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Residual Stress of Multilayer Ceramic Capacitors with Ni-Electrodes (Ni-MLCCs)

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The residual stress of multilayer ceramic capacitors (MLCCs) has been studied. The capacitance decreased significantly under external compressive stress applied to MLCCs in the thickness direction, on the other hand, the capacitance increased under external stress in the width direction. These capacitance changes depended on the number of dielectric layers in MLCCs. The compressive residual stress at the surface of MLCCs has been shown by X-ray diffraction (XRD) analysis. The stress increased with the number of dielectric layers in MLCCs. Moreover the tensile stress was confirmed in the thickness direction of MLCCs by XRD analysis also. Therefore the dependence of electrical characteristics dependence on the number of dielectric layers, *i.e.*, apparent dielectric constant, temperature dependence of capacitance, and aging deterioration can be explained by the residual stress. [DOI: 10.1143/JJAP.42.6041]

KEYWORDS: MLCCs, residual stress, dielectric constant, capacitance change, capacitance aging

1. Introduction

The high capacitance and miniaturization of multilayer ceramic capacitors (MLCCs) have been rapidly progressing in response to the demand for the downsizing and high efficiency of electronic devices. A greater number of thinner dielectric layers is highly desired for MLCCs. Ni is the preferred internal electrode material owing to its cost advantage with high capacitance. However, Ni is easily oxidized, so that the Ni-MLCCs must be fired in a reducing atmosphere. Therefore, many studies have been carried out to develop the reduction-resistant dielectrics and to attain the high capacitance Ni-MLCCs with high reliability.[1–9] Ni-MLCCs have already been manufactured, in which the dielectric layer thickness is almost the same as that of the internal electrode, 1 μm, and the number of dielectric layers is over 300. The market for these Ni-MLCCs is becoming more widespread. However, since different materials, *i.e.*, dielectrics and internal electrode metal, must be cofired, it is difficult to reduce the thickness and increase the number of layers in MLCCs. The defects often appear because of the difference between the properties of dielectrics and the internal electrode, such as density, thermal expansion and other physical differences. Even if defects are not generated, it is expected that residual stress remains in MLCCs. Therefore, to achieve high capacitance, it is critical to solve this problem of residual stress. In the previous paper, the authors reported the existence of the residual stress in MLCCs and proposed a means of estimating the residual stress.[10–12] The purpose of this present paper is to clarify the effect of the residual stress on the electrical characteristics using MLCCs with different numbers of identical dielectric layers.

2. Experimental Procedure

In this study, $BaTiO_3$-based Ni-MLCCs with X7R characteristics were employed for the experiments. The dielectric sheets with printed Ni internal electrodes were laminated and pressed, which was followed by firing in a reducing atmosphere at 1200–1300°C. The shape of MLCC was 3216 type (3.2 mm length by 1.6 mm width). The numbers of effective dielectric layers in MLCCs were 10, 50, 100 and 200. These were prepared to confirm the effect of the number of dielectric layers. The thickness of the dielectric layer is 3 μm after firing in all MLCCs independent of the number of dielectric layers. For comparison, the dielectric-only-body without internal electrode and of identical shape as MLCC was also fabricated.

The residual stress was estimated using X-ray diffraction (XRD). X-rays were applied to the surface of the MLCCs, the residual stress was calculated from the shift of the peak of $BaTiO_3$ (310). The internal stress was also estimated by XRD using polished MLCCs.

The capacitance and temperature dependence at 1 kHz with 1 Vrms were measured using an Impedance analyzer (HP-4284A). The apparent dielectric constant was calculated from that capacitance.

In order to examine the external stress on capacitance, the capacitance was measured with a load on the MLCCs using a hydraulic press. The capacitance change to compressive stress and its temperature dependence under external stress were measured. The capacitance aging under no dc field at room temperature was also measured.

