Microwave Coffing of Base Metal Electrode Multilayer Capacitors

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ABSTRACT
Multilayer capacitors (MLCs) with base metal electrodes were cofired by microwave processing. Commercial green chips of MLCs with nickel electrodes were used in the microwave sintering study. Binder burnout was carried out in a conventional furnace. The cofiring experiments were conducted in a multimode microwave cavity operating at 2.45 GHz under an inert atmosphere. Microstructure of the microwave processed MLC was studied. The dielectric properties of the microwave sintered MLCs were measured and compared with those sintered by conventional processing. The results show that the properties of the microwave-sintered samples are comparable to or better than the conventional samples. Also the microwave processing was found to have enhanced sintering kinetics and lowered the processing temperature and time substantially.

INTRODUCTION
Microwave processing of ceramic materials has been widely studied in the past twenty years. The microwave processing lab at Penn State has been working on the microwave sintering of metals, magnetic materials and many kinds of ceramics for over a decade. The use of microwave energy for processing multilayer ceramic capacitors is a rather new development and has great potential to improve productivity and the performance of the products. Several patents such as 2,4 have been filed on utilization of microwave radiation in ceramic processing. The patent by Lauf et al. 4 describes the use of microwave radiation for fabrication of multilayer capacitors (MLCs) with Ag-rich electrodes. However, fabrication of base metal electrode MLCs has not been reported.

There are many complex processes during the heat treatment of a multilayer ceramic capacitor. First, the binder must be removed at low temperature, leaving no residual carbon in the body before pore closure. In X7R (a doped-BaTiO3 ceramic material with a core-shell structure) formulated capacitors, chemical modifiers must diffuse from the grain boundary to the grain interior to form the core-shell structure. Finally, the ceramic must be fully sintered at high temperature with no porosity. For base-metal capacitors, the oxidation of the Ni electrodes must also be controlled. Microwave sintering may change the kinetics of these competing processes, which will be important as the grain size decreases for thin-layer X7R capacitors.

The main objective of this study is to apply the microwave technology for processing base metal electrode multilayer ceramic capacitors. The BaTiO3 bulk material is not a good microwave coupler at low temperature. Because of this, susceptors that enhance the microwave absorption of the sintering system must be added around the samples. It has been successfully proven that this kind of sintering system design is suitable for sintering the X7R bulk materials and, more importantly, the X7R-based MLCs.

The newly developed process partitions the microwave energy between the susceptor and the multilayer ceramic capacitors. The principal of this process is based on the interaction between the microwaves and all of the materials in the microwave furnace. The susceptor absorbs part of the microwave energy and radiates thermal energy. Since the susceptor surrounds the MLCs, a more stable and uniform hot zone is maintained. In addition, the thermally heated MLCs will be heated initially from their surfaces. The microwaves also interact directly with the MLCs, in which they are heated as a whole (volumetric heating) and thereby providing very uniform and rapid heating of the sample. The metal powders (Ag-Pd or Ni) in MLCs can be self-heated in a microwave field. The heating rate of the load is dependent upon input power, frequency and the microwave absorption properties of the materials. The energy partition can be controlled by the type and amount of susceptor used in the microwave furnace.

Our previous testing on microwave sintering of Ag-Pd found that the processing was reproducible and the heating was uniform. In the last quarter, we started the initial trials on the target of the project: microwave sintering of BME MLCs. The green chips of the commercial nickel electrode X7R 0603 MLCs with nominal size of 1.52 mm × 0.76 mm × 0.76 mm (0.06" × 0.03" × 0.03") were used for the microwave sintering. The focus of this work was on the microstructural development of the X7R BME size 0603 multilayer capacitors in microwave sintering. The preliminary results show that microwave sintering of BME X7R MLCs is promising.

EXPERIMENTAL
The microwave sintering experiments of MLCs were conducted in a 6 KW, 2.45 GHz multimode microwave furnace. An atmosphere control system has been used to control the input gas and flow rate through the applicator. An optical pyrometer has been placed on the top middle of the applicator to monitor the temperature of the sample load. A special susceptor package has been developed to enhance microwave sintering the MLCs in the microwave applicator. This
specially-designed susceptor is for the purpose of: a) minimizing the temperature gradient throughout the sintering area at sintering temperature, b) providing very precise temperature control which enables variable holding time at sintering temperature.

The microwave sintering of Ni-electrode MLC chips was carried out in the temperature range of from 1100°C to 1250°C at 2.45 GHz. The total heating time was within 2 h, with about 20 min soak at the peak temperature.

Microwave sintering of BME X7R 0603 MLCs

The sintering experiments were conducted with a sintering package using either SiC or ferrite as a susceptor. The configuration of the susceptor is to fill the space between two mullite tubes with a mixture of coarse SiC and alumina, or pre-sintered crushed coarse ferrite. Both SiC and ferrite are excellent microwave absorbers thus at low temperature the susceptor will be heated first to enhance the heating of the MLC samples. The difference is that SiC can withstand higher temperature than ferrite. The working temperature for SiC can go up to 1400°C or even higher, whereas ferrite is only good up to 1300°C or so. The use of the susceptor is a must to compensate the heat loss from the samples and get uniform temperature distribution.

