ELSEVIER
Journal of Power Sources 60 (1996) 199–203
JOURNAL OF POWER SOURCES

Reliability of multilayer ceramic capacitors with nickel electrodes

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Received 4 January 1995

Abstract

The reliability of multilayer ceramic capacitors (MLCCs) with Ni internal electrodes has been studied from the viewpoint of partial oxygen pressure (P_{O_2}) during firing. It is shown that the load-life time of the insulation resistance (IR) was prolonged by firing under low P_{O_2}, annealing after firing, and the addition of dopants. It is also shown that the generation of oxygen vacancies led to the degradation of IR. Annealing treatment for the oxidation of the dielectric body accelerates the dielectric aging of MLCCs. It is found that the appropriate control of the P_{O_2} during firing can improve the reliability of MLCCs with Ni electrodes to a level as high as that of MLCCs with precious metal electrodes. Thus, we have developed an MLCC with Ni electrodes that features high reliability and a large capacitance of 10 μF for the Y5V characteristic and 4.7 μF for the X7R characteristic, both in the case of the C3216 (3.2 mm × 1.6 mm × 1.4 mm) form.

Keywords: Multilayer ceramic capacitors; Nickel electrodes; Degradation; Aging; Reliability

1. Introduction

Keeping up with the trend in miniaturization of electronic components, the demand for MLCC has grown because of the large capacitance despite its small size. MLCCs consist of alternately thin dielectric layers and internal electrode layers in one body, and both ends are terminated by external electrodes. Capacitance can be increased with thinning the dielectric layers and increasing the number of dielectric layers. So far, the majority of MLCCs have employed a Pd internal electrode, an Ag external electrode, and barium titanate based dielectric materials. While precious metals have been conventionally used as the electrode material, MLCCs that use Ni, base metal, for the internal electrode have been successfully developed to meet the growing need for low cost capacitors.

Dielectric layers are made thinner and the number of these layers has been increased in order to meet the needs for MLCCs being smaller in size but providing large capacitance. The cost of internal electrodes has, as a result, becomes a greater part of the total cost. Therefore, if Ni, a base metal, can be used as the internal electrode, it becomes a very effective means for lowering production cost. An Ni internal electrode is, however, easily oxidized during firing under ambient conditions. Firing should be therefore carried out in a reducing atmosphere using a reduction-resistive dielectric material. These are the major features of the MLCCs with Ni electrodes. When a reduction-resistive material is used and fired in a reducing atmosphere, the capacitors with internal Ni electrodes can provide initial characteristics similar to those provided by capacitors that use Pd as the internal electrode. Major problems involved regarding the reliability of such capacitors are: (i) a short lifetime of IR under a highly accelerated life test; (ii) aging of the capacitance, and (iii) the reliability problems such thermally-induced cracking, caused by the discrepancy in the thermal expansion coefficient between the electrodes and dielectrics, is common to all kinds of ceramic capacitors.

The authors have reported some papers on the reliability of the MLCCs with Ni internal electrodes. As a serial report of this program [1–17], the present paper focuses on the reliability of MLCCs with Ni electrodes, with special attention to P_{O_2} firing.

2. Experimental

The dielectric materials employed in this work are those with an Y5V characteristic whose main composition is $[(Ba_{1-x}Ca_x)O]_m[(Ti_{1-y}Zr_y)O_2] + aSiO_2$, where $x = 0.004$, $y = 0.18$, $m = 1.004$ and $a = 0.1$ wt.% with 0.2 wt.% each of MnO and Y_2O_3 added, and those with an X7R characteristic whose main composition is $BaTiO_3$ (95 mol%) + $SrTiO_3$ (3 mol%) + $Ba_{0.4}Ca_{0.6}SiO_3$ (2 mol%) with MnO (0.375 mol%) and Nb_2O_5 (0.05 mol%) added. These dielectric material powders were well mixed with an acrylic binder

SSDI 0378-7753(95)02283-1

solution. Then, green sheets were cast using these slurries by so-called doctor-blade method. After Ni electrodes were printed on these green sheets, they were laminated and stacked. Then they were cut to green chips. The chips were then heated in air at 300 °C for 2 h in order to eliminate the binder. Then they were fired under the following conditions: $P_{O_2} = 10^{-11}$ to 10^{-13} MPa and the temperature between 1250 and 1350 °C. After firing, they were annealed in order to oxidize the dielectric body under the following conditions: $P_{O_2} = 10^{-6}$ to 10^{-19} MPa and the temperature between 900 and 1100 °C.

