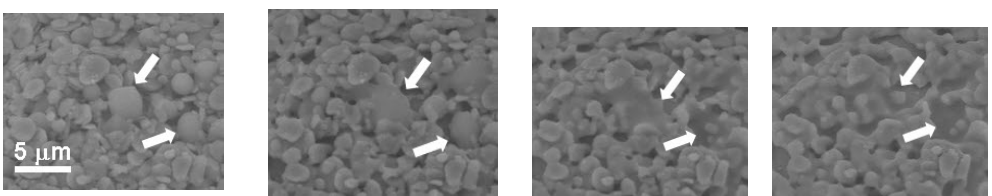
Compared to the paste using flaky Cu powders, the paste using spherical powders showed a similar microstructural evolution at lower temperatures (Fig. 4). Necking between the Cu powders was formed at 529^{o}C and the softening of glass frits started at 672^{o}C. The densification starting at 770^{o}C progressed until the sintering ended. Although the compositions of glass frits and the size of Cu powders are different, the flaky and spherical powders have a fundamental difference in the sintering behavior of termination. While the flaky powders conform well to the liquid phase sintering behavior, i.e., formation of liquid phase leading to rearrangement and compacting of solid particles [3], the spherical powders seemed to have a higher driving force to sintering, which is attributed to a larger number of contact points to adjacent powders. As a consequence, the spherical powders started to be connected to neighbors even before the glass frit formed a liquid phase. In this case, the role of glass frit in the sintering of termination would be rather to somehow inhibit or control the shrinkage of Cu powders than to facilitate it. In addition to the earlier commencement of powder necking, the spherical powders could give an unfavorable effect in terms of binder burn-out.

As shown in Fig. 2, the termination formed using the flaky powders had a better coverage on the corner than that from the spherical powders. To understand this difference, the chips which were heat treated at 600^{o}C just to sufficiently remove binders in the termination were loaded in ESEM and heated up to 900^{o}C while being *in-situ* investigated (Fig. 5). Since the ESEM investigation was performed in 100 Pa of H_2O environment, the temperature that the specimen experienced was not matched to the temperature in sintering profile for termination. Nevertheless, the relative comparison in the sintering behavior of different specimens was possible. Fig. 5 shows the corner area of the termination formed using spherical Cu powders. As indicated by an arrow, the spherical powder was surrounded by glass frits, and at about 750^{o}C, the glass frits were softened and melted down to fill the spaces between the Cu powders. On further heating, the Cu powders were dragged by the liquid glass phase and rearranged so that the Cu to Cu distance was decreased which in turn leaded to the empty spaces not covered by the Cu powders larger. In case of flaky powders in Fig. 6, however, the whole termination area was more covered with Cu powders due to the enhanced area of the flake. Once the flaky powders formed necking to each other, the connection of powders could act as a framework in which the dragging effect of glass phase is weakened [4]. As a result, it is considered that the termination formed using the flaky powders would have a better coverage on the corner compared to that from the spherical powders.



(a) (b) (c) (d)

Fig. 5. *In-situ* ESEM observation of the corner area of termination formed from the spherical Cu powders during heating; (a) 710^{o}C, (b) 750^{o}C, (c) 790^{o}C, (d) 840^{o}C. The arrow indicates a spherical Cu powder.



(a) (b) (c) (d)

Fig. 6. *In-situ* ESEM observation of the corner area of termination formed from the flaky Cu powders during heating; (a) 710^{o}C, (b) 750^{o}C, (c) 790^{o}C, (d) 840^{o}C. The arrow indicates glass frits.

Conclusions

To understand the effects of material characteristics of the copper paste on the sintering behavior of termination, the pastes using different types of copper powders (spherical and flaky) were used to form the termination on MLCC chips, and the microstructure of the sintered termination was investigated. Both of terminations showed a full densified microstructure after sintering, but the distribution of glass phase was somewhat different which is attributed to the larger spaces between the flaky powders to be filled out by the liquid glass phase.

The investigation of the termination microstructure during sintering revealed that the paste using spherical powders experienced a microstructural evolution at lower temperatures compared to the case of flaky powders conforming well to the liquid phase sintering behavior. It is considered that the larger number of contact points of the spherical powders leaded to earlier forming the powder-to-powder connection even before the glass frit formed a liquid phase. As a result, the role of glass frit in the sintering of termination from the spherical powders would be rather to somehow inhibit or control the shrinkage of Cu powders than to facilitate it.

The plan view microstructure of the termination showed that the case of spherical powders had less coverage at the corner area than that of flaky powders. The *in-situ* observation of the termination on heating showed that the flaky powders would form a connection, in which the dragging effect of glass is weakened, and leave the empty spaces not covered by the Cu powders smaller.

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