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Binder Burnout and Sintering Process of Copper Internal Electrode Multilayer Capacitors

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In copper internal electrode multilayer capacitors with 2μF capacitance, a binder burnout process and a sintering process were discussed with regard to a small scale mass production. In the binder burnout process, secondary phases, pyrochlore and metal lead, were observed. The secondary phase was found only in a reduced atmospheric condition. It is found that the formation of those secondary phases are avoidable by controlling the gas flow condition and temperature. In the sintering process, a closed crucible system resulted in an anomalous grain growth and a short life time, though the closed crucible is normally used among lead perovskite materials. Using an open crucible system those problems could be solved. Combining the binder burnout process and the sintering process, a small scale mass production process was established.

1. INTRODUCTION

As multilayer capacitors, palladium, silver-palladium alloy and nickel metals are used widely. Among multilayer ceramic capacitors, copper internal electrodes are quite applicable because of its high conductivity and low cost. However the material is easily oxidized by heat treatments in air. Multilayer ceramic capacitors are obtained by the cofiring process of dielectrics and electrode metals, In that case, heat treatments in reduced atmosphere are essential to obtain copper internal electrode capacitors. The melting temperature of copper is rather low, 1083°C, so that the dielectric material should have both low temperature sintering capability and stability against reducing atmosphere.

Two approaches of the copper internal electrode capacitors have been tried. Combining with low dielectric materials, high Q capacitors have been developed [1-2]. This application makes use of the high conductivity of copper. The other application is low cost and high capacitance capacitors combining with lead complex perovskite dielectrics [3-5]. Lead complex perovskite materials generally have low sintering temperature and high dielectric constant. Moreover lead complex perovskite material shows less bias field dependence of the dielectric constant than conventional systems, barium-titanate.

To obtain high capacitance such as 10μF, less than 10μm layer thickness and more than 100 layers are required. The bias field dependence of the dielectric constant and the metal cost become important to obtain high capacitance capacitors. Thus the combination of copper and lead complex perovskite is one of the promising applications.

However, lead complex perovskite material is sensitive to atmosphere in the heat treatment. PbO has high vapor pressure, and the vapor-out of PbO is a problem. In the combination of silver-palladium and lead complex perovskite, the treatment is performed in air, and usually PbO vapor-out is suppressed by a closed crucible system.

In copper electrode capacitors, all of the heat treatments have to be performed in reduced atmosphere. Thus both oxygen partial pressure (PO_2) and PbO vapor have to be controlled. It is found that the quite complicated atmospheric control are essential. Indeed a few reports have been published in copper internal multilayer capacitors, and they have not been commercialized yet. With increase of the number of pieces in one batch, the carbon residue and PbO vapor accumulate more, because the specimens emit them more densely. The

fact suggests that in a mass production process the atmospheric control becomes very difficult.

In the present paper, based on small scale mass production process, 300 pieces per batch, both the binder burnout process and the sintering process are discussed.

2. EXPERIMENTAL PROCEDURE

The dielectric material used in this study was based on $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, and the ratio was 95-5. The material looses its insulating resistance after a reduced atmospheric sintering [6]. Excess MgO accomplished the anti-reduction of the material [7]. Excess MgO means B-site rich and a high sintering temperature. As a A-site material, CaO was added in order to decrease its sintering temperature. Additionally, $PbSiO_3$ was used to improve the sintering behavior. The final composition used in the study was $95Pb(Mg_{1/3}Nb_{2/3})O_3$-$5PbTiO_3$-1MgO-0.3CaO-$0.1PbSiO_3$.

Powder preparations and green chip fabrications were described in refs. 4, 5. The detail will not be explained in the present paper. The particle size of copper powder for the internal electrode was about 0.3μm. The designed chip size was 3.2mm x 1.6mm x 1.0mm, the layer thickness was about 14 μm and the number of the layer was 40. A small scale mass production batch, as many as 300 pieces was performed in the heat treatment.

3. RESULTS AND DISCUSSION

3. 1 Binder burnout process

In the case of a small batch, less than 50 pieces, the binder burnout condition written in Table 1 was used. However, in the case of large scale batch, a deposition of metal lead and a formation of pyrochlore phases were found on the surface of the specimen. According to the X-ray diffraction pattern, air binder burnout samples and small batch samples show only perovskite phases. Thus the phenomenon is unique in a large number and a reduces atmospheric treatment.

The specimen was placed on a magnesia plate during the binder burnout process. Lead metal deposited on the center in the batch. On the contrary the pyrochlore phase was formed near the edge. It is thought that the carbon gas was abundant around center, and PbO vapor-out was accelerated around the edge. The inhomogeneous gas circulation inside the batch is found to be responsible for the lead metal and the pyrochlore phase.

