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The effects of sintering conditions and Ni powder size on the dielectric properties of a X7R multilayer ceramic capacitor

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The effects of the Ni powder size and the sintering conditions on the electrical properties, especially in regards to the reliability, of a X7R multilayer ceramic capacitor (MLCC) possessing a Ni internal electrode and thin layers were investigated. This research also attempts to use a paste made from 200 nm and 400 nm Ni powder in order to compare the MLCC properties. The ceramic was sintered at the increasing temperatures of 1230 °C, 1250 °C and 1270 °C at a fixed heating rate of 60 K·minute^{-1} which caused the internal electrode connectivity to decrease. The MLCC sintered at 1270 °C suffered from an Ni internal electrode contraction with an increased ceramic thickness. Conversely, the internal electrode connectivity was improved when the sintering temperature was fixed at 1270 °C with the heating rate being varied at 20, 40, and 60 K·minute^{-1}. The ceramic treated with dense sintering (1250 °C, 60 K·minute^{-1}) had a 10% higher breakdown voltage (BDV) compared to less densely sintered ceramic (1230 °C, 60 K·minute^{-1}). In addition, there was a decrease in the degree of internal electrode disconnection. Therefore, the high temperature insulation resistance (IR) voltage properties were fine for a relatively high sintering temperature and a good internal electrode connectivity. The best result was found for a sintering condition of 1250 °C, at 60 K·minute^{-1}. The effects on the capacity and breakdown voltage of the high temperature IR for different Ni powder sizes were tested. The MLCC using 200 nm Ni powder had a 2% larger capacity and a 60% higher internal resistance when compared to the MLCC using 400 nm Ni powder. The MLCC using 200 nm Ni powder had a high temperature IR value of 9 Vr and the one using 400 nm Ni powder had high temperature IR value of 5 Vr, both showing good high temperature IR values when the internal electrode connectivity was good.

Key words: MLCC, BDV IR

Introduction

Surface mount technology has been developed in order to make high density and high electrical performance circuits. This trend has resulted in a rapid increase in the demand for multilayer ceramic capacitors (MLCCs). The employment of base metals for the inner electrodes, such as Ni, is essential in reducing the cost. Base metals, however, are easily oxidized when they are heated in air and so lose their electrical conductivity. Therefore, the sintering of MLCCs using base metal electrodes needs to be performed under a reducing atmosphere. Unfortunately, dielectrics containing titanium oxides lose part of their oxygen during this process, and end up becoming n-type semiconductors. In order to prevent the dielectrics from losing their high insulation resistance, acceptor impurities are added that produce non-reducible dielectric compositions. However, since the oxygen vacancy is the most mobile species in $BaTiO_3$ lattices, the electromigration of the extrinsic oxygen vacancies introduced by the addition of acceptor impurities is the main cause of electrical degradation in $BaTiO_3$-based ceramic capacitors [1-2].

Electronic products are becoming smaller and require high performance capabilities, necessitating a reduction in component size. There are three ways to make high capacity MLCC : thinning the ceramics, increasing the surface area, and reducing the electrode coating. A thin electrode coating has a drawback in that it is difficult to maintain the internal electrode coverage after sintering. Therefore a smaller sized Ni powder needs to be used for coating in order to increase the film density. Low temperature sintering is also needed in order to prevent coverage shrinkage. Reducing the size of multilayer ceramic capacitors (MLCCs) as well as increasing their capacitance is a predominant issue for capacitors now in use; the thickness of the dielectric layers is continuously decreasing [3]. The reduction of the dielectric layer thickness causes an increase in the electric field strength applied to the dielectric layers of MLCCs, and so the reliability of the dielectric materials under large DC electric fields has become a major issue [4-7]. This issue has become one of the most serious problems in fabricating highly reliable MLCCs as well as the issue of the degradation that occurs in the insulation resistance (IR) [8-9]. In order to study this, we prepared X7R MLCCs with a capacitance of 1 μF and a rated voltage of 25 V and investigated the electrical properties regarding the MLCC's high temperature insulation resistance (IR)

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using a sintering condition test. In addition, attempts were made to use paste made from 200 nm and 400 nm Ni powders in order to compare the MLCC properties.

