The Influence of Microwave Sintering on Microstructure and Dielectric Property of (Zn,Mg)TiO_3-based Mulitlayer Ceramic Capacitor

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ABSTRACT

The effects of microwave sintering on the sintering behaviour, the microstructure and the silver diffusion of (Zn,Mg)TiO_3 based multilayer ceramic capacitors (ZMT' MLCCs) with pure silver electrodes were investigated in this study,. The energy dispersive spectroscopy results showed that the silver ions diffused into the dielectric layer significantly when ZMT' MLCC was sintered directly up to 900°C (conventional sintering). However, ZMT' MLCC was fired at 900°C using microwave sintering; it was found to effectively suppress silver ion diffusion into the dielectric layer. For example, the concentration of silver ions was identified by energy dispersive spectrometer, and both the Ag ion concentrations for conventional and microwave sintering are 2.0 and 0.1 at.% respectively. The result for this is may be due to different sintering kinetics between conventional and microwave sintering. To prove the effect of silver ion diffusion on the insulation resistance of ZMT' MLCCs, the insulation resistance under different sintering conditions was measured at 85°C and 95% relative humidity atmosphere. The insulation resistance of ZMT' MLCCs with conventional sintering was degraded obviously, which was compared with that with the microwave sintering.

Introduction

Cost saving, performance, and miniaturization are the major drivers in the manufacture of multilayer ceramic, although many manufacturers have switched over from Ag-Pd electrodes to base metal electrode systems.[1,2] In some cases, 95Ag-5Pd or pure silver of inner electrodes has the advantage of cost when compared based metal system, and silver is also the most conductive element, facilitating lower ESR (Equivalent Series Resistance) & higher frequency requirements. However, ceramic capacitors are one of the most widely used discrete electronic components which play a very important role in electronic industry. The use of silver-palladium alloy as the conductor of MLCCs, rather than pure palladium alloy, is one way to reduce costs.[3-5] Therefore, on the basis of development of many low-sintering ceramic formulations, pastes of Ag and Ag-Pd have been widely used as internal electrodes in the metal-ceramic cofiring step during fabricating these multilayer ceramic devices.[6] However, during the co-firing of the ceramic layers and silver/palladium inner electrodes, potential for the chemical reaction and the inter-diffusion at the interfaces, and their influence on the co-firing behaviors of MLCCs must be considered. The interaction and inter-diffusion may change the sintering behavior and final properties of MLCCs.[7,8]

It is well known that zinc titanates ($ZnTiO_3$) can be sintered at 1100°C without the use of sintering aids.[9,10] When a sintering aid is added, it can be sintered at the temperatures below 900°C.[9-11] $ZnTiO_3$ has a perovskite type oxide structure and should be useful as a microwave resonator material.[10] $ZnTiO_3$ material has a permittivity (ε_r) of 19, Q value of 3000 at 10 GHz, and a temperature coefficient of resonant frequency (τ_f) of –55 ppm/°C.[11-12]

Microwave sintering is method having do self-heating from the internal by absorption of microwave power. Therefore, the microwave sintering is possible compared with external sintering by thermal conduction or radiation. When this method is utilized in processing of ceramics, the fine grain, uniformity and high densification are expected, and electric and mechanical properties can be improved.[13]

It is well known, silver migration into ceramics in the co-firing process of low sintering temperature MLCCs is another important reason which influences the reliability and dielectric characteristics.[14]

In previous study,[15]) the effect of heating rates and two-steps sintering on the Ag diffusion into ZMT' dielectric have been investigated. It was found that the two-steps sintering can effectively prevent the Ag ions from diffusing into the dielectric layer. In this paper, the effects of microwave sintering on the sintering behavior, microstructure and silver diffusion of ZMT' MLCC with pure silver electrodes were investigated.