With increase of the sample number, the atmosphere becomes more reduced. In order to compensate PO_2, H_2 gas wasn't used, and the binder burnout was performed in N_2-H_2O gas mixture. For avoiding PbO vapor-out, the kept time at high temperature around 600°C was decreased to 8.5h. The final temperature was increased at 620°C to achieve effective binder burnout in a short time.. Moreover, the direction of the gas flow was changed every 1h, though the gas flow direction was one way in the conventional treatment, The summary of the binder burnout condition is shown in Table 2. Applying the binder burnout condition, less than 100ppm carbon residue was obtained and the secondary phase disappeared.

Table 1
Binder burnout condition for small batch. H_2(8ppm)-H_2O-N_2 ΔT = 1°C/min

Step No.	Hold temp. (°C)	Hold time (°C)
I	250	10
II	400	10
III	600	40

Table 2
Binder burnout condition for 300 pieces batch. H_2O-N_2 ΔT = 0.55°C/min below 400°C, 1.2°C/min below 620°C

Step No.	Hold temp. (°C)	Hold time (h)
I	400	10
II	620	8.5

3. 2 Sintering process

Sintering was performed at 950°C. In conventional sintering process of lead perovskite materials, closed crucibles were used in order to avoid PbO vapor-out. In a large batch, even 100ppm carbon residue becomes a problem. The carbon residue induces the reduction of dielectric materials, resulting in a short life time. Simultaneously, closed

crucible system causes an anomalous grain growth because of too much PbO atmosphere. These problems take place only in large batches.

In our study an open crucible shown in Fig. 1 was used. To remove carbon residues, the sample should be placed in fresh atmosphere. On the contrary, to retain PbO atmosphere the sample should be placed in a closed crucible. As is shown in Fig. 1, the top cover was removed. The carbon atmosphere, CO, is much lighter than lead atmosphere, PbO. Thus the mobility of CO is much higher than that of PbO. By removing the top cover, it is expected that CO goes away from the crucible selectively and PbO remain with appropriate concentration.

In the case of a small amount sintering, the gas mixture of H_2(40ppm)-H_2O-N_2 with 1000 cc/min flow rate was used. In the open crucible system, the flow rate was adjusted to 200 cc/min to avoid too much PbO vapor-out.

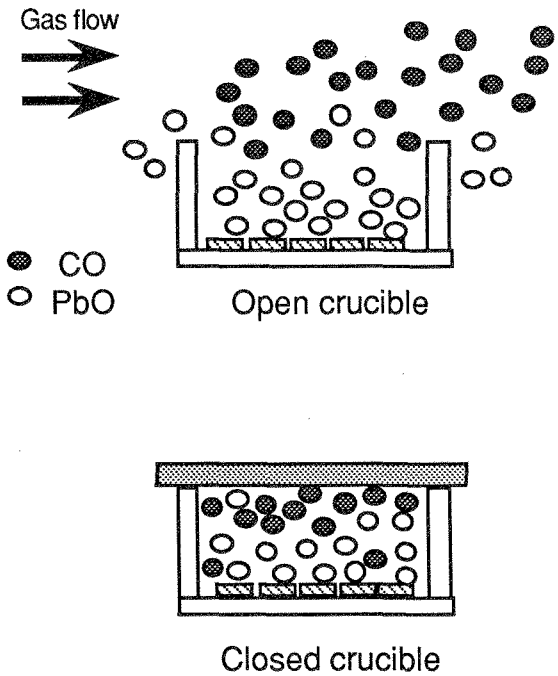

Figure 1. Open and closed crucible system.

Figure 2 shows the cross sectional view of the specimen. It is found that the both specimen sintered densely, and the grain size of the open crucible specimen is much smaller than that of the closed crucible specimen. Figure 3 shows the result of the life test. Both curves are a typical case of the open crucible sample and the closed crucible sample. It is clear that the leak current of open crucible sample is suppressed at a low level and the level is enough for practical use.