Experimental

Additives MgO(IMA, 99.9%), Dy_2O_3(Rhodia, 99.5%), Mn_3O_4(Suk-Kyung AT, MN001), $BaCO_3$(Sakai, BW-KHR20) and SiO_2(AEROSIL®, AEROSIL OX50) were added to the basic $BaTiO_3$ material (Samsung Fine Chemicals, SBT03). The mixture was weighed to an appropriate value of 0.1-2 mol in order to form a slurry by employing a bead mill (DnTek, Nanoset Mill) using 0.3 mmΦ beads wherein the solvent and dispersant (BYK103) were first mixed. Subsequently, a binder (BH-3, S/R = 10) was added and milled in order to make the final slurry. A 2.2 μm sheet was coated using a die coater. A paste made from 400 nm Ni (Smittomo YH-6) powder and a paste made from(200 nm) Ni (JFE, NFE201S) powder were subsequently coated on the sheet. The green chip (G/C) was manufactured by compressing 170 multi-layer at a hydraulic pressure of 1200 pressure in MPa. The manufactured G/C was then burned out in air for over 40 hours at 240-260 °C followed by a second burn out for 5 hours at 700-800 °C for debinding. Sintering was carried out at 1230-1270 °C employing a 0.05% hydrogen atmosphere at heating rates of 20-60 K·minute^{-1}. An SEM (Jeol, JSM-840) was used to check the ceramic's degree of sintering and the Ni internal electrode. An optical microscope was used to check the bending characteristics of the internal electrodes. The MLCCs were manufactured by coating Cu paste onto the edges in order to measure the dielectric properties. The capacitance and dissipation factor were measured using an Agilent 4284A LCR meter. The insulation resistance was measured using an Agilent 4339B LCR meter after charging the capacitor for 60 seconds at a rated voltage of 6.3 V.

The MLCC reliability was tested by evaluating the high temperature insulation resistance value at 150 °C at 10 minute time intervals with a rated voltage increase until the insulation resistance was below 10^5 Ω.

Results and Discussion

The sintering condition tests

The sintered green chips [1.0 mm × 0.5 mm] were polished in the L direction in order to reveal the internal electrode cross section. The MLCCs sintered under different conditions were mounted to check the change with respect to the step difference between the available area and the margin area. The final product was then polished for optical microscopic analysis. Fig. 1 illustrates the differences in the internal electrode bending. Table 1 enumerates the MLCC sintering conditions.

Fig. 2 shows the results with respect to the sintering conditions of the MLCCs. An increase in the sintering temperature or heating rate caused an increase in the change.

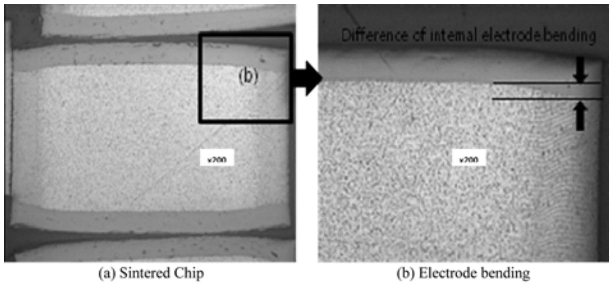


Fig. 1. The differences in the internal electrode bending.

Table 1. The Sintering Conditions

	Sintering condition		
Sintering Temperaure[°C] at 60 K·minute^{-1}speed	1230	1250	1270
Sintering Speed [K·minute^{-1}] at 1270 °C	20 K·minute^{-1}	40 K·minute^{-1}	60 K·minute^{-1}