3. Results and discussion

3.1 *Effect of the number of dielectric layers on the dielectric constant*

The capacitance is the most basic characteristic of capacitors. With the thinning of the dielectric layers and the increase in their number, it is known that the apparent dielectric constant calculated from the capacitance increases and the temperature dependence also increases, even though identical dielectric layers are used. However, there seems to be no established explanation for this. The electric field has been named as one of the causes of the increase in dielectric constant with thinner dielectric layers.[13] Figure 1 shows the temperature dependence of the apparent dielectric constant from −55°C to 160°C with various numbers of dielectric layers. The dielectric constant increased with increasing number of dielectric layers, although the electric field condition and the dielectric thickness remained the same. Therefore, this change in dielectric constant cannot be explained by the electric field. The diffusion of Ni to the dielectrics from the internal electrodes was then suggested as a possible cause and the effect of Ni addition to the dielectric was investigated.[10] However, no effect on the increase in the

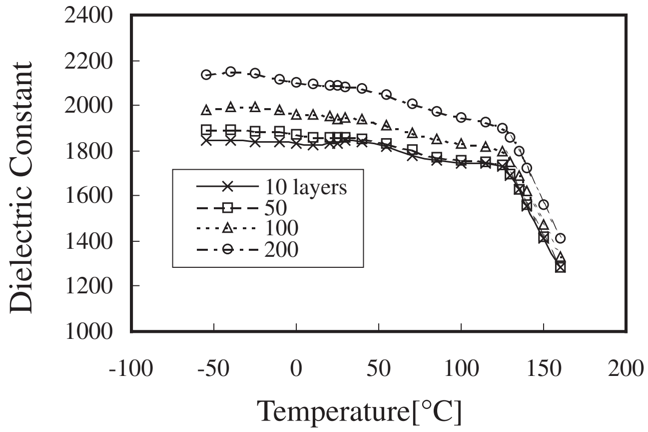

Fig. 1. Influence of the number of dielectric layers on the temperature dependence of apparent dielectric constant under 1 kHz with 1 Vrms.

dielectric constant was found. Here we propose that residual stress is behind the increase in the dielectric constant with increasing number of dielectric layers, and investigate the effect of residual stress on the capacitance change in MLCCs with various numbers of dielectric layers.

3.2 *Effect of the external compressive stress on capacitance*

With the aim of elucidating the relationship between residual stress and electrical characteristics, the capacitance of MLCCs was measured under external compressive stress. Mass produced MLCCs with capacitance of 10 μF with 3216 case size were used for this experiment. The capacitance was measured while adding a load to the MLCC using a hydraulic press in both the thickness and width directions. Figure 2 shows the result of the capacitance change under external compressive stress. With the load on MLCC in the thickness direction, the capacitance significantly decreased. On the other hand, the capacitance slightly increased with load in the width direction. Figures 3(a) and 3(b) show the temperature dependence of capacitance under external stress. The tendency does not depend on the temperature, that is, the capacitance decreases with the load in the thickness direction and increases in the width direction

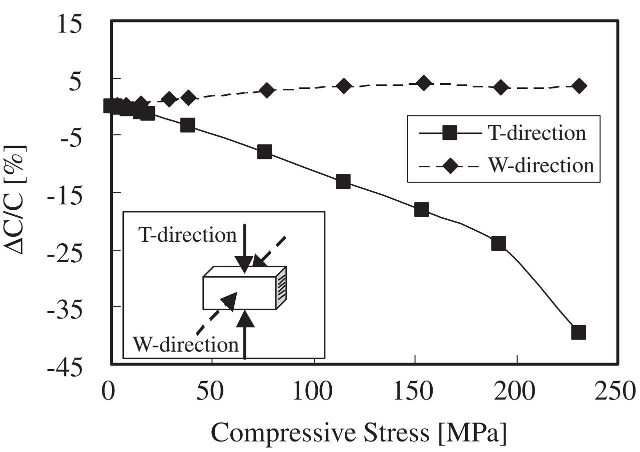

Fig. 2. Effect of the external compressive stress on the capacitance change of MLCCs(C3216JB106K).