Experimental

1 Preparation of the ZMT' powders

ZMT' powders were synthesized by conventional solid-state methods from individual high-purity oxide powders: ZnO (99.8% Umicore Zinc Chemicals, France), TiO_2 (99.9% Showa Denko Inc., Japan) and MgO (99% Pharmacie Central Inc., France). They were mixed and ground in deionized water with 2mm Zirconia beads for 24 h, and the mean particle size (D_{50}) of milled powder was about 0.35m. The powders were calcined in air at 900°C for 5 h after ball milling. The $3ZnO-B_2O_3$ (ZnBO) glass with 1m particle size was chosen as sintering aid, and it was added with the amounts of 1.0 wt%. Then the calcined powders were milled again for 6 h. The mean particle size was measured to be about 0.5 um.

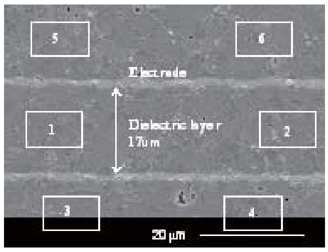

Fig. 1: The analysis position of EDS for ZMT' MLCC; total six points are measured.

2 Fabrication of multilayered ZMT' capacitors

In this experiment, MLCC consists of ten active layers with an overall size of 2.0 x 1.25 x 0.6 mm, and a distance of 17um between the internal electrodes. The ZMT' powders were mixed with resin (polyvinyl butyral), plasticizer (butyl benzyl phthalate) and solvent (toluene and ethanol). The resultant slurry was tape-casted to a green sheet with 30 um thickness using the doctor-blade method.

A silver paste composing of silver particles, binder and solvent was prepared for screen printing. A silver powder (Ag C200ED, Ferro Co., USA) with average particle size of 1.1 μm was used. The powder/organic vehicle ratio was 90/10 in weight. The pastes were prepared and homogenized on a standard three-roller mill. The paste properties consist of 60% solid content and 25 Pa.s of viscosity by 10 rpm.

Ag pastes were printed as an inner electrode onto the green sheet. These printed sheets were stacked, pressed at 60°C under a pressure of $5.2x10^7$ Pa and cut into chips. The lamainated green chip was sintered in microwave oven after binder burn out (320°C). The samples were sintered in air by microwave processing ramping at 25°C/min. Temperature of the sample was monitored with a type-R thermocouple shielded with platinum foil and grounded to the inner metallic wall of the microwave furnace. The samples were sintered at various temperatures from 800°C to 900°C, holding 120 min at the peak temperature. Comparative conventional sintering was carried out in a regular resistance furnace at the same heating rate and holding time.

3 Measurements

The sintering shrinkage of ZMT' dielectrics and silver powders was measured at a heating rate of 5°C/min in air by a thermo-mechanical analyzer (TMA, Netzsch DIL 402C, Germany). Both ZMT' dielectrics and silver powders are pressed to form a disc with φ10 mm diameter and 1 mm thickness. The capacitance and dissipation factor were measured at 1MHz and 23°C by impedance analyser (HP 4278A Palo Alto, CA). Microstructural observation of the sintered MLCC was performed by scanning electron microscopy (SEM, Jeol. JEL-6400 Japan) equipped with energy-dispersive spectroscopy (EDS). Each test analyzed two samples; 6 points were analyzed on each sample as shown in Fig. 1, for a total of 12 points, to ensure EDS reliability and reduce errors. The insulation resistance was measured with a high resistance meter (HP 4140A Palo Alto, CA) at a dc voltage of 50 V for 1 min.