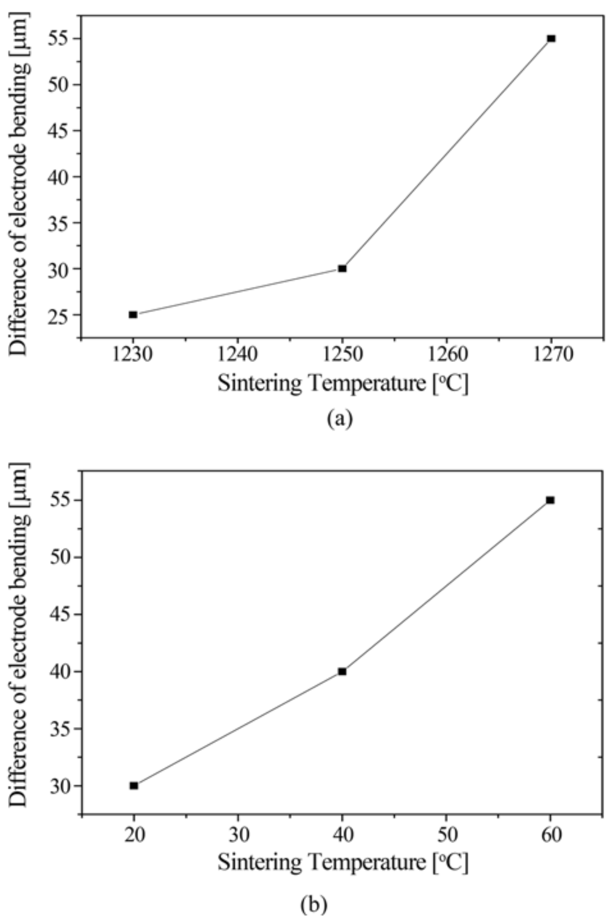


Fig. 2. The internal electrode bending caused by the sintering conditions: (a) sintering temperature, (b) sintering speed.

The MLCCs were sintered in a rapidly heating tunnel furnace [Noritake]. The sintering temperature and the heating rate were all controlled by the speed of the furnace movement. It is reasonable to state that in both cases the rate of heating was increased. Lewis *et al*. stated that

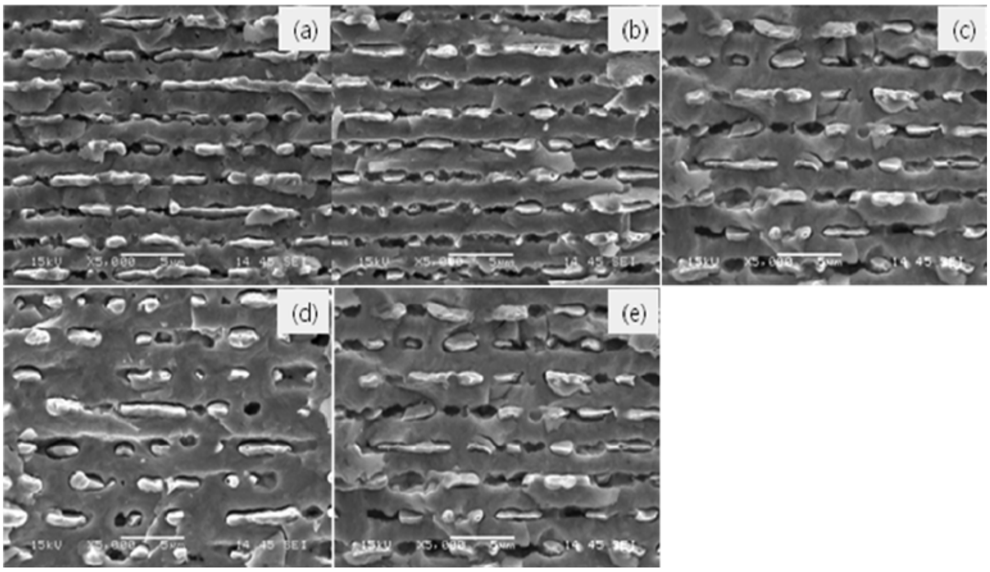
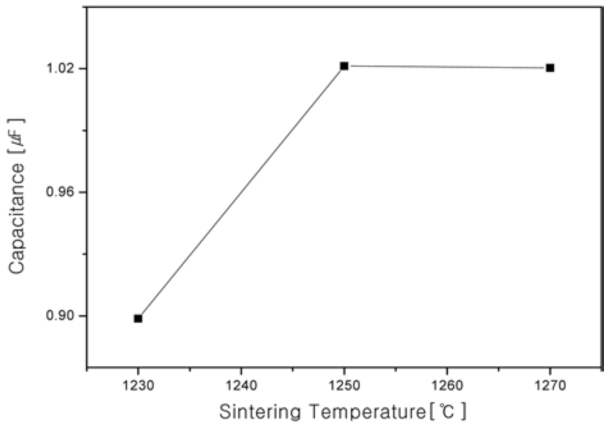
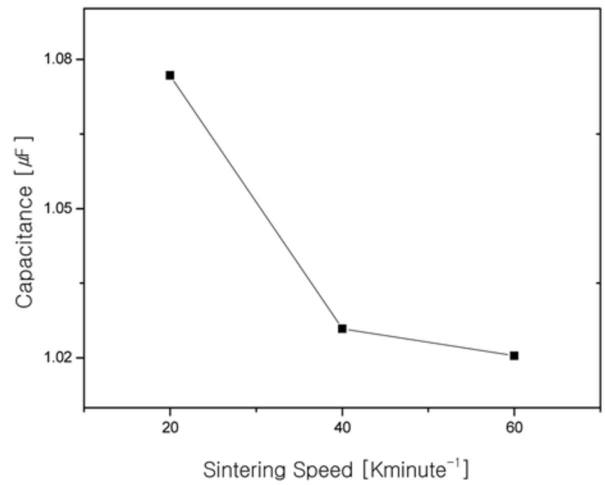