The IR life was tested in a highly accelerated life test (HALT) in which the acceleration was done by temperature and voltage stresses. The leakage current was measured in a high-temperature oven under voltage stresses. The IR lifetime was determined as the time needed to fall to the 10^6 Ω level. Capacitance aging under a d.c. field was evaluated by the following procedure. A voltage of 1.8 V/μm was applied at 40 °C for a certain period, then the voltage stress was removed. The capacitance was measured after aging for 24 h. The microstructure was observed by using scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM).

3. Results and discussion

3.1. Life of insulation resistance under highly accelerated life test

According to JIS (Japanese Industry Standard), the product of capacitance and resistance should be greater than 20 MΩ F, after the life test when applying 200% of the rated voltage at 85 °C for 1000 h. Highly accelerated life test (HALT), in which the samples under temperature and voltage stresses, is generally used in order to qualify the reliability of a large number of MLCCs in a short time. The accelerated life is well known to follow the empirical equation (1) [18]:

$$t_1/t_2 = (V_2/V_1)^N \exp[Es/k(1/T_1 - 1/T_2)] \quad (1)$$

where t is the mean time to failure, V the applied d.c. voltage, and T the absolute temperature. Suffix shows the measuring condition, 1 and 2. Es is the activation energy of the IR degradation, N the voltage acceleration factor, and k the Boltzmann constant. It has already been confirmed that the accelerated life is well correlated with those under conditions of the JIS or MIL-STD (Military standard) [19,20].

Table 1
The activation energy (Es) of the IR degradation of various MLCCs

Sample			Es	Applied voltage
Dielectric material	Internal electrode	Characteristics	(eV)	(V/μm)
$BaTiO_3$	Pd	Y5V	1.42	25
$BaTiO_3$	Pd	X7R	1.73	35
$BaTiO_3$	Ni	Y5V	1.42	10
$BaTiO_3$	Ni	X7R	1.51	20
Lead-based perovskite	Ag–Pd	Y5V	1.33	20

Table 1 shows the results of the HALT on several MLCCs, those using Pd internal electrodes, Ni internal electrodes, and those composed of relaxor material. The Pd capacitors have a longer life than Ni capacitors, even though it was measured under a greater electric field strength. In the case of Pd capacitors, the leakage current gradually increased with time, requiring a certain period before the breakdown. In the case of Ni capacitors, in contrast, the leakage current did not increase at all at the beginning, but abruptly and sharply increased after an induction period. The effect of P_{O_2} during firing on the IR life of MLCCs with Ni electrodes is shown in Fig. 1. The life was extended by lowering P_{O_2} during firing. In the case of high P_{O_2} firing, the life of the capacitors was short, and IR degraded in a similar way as the MLCCs with Pd electrodes, in which gradual deterioration of IR with time was observed.

Rawal and Chan [21] reported that IR degradation under HALT could be classified into two modes: avalanche breakdown (ABD) and thermal runaway (TRA). ABD refers to the sudden breakdown accompanied by an abrupt leakage of current. TRA refers to the breakdown which results from a gradual increase in the leakage current. Degradation modes may vary depending on the test conditions. ABD generally occurs when the test is accelerated by voltage. On the other hand, TRA generally occurs when the test is accelerated by temperature. Both ABD and TRA may be observed at the same time in some cases, depending on the test conditions.

Imperfections in ceramics can be generally classified into two categories, intrinsic and extrinsic factors. Intrinsic factors are electronic disorders, dislocations, grain boundaries, defects, etc. Extrinsic factors are delamination, cracks, voids, pores, etc. ABD is said to be caused by extrinsic factors and TRA to be caused by intrinsic factors. Rawal and Chan [21]

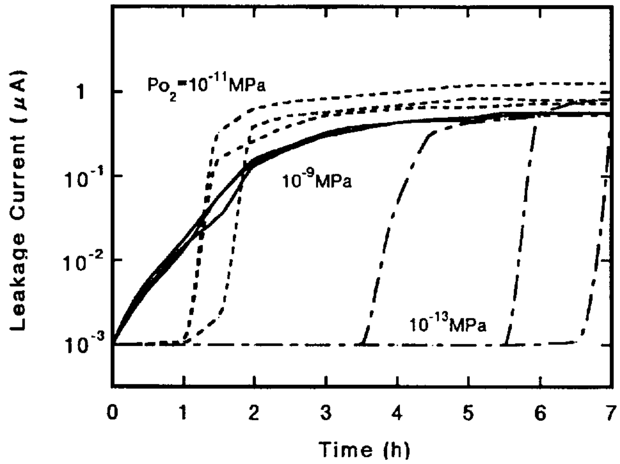

Fig. 1. Effect of oxygen partial pressure during firing on the variation of leakage current with time during highly accelerated life test. Three specimens were measured for each condition.