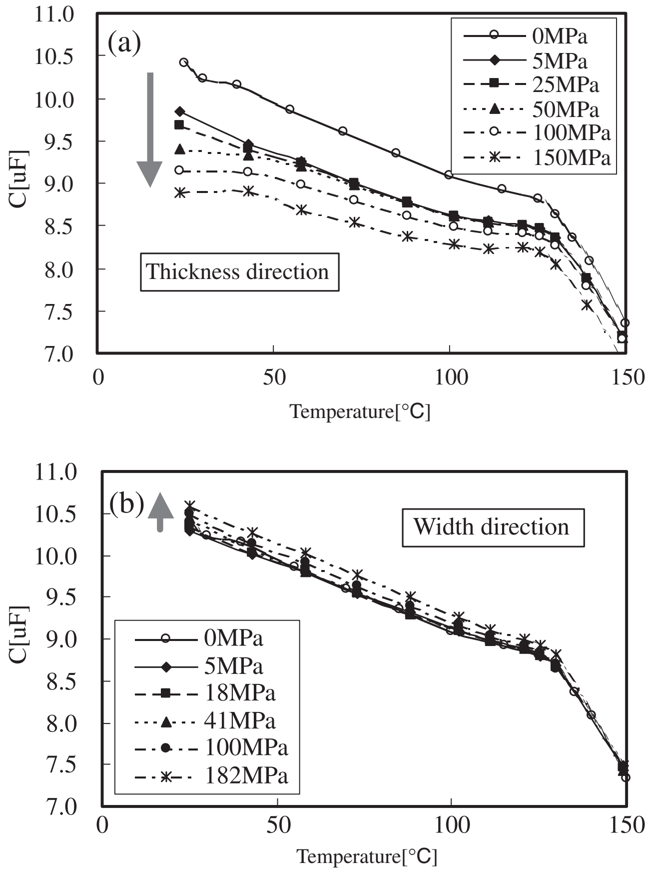

Fig. 3. (a) Effect of the external stress in the thickness direction on the temperature dependence of capacitance. (b) Effect of the external stress in the width direction on the temperature dependence of capacitance.

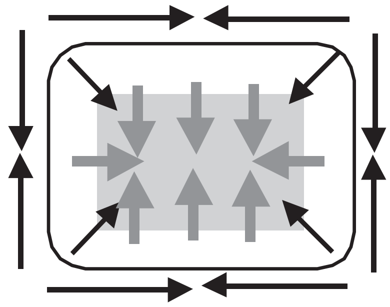

Fig. 4. Schematic of residual stress in MLCCs.

regardless of the temperature. The ratio of capacitance change decreases with increasing temperature. The Curie point is not shifted by external stress.

Figure 4 shows the schematic of residual stress in MLCCs. The source of the residual stress is expected to be the difference in the shrinkage behavior during firing and the discrepancy of the thermal expansion coefficient between the Ni internal electrode and the dielectrics. The authors have previously reported that the addition of sintering aids to dielectric material could decrease the sintering temperature of dielectrics to fit the Ni shrinking temperature, but it could not decrease the residual stress.[11] Table I shows the thermal expansion coefficient of Ni and dielectrics in a reducing atmosphere. It is hypothesized that this difference is the

Table I. Thermal expansion coefficient in reducing atmosphere from 200 to 1200°C.

	10^{-6}/deg
Ni	7.3
$BaTiO_3$-based	12.6

source of the residual stress. It is considered that the tensile stress increases in the thickness direction with increasing number of layers.

It also seems that this external compressive stress on MLCCs in the thickness direction cancels the residual stress in MLCCs; conversely, the external compressive stress in the width direction enhances the internal tensile stress in the thickness direction of MLCCs. It is thought that the stress perpendicular to the electric field increases the capacitance, whereas the stress in the same direction as the electric field decreases the capacitance.

3.3 *Estimation of residual stress by XRD analysis*

X-rays were applied to the top surface (length-width area) of the MLCCs, and the residual stresses in the length direction were analyzed, as shown in Fig. 5. The residual stress of the dielectric-only body was almost zero. Similarly, −53 MPa was calculated for the MLCC with 10 layers and −430 MPa for 200 layers. In general, "+" stands for tensile stress and "−" denotes compressive stress. Therefore, it is confirmed that compressive stress exists on the surface of MLCCs and that compressive residual stress increases with increasing number of dielectric layers.

To examin the internal stress of MLCCs, the MLCCs with 200 effective layers were lapped and polished from the side to the center. The lapped thicknesses were 0.1 and 0.7 mm. In the case of the lapped thickness of 0.1 mm, only the margin area was eliminated, and the Ni electrode could not be seen on the lapped surface. The thickness of 0.7 mm is almost half the width of MLCCs. The X-rays were applied to the lapped surfaces and the residual stresses in the thickness direction were estimated. Figure 6 shows the effect of lapping thickness on the residual stress. The unlapped MLCCs and only the margin-eliminated MLCCs show almost the same residual compressive stresses. Accordingly, there is no effect of lapping. With the lapping of half the MLCC thickness, tensile stress was observed. Therefore, there is tensile stress in MLCCs with 200 effective layers in the thickness direction. It is regarded that the tensile stress in the thickness direction equals the external stress in the width direction. Figure 2 shows that external stress in the width direction increases the capacitance. Therefore, tensile stress in the thickness direction increases the capacitance. Consequently, the increase in the apparent dielectric constant of MLCCs with increasing number of layers, as shown in Fig. 1, is attributed to the residual tensile stress in MLCCs.