Fig. 3. The microstructure of the MLCCs under various sintering conditions: (a) 1230 °C, 60 K·minute^{-1}, (b) 1250 °C, 60 K·minute^{-1}, (c) 1270 °C, 60 K·minute^{-1}, (d) 1270 °C, 20 K·minute^{-1}, (e) 1270 °C, 40 K·minute^{-1}.

an increase in the sintering heating rate results in a decrease in the ceramic density, causing the maximum densification temperature to increase which has been explained to be related to xanthan [10]. Therefore, the difference in the amount of xanthan left in the internal ceramic and the xanthan in the cover causes electrode bending. Fig. 3 shows the SEM images of the chips' internal microstructure according to the sintering conditions. The ceramic was sintered at the increasing temperatures of 1230 °C, 1250 °C and 1270 °C at a fixed heating rate of 60 K·minute^{-1}, which caused an internal electrode connectivity decrease. The MLCC sintered at 1270 °C had an Ni internal electrode contraction with an increased ceramic thickness. Conversely, the internal electrode connectivity was improved when the sintering temperature was fixed at 1270 °C with the different heating rates of 20, 40, and 60 K·minute^{-1}. There was a severe internal electrode contraction for the MLCC run at the temperature of 1270 °C and the heating rate of 20 K·minute^{-1}, which is thought to be the effect of receiving the highest thermal energy. The ceramic sintering and the internal electrode connectivity were best under the 1250 °C, 60 K·minute^{-1} conditions. Fig. 4 shows the change in capacity with respect to the sintering conditions. When the heating rate was fixed at 60 K·minute^{-1} with an increasing sintering temperature, the capacity increased up to the temperature of 1250 °C. It can be surmised that sintering takes place until 1250 °C, whereas above that temperature a destructive interference occurs between the internal electrode disconnection (capacity decrease) and the ceramic sintering (capacity increase). In addition, when the sintering temperature was fixed at 1270 °C with an increasing heating rate the capacity decreased. There was a noticeable capacity decrease when the heating rate was increased from 20 K·minute^{-1} to 40 K·minute^{-1}. Sintering at 20 K·minute^{-1} results in much more heat energy,



(a)



(b)

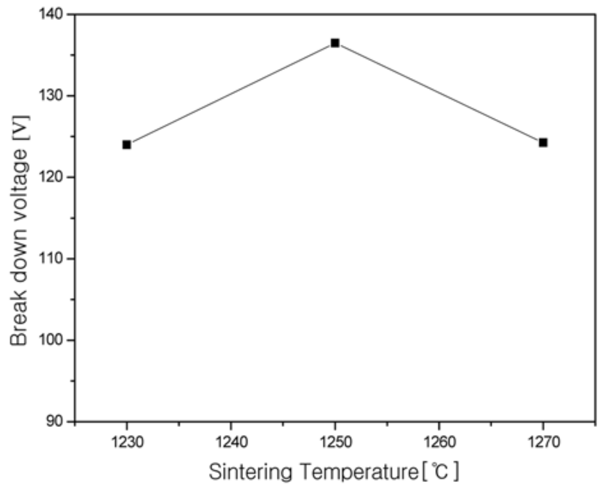
Fig. 4. The MLCC capacitance vs the sintering conditions: (a) sintering temperature, (b) sintering speed .