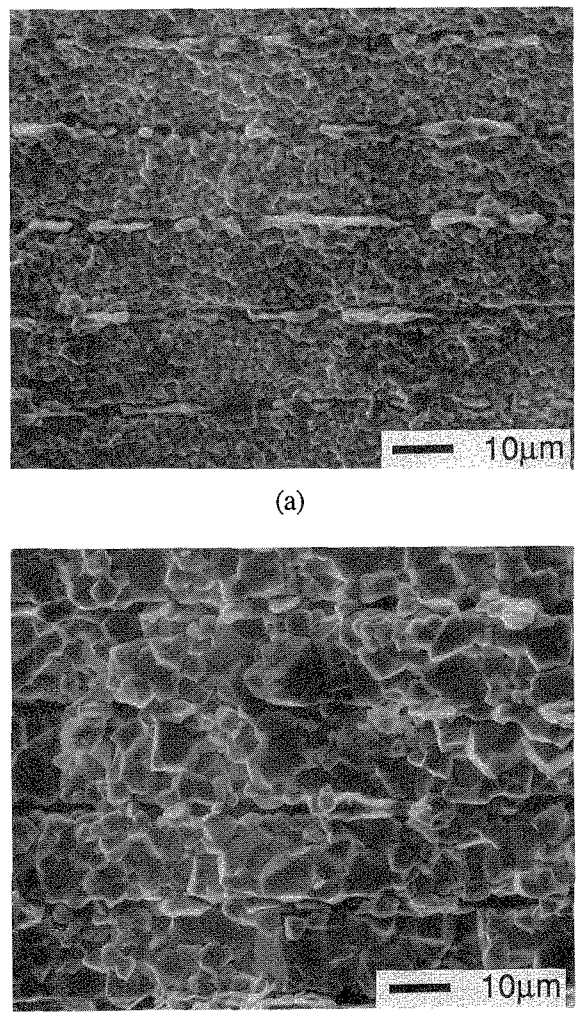

Figure 2. Cross sectional view of copper internal electrode capacitor. (a) open crucible, (b) closed crucible.

Figure 4 shows cross sectional view of the 2μF copper internal electrode capacitor at low magnification. In the small scale mass production level, 300 pieces batch, defect free devices can be obtained. Table 3 shows the summary of the obtained copper internal electrode multilayer capacitor.

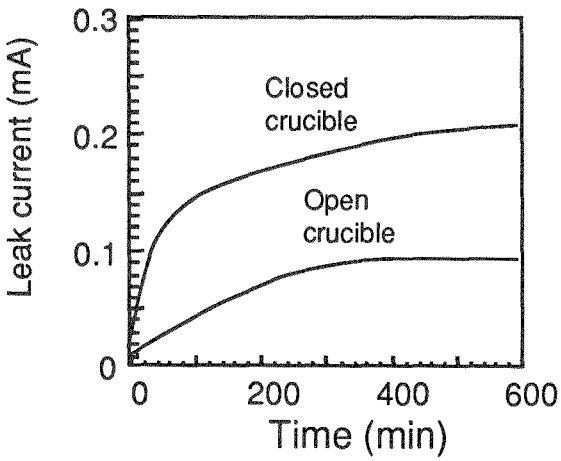

Figure 3. Results of the life test. 200°C, 8V/μm.

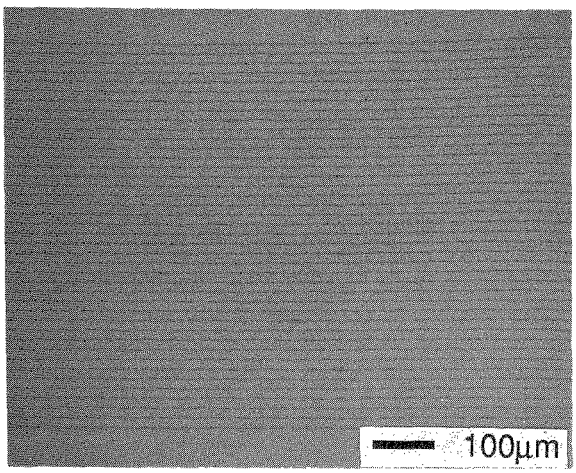

Figure 4. Cross sectional view of 2μF copper internal electrode capacitor.

Table 3
Summary of the device specification obtained in the study, based on 300 pieces batch.

Capacitance (μF)	Dimension (mm)	IR (MΩ)
2.0 EIA Y5V	3.2x1.6x1.0	10000

4. Conclusion

In copper internal electrode multilayer capacitors with 2μF capacitance, a binder burnout process and sintering process were discussed with regard to a small scale mass production. In the binder burnout process, secondary phases, pyrochlore, and lead depositions were observed. The formation of pyrochlore and the deposition of metal lead were avoidable by controlling the gas flow condition and temperature. In the sintering process, a closed crucible system resulted in an anomalous grain growth and a short life time. Using an open crucible system both problems could been solved. Combining the binder burnout process and the sintering process, the small scale mass production process was established.

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