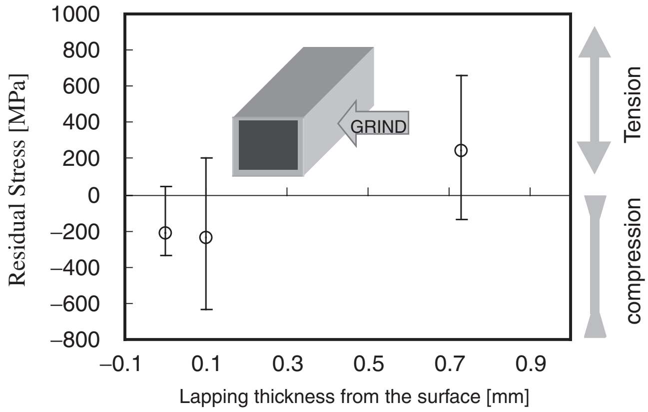

Fig. 6. Effect of the lapped thickness on the residual stress at the surface of MLCCs in the thickness direction.

3.4 *Dependence of capacitance change on number of dielectric layers under external stress*

The effect of external stress on capacitance change in the width direction with various numbers of dielectric layers has been investigated. Compressive stresses of 10, 50, and 100 MPa were added and the capacitance changes were compared. Figure 7 shows the dependence of capacitance change on the number of dielectric layers. With increasing number of dielectric layers, capacitance change under external stress decreased. It is thought that the capacitance had already been changed by the internal residual stress in MLCC with many layers before the external stress was added. Therefore, the capacitance of MLCCs with many layers was only slightly changed by the external stress.

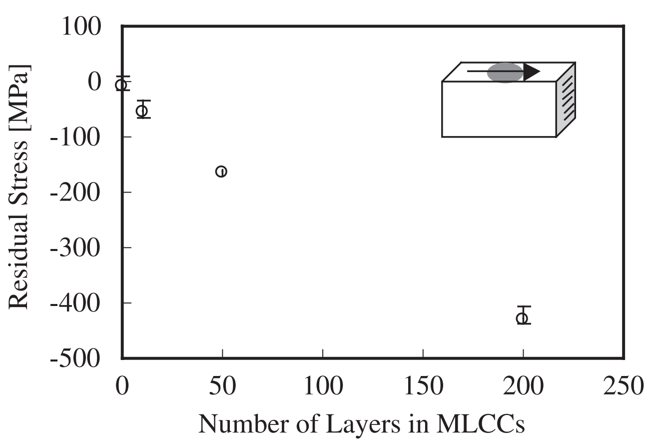

Fig. 5. Change in residual stress in the length direction at the surface of MLCCs as a function of the number of dielectric layers.

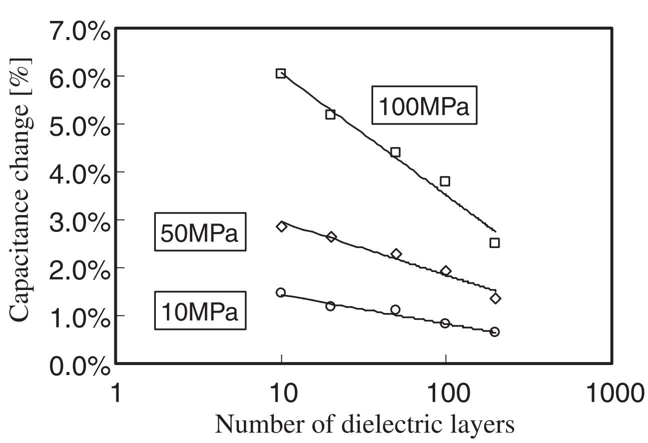

Fig. 7. Effect of the number of dielectric layers on the capacitance change under external stress in the width direction.