causing a poor internal electrode connectivity. However, the Dy-type grain growth dielectric properties are thought to be increased. Kum-Jin et al. have stated that Dy and BT are reactive with each other, causing the substitution of Ba or Ti into the BT lattice [11]. The good grain growth is caused by the small amount of energy required. Fig. 5 shows the breakdown voltage according to the sintering conditions. The ceramic with dense sintering (1250 °C, 60 K·minute^{-1}) had a 10% higher breakdown voltage compared to the less densely sintered ceramic (1230 °C, 60 K·minute^{-1}). There was also a decrease in the degree of internal electrode disconnection. This can be explained by the increase in the thermal energy causing the internal electrode contraction. At the sintered ceramic interface, enough shear stress remains that is not strong enough to cause a crack but starts a degradation when voltage is applied. At the sintering conditions of 1270 °C, 20 K·minute^{-1}, there was a 44.5% insulation voltage decrease compared to the sintering conditions of 1250 °C, 60 K·minute^{-1}.

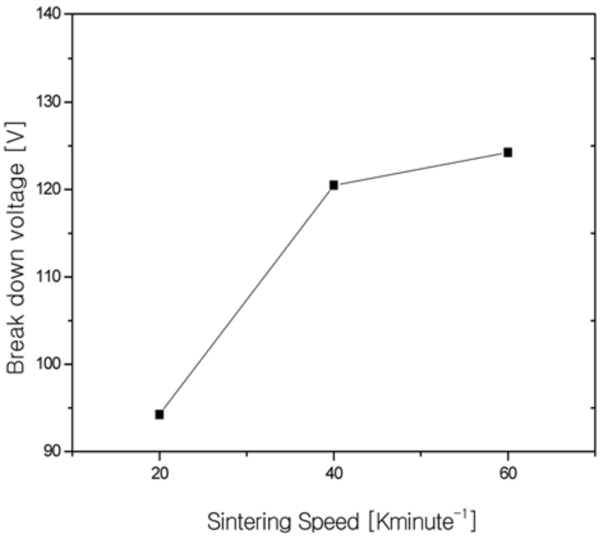
The MLCCs under each sintering condition were tested for reliability. Fig. 6 shows the insulation resistance at 125 °C with voltage steps of 6.3 V. The results were fine for all of the sintered chips except for the 1230 °C device. These results are very similar to the above-mentioned breakdown voltage results. Therefore, the high temperature IR voltage properties were fine for a relatively high sintering temperature and a good internal electrode connectivity. The best result was found for the 1250 °C, 60 K·minute^{-1} sintering condition. The good MLCC reliability was the result of adding the Dy, which delayed the IR deterioration in the thick shell structure of the core-shell [12].

The Ni powder size tests

Fig. 7 shows the fracture test of the MLCCs sintered at 1270 °C and 60 K·minute^{-1} using either 200 nm or 400 nm Ni powder. For the same sintering conditions, the product made from the 400 nm powder had an internal electrode disconnection. The thickness of the paste coating on the green sheet was almost the same for both the 200 nm (1.2 μm) and 400 nm (1.3 μm) devices. However due to the low film density (200 nm : 5.2 g/cm^3, 400 nm :

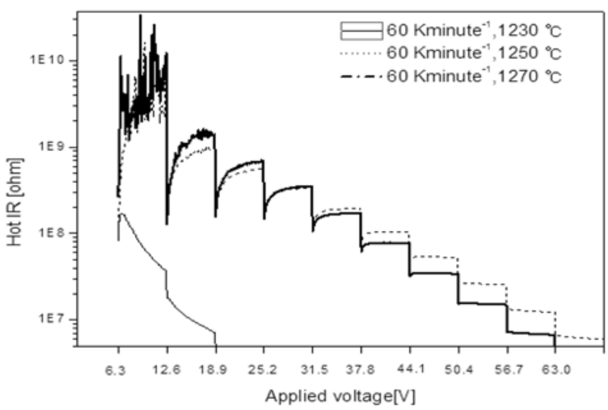


(a)

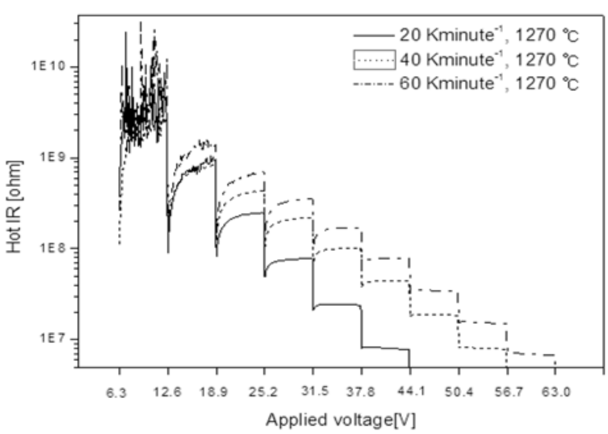


(b)

Fig. 5. The MLCC breakdown voltage vs the sintering conditions : (a) sintering temperature, (b) sintering speed.