Results and Discussion

3.1 Effect of microwave sintering on the density and microstructure of ZMT' dielectric

Figure 2 shows the bulk density of the ZMT' ceramic pellets from each sintering process as a function of the sintering temperature. The density of ZMT' ceramics sintered at different temperatures depends on the heating mode. For the ZMT' ceramics sintered by the conventional process, the density is much lower than those sintered by microwave processing at temperatures < 880°C. The theoretical density of the ZMT' ceramic is ~4.95 g/cm[3.14] The ZMT' ceramics produced by microwave processing can reach over 95% of the theoretical density (4.75 g/cm^3) at 840°C. For conventional processing, the material must be sintered at 900°C to obtain a 95% theoretical density. In other words, the microwave sintering can achieve a high-density ZMT' ceramic at a lower heating temperature (840°C), while in the conventional sintering, there was no significant densification below 880°C. The microwave sintering temperature was 60 °C lower than the conventional sintering. The maximum densities achieved for microwave and conventional sintering were 4.92 g/cm^3 at 900°C and 4.90 g/cm^3 at 920°C, respectively. This clearly indicates that microwave sintering substantially enhanced the densification of ZMT' ceramics. The densification effect was evaluated by linear shrinkage ($\Delta L/L_0$) of the ZMT' ceramics as shown in Fig. 3. The results show that microwave sintering enhanced the sintering of the samples. It was found that the microwave densification enhancement of ZMT' ceramics was temperature-dependant. The microwave heating at 840°C produced the same densification as conventional heating at 900°C (60°C lower). No significant microwave densification enhancement was observed below 800°C, which indicates significantly accelerated sintering kinetics by microwave processing. On the other hand, the linear shrinkage ($\Delta L/L_0$) of the Ag electrode was evaluated as shown in Fig. 4. The results were exhibited that microwave sintering also enhanced the sintering of the samples.

The effect of different sintering modes on the microstructure of Ag electrodes was observed. SEM micrographs of the surface of the specimens sintered at 700°C are shown in Fig. 5. In Figure 5 (a), it can be seen that the Ag electrodes produced by conventional processing are densification; but the grain size is not clear. For microwave processing, the densification in the sintered specimen is enhanced considerably, as shown in Fig. 5 (b), since the growth of grains are significantly..

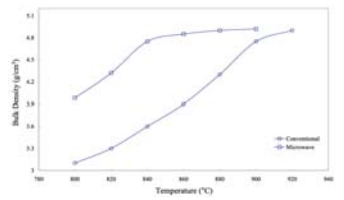

Fig. 2: The bulk density of ZMT' ceramics produced by both sintering methods as a function of the sintering temperature.

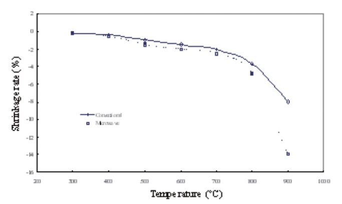

Fig. 3: The shrinkage rate of ZMT' ceramics produced by both sintering methods as a function of the temperature.

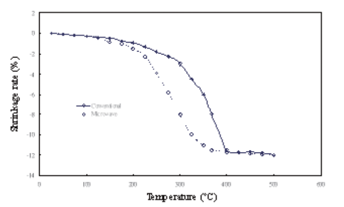

Fig. 4: The shrinkage rate of Ag electrodes produced by both sintering methods as a function of the temperature.

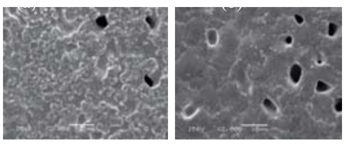
Fig. 5: SEM microstructures for Ag electrode sintered at 700°C (a)conventional sintering and (b) microwave sintering.

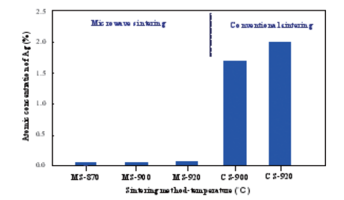

Fig. 6: Average Ag concentration in the dielectric layer of ZMT' MLCC with different sintering temperature and method

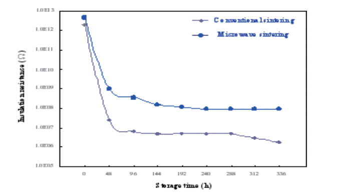

Fig. 7: The electrical resistances measured under a temperature of 85°C and relative humidity of 95% when ZMT' MLCC undergoes different sintering method and storage times

Table. The electrical properties of ZMT MLCC sintered under different conditions

Microwave-sintering temperature (°C)	Permittivity	Dielectric Loss (x10^{-4})	Insulation Resistance (MOhm)	Breakdown Voltage (V/um)
870	27.1	3.6	45000	45.7
900	29.9	2.1	250000	49.3
920	36.0	6.6	380000	47.1
Conventional	29.0	2.2	150000	39.7