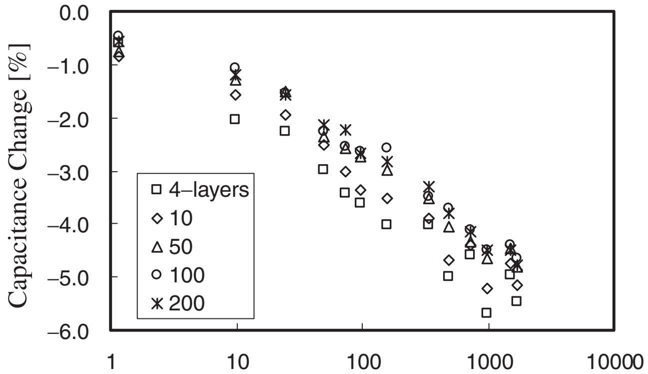

Fig. 8. Capacitance aging behavior of MLCCs with various numbers of dielectric layers at room temperature.

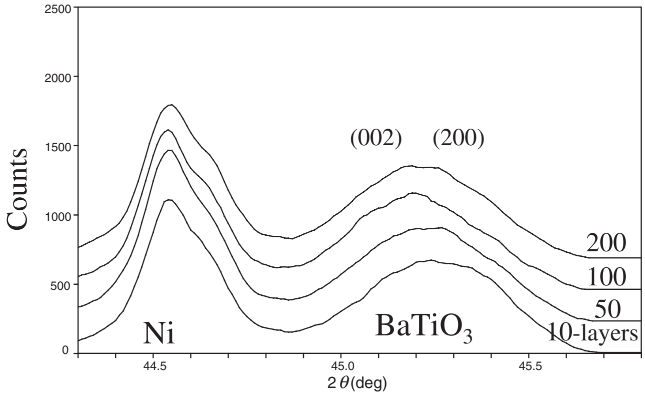

Fig. 9. X-ray profiles at the lapped surface in the center of MLCCs with different numbers of dielectric layers.

3.5 Capacitance aging

To clarify the effect of residual stress on capacitance, capacitance aging under no dc field at room temperature was measured on MLCCs with various numbers of effective active layers. Twenty-four hours after heat treatment at 150°C for 1 hour, the initial value of capacitance was measured. At a fixed time after the heat treatment, the capacitance was measured, and the capacitance change from the initial value was calculated. Figure 8 shows the effect of the number of dielectric layers on capacitance aging. It was found that the capacitance aging deterioration significantly depends on the number of dielectric layers. It decreased with increasing number of dielectric layers. The results have already shown that the residual stress in MLCCs increased with increasing number of layers. Therefore, Fig. 8 is interpreted to mean that capacitance aging decreases with increasing residual stress. Well-known factors affecting capacitance aging are internal bias field, space charge effect, lattice defect, mechanical stress, and domain wall pinning.[14–18] Figure 8 indicates that the increasing residual stress with increasing number of dielectric layers suppresses capacitance aging. The mechanical stress is one of the reasons for capacitance aging. The relationship between residual stress and capacitance aging should be examined further.

3.6 X-ray diffraction profiles of MLCCs with different number of dielectric layers

X-ray profiles of MLCCs with different numbers of dielectric layers were compared in (200) and (002) in $BaTiO_3$. Figure 9 shows the layer number dependence of the X-ray profiles at the lapped surface in the center of MLCCs, which has already been explained in Fig. 6. The compositions of these MLCCs are that of the $BaTiO_3$-based system, and the peaks of (200) and (002) are not split but pseudo-cubic. The peak-tops shift to low angles whom an increasing number of dielectric layers is observed. Accordingly, the lattice parameter increases with increasing number of dielectric layers. Therefore, this increase in lattice constant can explain the increase in the apparent dielectric constant with increasing number of dielectric layers. The c-axis orientation is expected from the tensile stress in the thickness direction.

4. Conclusions

The residual stress increased with increasing number of dielectric layers of MLCCs. The electrical characteristics were changed according to the increasing number of dielectric layers.

1) The apparent dielectric constant increased.
2) The capacitance change decreased under external stress in the width direction.
3) The capacitance aging decreased.

The lattice parameter of $BaTiO_3$ increased with increasing number of dielectric layers. Furthermore the tensile stress was confirmed to exist in the thickness direction of MLCCs. Therefore, the dependence of these electrical characteristics on the number of dielectric layers can be explained well by the enhanced residual stress in MLCCs.

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