(a)



(b)

Fig. 6. The changes in the hot IR for various sintering conditions: (a) sintering temperature, (b) sintering speed.

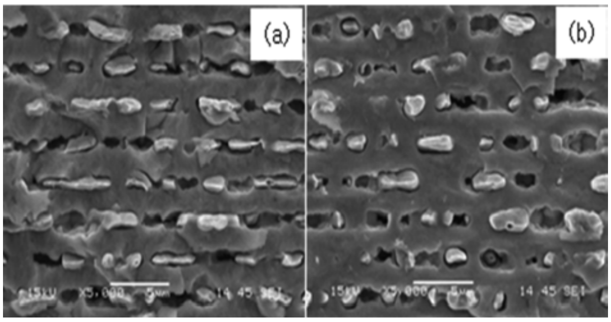
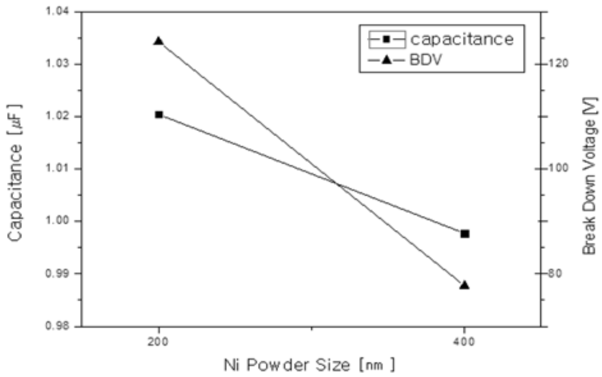


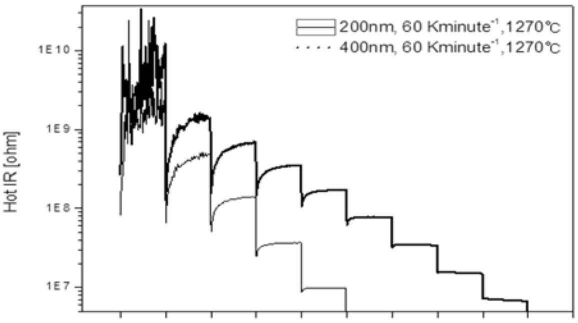
Fig. 7. The scaning electron micrographs of the fracture surfaces sintered at 1270 °C regarding the Ni powder size: (a) 200 nm Ni, (b) 400 nm Ni.

4.8 g/cm^3), the internal electrode thickness became partially irregular during the G/C compression and worsened during sintering.

Fig. 8 shows the effects of the capacity and the breakdown voltage of the high temperature IR for the different Ni powder sizes. The device using the 200 nm Ni powder had a 2% larger capacity and an internal resistance 60% higher than the 400 nm Ni powder device. The large capacity and breakdown voltage is considered to have come from the internal electrode coverage. The 200 nm Ni powder device had the high temperature IR value of 9 Vr and the 400 nm Ni powder device had a high temperature IR value of 5 Vr, both showing good high temperature IR values when the internal electrode connectivity was good. Polotai et al. investigated Ni ceramic interface dielectric properties. They found that a large interfacial area or a high diffusion of Ni in the ceramic degraded the dielectric properties. In this study, the MLCC using the 400 nm Ni powder had a small internal electrode coverage, causing an increase in the interface which had a negative effect on the dielectric properties and reliability [13].



(a)



(b)

Fig. 8. The dielectric properties and reliability regarding Ni Powder size : (a) the capacitance and break down voltage, (b) the hot IR.

Conclusions

The effects of the Ni powder size and the sintering conditions on the electrical properties, especially in regards to the reliability, on X7R multilayer ceramic capacitors (MLCC) possessing a Ni internal electrode and thin layers were investigated. This research also used paste made from 200 nm and 400 nm Ni powders in order to compare the MLCC properties.