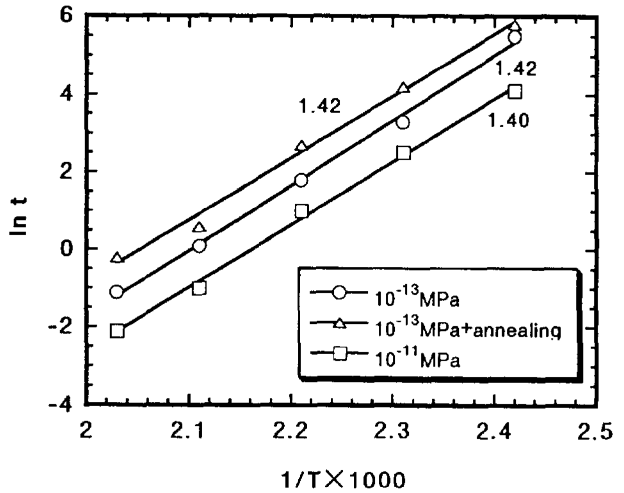

Fig. 2. Arrhenius plot of mean time to failure under highly accelerated life testing for conventional Ni electrode MLCCs.

reported *Es* values of 1.87 eV for TRA and 1.49 eV for ABD. The *Es* of the samples fired under the reducing atmosphere obtained in this work are in accordance with Eq. (1), see Fig. 2. Although the mode of IR degradation varied with the P_{O_2} during firing, the *Es* was about 1.4 eV in all cases. According to the classification proposed by Rawal and Chan, this indicates that the ABD mode, in spite that the time dependence of IR under HALT shows TRA mode.

3.2. Causes of IR degradation

On the degradation of IR, many investigations have been done and two major models are proposed: (i) the grain boundary model, and (ii) the reduction model [22–25]. Loh [26] suggested that the deterioration of the grain boundary under d.c. field was responsible for the IR degradation. In general, the electrical resistance of the grain boundaries is well known to be higher than that of grains. The grain boundary model supposes local breakdown of grain boundary caused by the high electrical field. Many studies suggested the electrolytic migration of oxygen vacancies. It is based on an injection of oxygen vacancies from the anode, which is accompanied by a reduction of dielectric oxide. Oxygen vacancies, which have a positive space charge, slowly diffuse towards the cathode. When the oxygen vacancies arrive at the cathode, the positive charge is neutralized by the Schottky emission.

In order to prolong the IR life of MLCCs with Ni electrodes under HALT, the effect of the processing parameters on the IR life has been studied. As mentioned above (Fig. 1), low P_{O_2} firing is effective to prolong the IR life. In such a condition, the dissociation of oxygen generates oxygen vacancies ($V_{\ddot{o}}$). This reaction can be expressed as follows, using the defect notation of Kröger–Vink [27].

$$Oo \rightarrow V_{\ddot{o}} + 2e + 1/2O_2 \quad (2)$$

The effect of annealing after firing on the IR life under HALT was investigated. Annealing was much effective to prolong the IR life [7]. The effect of P_{O_2} during annealing on the IR life is shown in Fig. 3. The higher the P_{O_2} during annealing, the longer is the IR life time. It indicates that the oxidation during annealing is effective for prolonging the IR life. However, annealing under P_{O_2} of 10^{-5} MPa or more causes oxidation of Ni and prevents its functioning as the electrode.

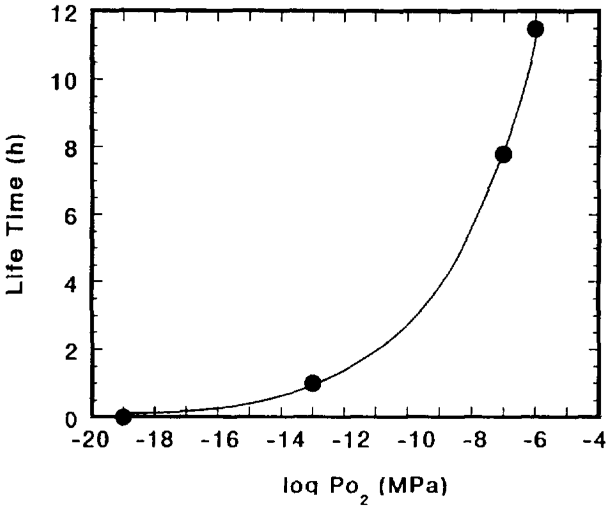

Fig. 3. Effect of oxygen partial pressure during annealing procedure on the life time at 200 °C, 10 V/μm; annealing procedure at 1000 °C for 3 h.