3.2 Effect of microwave sintering on the Ag diffusion and dielectric properties of ZMT' MLCCs

It has been reported that Ag diffusion from the inner electrode occurs during high-temperature cofiring between the ZMT' dielectric and the Ag/Pd inner electrode in $ZnTiO_3$-based MLCCs.[16)] To understand the diffusion of Ag after cofiring with microwave sintering, an analysis of the Ag element from the central region between the electrodes was carried out. Six positions on the central part were analysed on each sample to ensure EDS reproducibility and reliability. Figure 6 shows the EDS analysis for Ag diffusion in ZMT' MLCCs after different heating processes. When conventional heating is applied, significantly more Ag ions diffused into the dielectric layer. This result is the same as that of our previous study.[15)] According to the EDS analysis, the concentration of Ag in the ZMT' dielectrics resulting from microwave sintering is approximately 0.1 at.%, whereas that resulting from the diffusion of Ag ions during conventional sintering is approximately 2.0 at.%. This experimental result proves that microwave sintering can effectively prevent the diffusion of Ag ions into the dielectric layer. The reduction of Ag ionic diffusion into the dielectric layer during microwave sintering can be explained by the densification of ZMT' dielectrics. The microwave sintering process leads to increased densification of the ZMT' dielectric during heating (Fig. 2), reducing the porosity of the ZMT' dielectric and making it more difficult for Ag to diffuse into the dielectric layer. The microwave electromagnetic energy falls within the frequency range of 300 MHz to 300 GHz. Microwave heating is a process in which the materials couple with the microwaves, absorb the electromagnetic energy volumetrically, and transform into heat. It is different from the conventional process in which heat is transferred between objects by the mechanisms of conduction, radiation and convection.[17)] When MLCCs are sintered by conventional processing, the ZMT' dielectric surface is heated first, and the heat then moves inward. This inward movement means that there is a temperature gradient from the surface to the inside of the dielectric. However, microwave heating generates heat within the material first and then heats the entire volume.[18)]

Table I shows the electrical properties of ZMT' MLCCs with different sintering modes. The microwave sintering temperatures seem to have an effect on the dielectric properties of ZMT' MLCCs because the permittivity (ε_r) increases with increasing sinter temperature. In particular, the εr value of ZMT' MLCCs sintered at 920°C is higher than the value for those samples sintered at 900°C. This result is attributed to the increase in the amount of the rutile phase,11) as observed in the SEM analysis. As is well known,[10)] the existence of a small amount of the rutile phase can increase the dielectric constant of the ceramic because the dielectric constant of rutile, ε_r =105, is much higher than that of the hexagonal $ZnTiO_3$ phase, ε_r =19. However, some high dielectric loss is observed for MLCCs sintered at 920°C compared to samples sintered at 900°C. The breakdown voltage of the ZMT' MLCCs is highest for microwave sintering at 900°C. In addition, the lowest breakdown voltage (39.7 V/μm) is obtained for conventional sintering. This can be explained by Ag diffusion into the dielectric layer during cofiring because Ag migration leads to a local intensification of an applied field, lowering the breakdown strength. This result can also be confirmed by EDS analysis as shown in Fig. 6 because the concentration of Ag ions for conventional sintering of the ZMT' dielectric is higher than that for microwave sintering. In addition, the microwave sintering has been shown to typically enhance the kinetics of densification and grain growth (in some cases).[19)] This change in kinetics often leads to differences in microstructure.