An increase in sintering temperature or heating rate caused an increase in the electrode bending. The MLCCs were sintered in a rapidly heating tunnel furnace [Noritake]. The sintering temperature and heating rate were all controlled by the furnace movement speed. It is reasonable to state that in both cases the rate of heating was increased. Therefore, the difference in the amount of xanthan left in the internal ceramic and the xanthan in the cover causes electrode bending. The ceramic having dense sintering (1250 °C, 60 K·minute^{-1}) had a 10% higher breakdown voltage compared to the less densely sintered ceramic (1230 °C, 60 K·minute^{-1}). In addition, there was a decrease in the degree of internal electrode disconnection. This can be explained by the increase of thermal energy causing internal electrode contraction. For the sintered ceramic, a resulting shear stress remains that is not strong enough to cause a crack but enables degradation when a voltage is applied. At the sintering conditions of 1270 °C, 20 K·minute^{-1}, there was a 44.5% insulation voltage decrease compared to the sintering conditions of 1250 °C, 60 K·minute^{-1}. Therefore, the high temperature IR voltage properties were fine for a relatively high sintering temperature and good internal electrode connectivity. The best result was for the sintering condition of 1250 °C, 60 K·minute^{-1}. The good MLCC reliability is attributed to the added Dy, which delayed the IR deterioration in the thick shell structure of the core-shell. The device using 200 nm Ni powder had a 2% larger capacity and an internal resistance 60% higher than the 400 nm Ni powder device. The high capacity and breakdown voltage is considered to have come from the internal electrode coverage. The device using the 200 nm Ni powder had a high temperature IR value of 9 Vr and the device using the 400 nm Ni powder had a high temperature IR value of 5 Vr, both showing a good high temperature IR value when the internal electrode connectivity was good. In this study, the MLCC using the 400 nm Ni powder had a small internal electrode coverage, causing an increase in the interface which had a negative effect on the dielectric properties and reliability.

This research studied the effects of sintering conditions and Ni powder size in an MLCC's dielectric properties and reliability.

(1) An increase in the heating rate during sintering increased the internal electrode coverage but did not increase the capacity.
(2) An increase in the internal electrode connectivity increased the breakdown voltage and the high temperature IR reliability.
(3) The fine Ni powder was good for the dielectric properties and reliability.

References

1. R. Waser, T. Baiatu and K.H. Hardtl, J. Am. Ceram. Soc. 73 (1990) 1645-1990.
2. R. Merkle and J. Maier, Phys. Chem. Chem. Int. 5 (2003) 2297.
3. Z.L. Gui, Y.L. Wang and L.T. Li, Ceram. Int. 30 (2004) 1275-1278.
4. G.Y. Yang, E.C. Dickey, C.A. Randall, D.E. Barber, P. Pinceloup, M.A. Henderson, R.A. Hill, J.J. Beeson and D. Skamser, Jpn, J. Appl. Phys. 96 (2004) 7492-7499.
5. R. Waser, J. Am. Soc. 73 (1990) 1645-1653.
6. J.L. Cao, X.H. Wang, N.X. Zhang and L.T. Li, J. Am. Soc. 86 (2003) 1856.
7. X.H. Wang, X.Y. Deng, H.L. Bai, H. Zhou, W.G. Qu, R. Chen and L.T. Li, J. Am. Soc. 89 (2006) 438-443.
8. T. Tsurumi, M. Shono, H. Kakemoto, S. Wada, K. Saito and H. Chazono, Jpn J. Appl. Phys. 44 (2005) 6989-6994.
9. T. Nomura, N. Kawano, J. Yamamatsu, T. Arashi, Y. Nakano and A. Sato, Jpn. U. Appl. Phys. 34 (1995) 5389-5395.
10. A.C. Lewis, D. Josell and T.P. Weihs, Scr. Mater., 48[8] (2003) 1079-1085.
11. K.-J. Park, C.-H. Kim, Y.-T. Kim and K.-H. Hur, Journal of the Korean Ceramic Society, 46[2] (2009) 181-188.
12. A.V. Polotai, G.Y. Yang, E.C. Dickey and C.A. Randall, J. Am. Ceram. Soc., 90[12] (2007) 3811-3817.
13. A.V. Polotai, I. Fujii, G.Y. Yang, E.C. Dickey and C.A. Randall, J. Am. Ceram. Soc., 91[8] (2007) 2540-2544.