It was found in this work that the bedding powder is critical to achieve homogeneous sintering by microwave processing. The microwave absorption of the bedding powder should be the same as or close to that of the MLC samples being processed. The bedding powder that is much more or much less absorbing to microwaves than the MLCs could lead to failure in microwave sintering.

In the earlier trials, with a powder that was more absorbing than the samples, we found some samples with burn marks on the surfaces of the sintered MLCs. In order to solve this problem, we chose a bedding powder with microwave absorbing property similar to that of the samples. With this innovation, the heating has been stable and the temperature distribution was more uniform. The sintered chips were uniform and free of burn marks. At about 1200°C, with a soaking period of 20 min or so, and the total heating time in the microwave sintering for about 120 min, the samples were sintered well. Based on literature results for sintering BME capacitors, conventional sintering process of the same materials requires soaking at a peak temperature over 1300°C, and the entire processing takes more than 15 h. The microwave process substantially lowered the processing temperature and time significantly.

In this study, an inert atmosphere was used to avoid the oxidation of the Ni electrodes. Before microwave heating, the chamber of the microwave furnace was evacuated to less than 10 Torr and flushed with ultra-high purity nitrogen. The microwave sintering was carried out in the atmosphere of ultra-high purity nitrogen with or without addition of a small portion of forming gas. The oxygen partial pressure in the microwave-sintering atmosphere was less than 10⁻⁵ atm. For comparison, conventional sintering was also conducted in an atmosphere with oxygen partial pressure pO₂ = 1.85 x 10⁻⁵ atm. The heating rate in the conventional sintering was 2°C/min. The samples were soaked for 2 h at 900°C and another 2 h at 1320°C.

RESULTS AND DISCUSSION

Overall, BME 0603 MLCs samples microwave sintered at temperature between 1200-1250°C were dense and uniform. The sintered chips were tan or light tan in colors. It was found that when the atmosphere was too reducing, the color of the sintered chips turned dark gray. The geometrical densities of up to 5.81 g/cc have been achieved.

State of the Electrodes

The electrodes remained metallic after both microwave and conventional sintering in the controlled atmosphere in this study. X-ray diffraction (XRD) on the as-sintered surface of the microwave sintered samples showed peaks of metallic Ni. No evidence of nickel oxide was observed (Figure 1). Figure 2 shows the powder XRD of the sintered BME X7R 0603 samples with the conventionally sintered sample and the sample with oxidized electrodes as a comparison.

![Figure 1. XRD of the as-sintered end surface of the electrodes of the microwave sintered BME 0603 showing that the electrodes maintained metallic after microwave sintering. The XRD pattern was obtained by scanning the as-sintered surface with the exposed electrodes of an array of 64 microwave-sintered chips.](image-url)
Figure 2. Powder XRD pattern of the BME 0603 microwave sintered at 1250°C, and that of the conventionally sintered sample, with the sample with oxidized electrodes for comparison, indicating that the nickel electrodes of the sintered MLCs remain metallic.

Microstructure
The fracture surface microstructure of the microwave sintered BME (Ni-electrode) chips (cross section) was studied under SEM. Representative SEM micrographs are shown in Figures 3-7.

Figure 3. The as-microwave sintered electrode surface showing that there are no delaminations or cracks during microwave sintering.

Figure 4. Microstructure of the BME MLC microwave sintered at 1200°C for 10 min showing (A) as-sintered surface, and (B) fracture surface. It is seen that the nickel electrodes have been sintered well whereas the matrix is still porous under this processing condition.

Figure 5. Fracture microstructure of BME 0603 MLC microwave sintered at 1235°C for 20 min.

Figure 6. Fracture microstructure of BME 0603 MLC microwave sintered at 1250°C for 10-20 min.
SUMMARY AND FUTURE WORK

Microwave sintering of Ni-electrode MLCs has been conducted in an inert atmosphere. It was found that in the temperature range of 1200°C to 1250°C, the X7R 0603 chips were sintered well. The shrinkage of the chips was found to be dense, uniform and free of delaminations or cracks.

It was found that the use of X7R as bedding powder favors the microwave sintering, since the bedding powder has the same microwave absorption as the BME MLCs substrate. By using X7R for bedding, the sintering was stable and the sintered chips were very uniform.

Compared to the conventional process that takes 15h in the whole heating process, the microwave process saves more than 80% in processing time. In addition, to achieve the comparable densification effect, the microwave sintering can be carried out at lower temperature. This indicates that the densification of BME dielectrics has been substantially enhanced by microwave sintering.

The correlation of sintered microstructure and the dielectric properties of the microwave sintered BME MLCs are in progress.

REFERENCES