To prove that Ag ion diffusion into the dielectric layer results in the degradation of the insulation resistance (IR) of ZMT' MLCCs, they are placed in a constant temperature and humidity environment (85°C and R.H. 95%) for a long-term IR measurement as shown in Fig. 7. The result indicates that microwave sintering produces a higher IR value. According to a previous study,[15] high Ag ion concentration in the dielectric layer is a known result of conventional sintering. The Ag ions in the dielectric layer of the MLCC can reduce the IR, especially under high temperature and high humidity conditions, which accelerate the decrease of the IR. Therefore, the IR of ZMT' MLCCs with microwave sintering is higher than that of ZMT' MLCC with conventional sintering. This outcome could be explained by the diffusion of Ag ions into the dielectric layer during cofiring because Ag migration leads to the local intensification of an applied field, which lowers the insulation resistance.[26]

Conclusion

The ZMT' MLCC with different sintering modes was investigated. The results can be summarized below.

1. Microwave sintering can achieve a high-density ZMT' ceramic at lower heating temperature (840 °C), while in the conventional sintering, there was no significant densification below 880 °C. The microwave sintering temperature was 60 °C lower than the conventional sintering.
2. The effect of microwave sintering on Ag diffusion into the ZMT' dielectric was investigated. According to the EDS analysis, the concentration of Ag in the ZMT' dielectrics using microwave sintering is approximately 0.1 at.%, whereas the use of conventional sintering results in an Ag ion concentration of approximately 2.0 at.%. This result indicates that microwave sintering can effectively prevent the Ag ions from the silver electrode from diffusing into the dielectric layer..

Acknowledgments

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References

[1] Di Zhou, Hong Wang, Xi Yao, and Li-Xia Pang, J. Am. Cream. Soc. 91 [10] (2008) 3419-3422.
[2] Do-Kyun Kwon, Michael T. Lanagan and Thomas R. Shrout,, J. Am. Cream. Soc. 88 [12] (2005) 3419–3422.
[3] X. X. Wang, W. P. Chen, H. L.W. Chan and C. L. Choy, Mater. Lett. 57 (2003) 4351.
[4] Jonathan L. Paulsen and Erik K. Reed, Microelectronics Reliability 42 (2002) 815.
[5] A. C. Caballero, E. Nieto, P. Duran, C. Moure, M. Kosec, Z. Samardzija and G. Drazic, J. Mater. Sci. 32 (1997) 3257.
[6] R. Z. Zuo, L. T. Li and Z. L. Gui, Ceram. International. 26 (2000) 673.
[7] R. Z. Zuo, L. T. Li, N. X. Zhang and Z. L. Gui, Ceram. Interna. 27 (2001) 85.
[8] C. H. Lu and J. Y. Lin, Ceram. Interna. 23 (1997) 223.
[9] F. H. Dulin and D. E. Ras, J. Am. Cream. Soc. 43 (1960)125.
[10] H. T. Kim, S. Nahm and J.D. Byun, J. Am. Cream. Soc. 82 (1999) 3476.
[11] H. T. Kim, S. H. Kim, S. Nahm and J.D. Byun, J. Am. Cream. Soc. 82 (1999) 3043.
[12] H. T. Kim, J. D. Byun and Y.H. Kim, Mat. Res. Bull. 33 [6] (1998) 963.
[13] H. Fukushima, H. Mori, T. Hatanaka, and M. Matsui, J. Ceram. Soc. Jpn., 103 [210] (1995) 1011.
[14] Y. C. Lee, W. H. Lee and F. T. Shiao, Jpn. J. Appl. Phys. 43 [11A] (2004) 7596.
[15] Wei-Hau Lu, Ying-Chieh Lee, Pei-Rong Tsai, Advances in Applied Ceramics. 110 [2] (2011) 99-107.
[16] Wei-Hau Lu, Ying-Chieh Lee, Pei-Rong Tsai, Advances in Applied Ceramics. 110 [2] (2011) 99-107.
[17] Y.C. Lee and W.H. Lee, Jpn. J. Appl. Phys. 44 [4A] (2005) 1838-1843.
[18] Morteza Oghbaei, Omid Mirzaee, Journal of Alloys and Compounds 494 (2010) 175–189.
[19] Y. Fang, M.T. Lanagan, D.K. Agrawal, G.Y. Yang, C.A. Randall, T.R. Shrout, A. Henderson, M. Randall and A. Tajuddin, Journal of Electroceramics, 15 (2005) 13–19.