It is confirmed that the addition of a donor such as Y_2O_3 is effective in prolonging the lifetime of IR [12]. Cation vacancies are considered to be generated by the addition of a donor. These are assumed to compensate the oxygen vacancies that have been generated during firing in a reducing atmosphere, or acceptor doping, thus realizing a longer lifetime.

$$Y_2O_3 \rightarrow 2Y_{Ba''} + 3Oo + V_{Ba''} \quad (3)$$

$$V_{\ddot{o}} + V_{Ba''} \rightarrow \text{null} \quad (4)$$

These facts indicate that reducing the amount of the oxygen vacancies by annealing procedure or donor doping is of prime importance for prolonging the IR life. Combination of annealing and donor doping is much effective. This result supports the reduction model. That is, the oxygen vacancies generated during firing are assumed to be concentrated on the cathode under HALT, thus causing a bias electric field, and the current suddenly starts to flow as a result of the Schottky effect.

Even though the oxygen providing is effective in ensuring a long life, this does not explain why the lifetime is longer when the P_{O_2} is lower during firing. In order to explain the discrepancy, the microstructure of the MLCCs has been studied. As shown in Fig. 4, the lower the P_{O_2} during firing, the more Fe included as an impurity is concentrated in the Ni electrode. Fe and other impurities were enriched at the grain boundary in the case of firing under high P_{O_2}. If it is assumed that the impurities at the grain boundary diffuse and segregate in the area of the Ni electrode, then the lifetime of a capacitor fired under a high P_{O_2} would be shorter and its breakdown would follow the grain boundary model. On the degradation

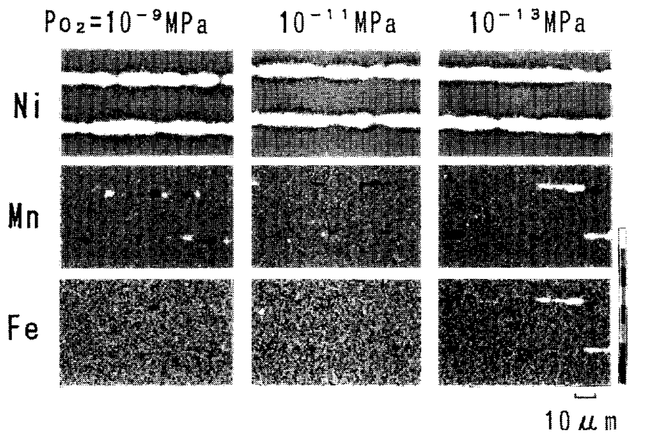

Fig. 4. Effect of oxygen partial pressure during firing on the microstructures.

Table 2
Representative characteristics of the newly developed MLCCs with Y5V characteristics

Type	C3216 (3.2 mm × 1.6 mm × 1.4 mm)
Rated voltage (V)	16
Number of layers	150
Thickness of layer (μm)	6.3
Capacitance (μF)	10.5
Dissipation factor (%)	4.9
Insulation resistance at 25 V d.c. (Ω)	2.7 × 10
Breakdown voltage (V)	368
Life time at 200 °C, 40 V d.c. (h)	32.5

of IR, both the reduction model and the grain boundary model are suggested in this work.

Using the techniques mentioned above for prolonging the IR lifetime, we have developed highly reliable MLCCs that feature a capacitance of 10 μF in a C3216 form (3.2 mm × 1.6 mm × 1.4 mm) with Y5V characteristics. Table 2 shows the electrical characteristics of the capacitor.

3.3. Capacitance aging

It is known that barium titanate shows dielectric aging [28,29]. Spontaneous polarization plays an important role in this phenomenon. When an electric field is applied, polarization remains even after the removal of the electric field, causing a decrease in the dielectric constant. The effect of P_{O_2} during firing on aging characteristics under the conditions of 40 °C and with a voltage of 1.8 V/μm was studied, see Fig. 5. Capacitance deterioration is stressed with the higher the P_{O_2} during firing.

It is well known that the dielectric aging could be suppressed by lowering the tetragonality of the perovskite structure, and by the so-called core–shell structure in which the electric field is concentrated to the phase of low dielectric constant [30]. Capacitance aging can be supposed as follows. High P_{O_2} during firing or annealing firing might introduce cation vacancies. This interpretation is not certain. Cation vacancies can easily move under the electric field, causing

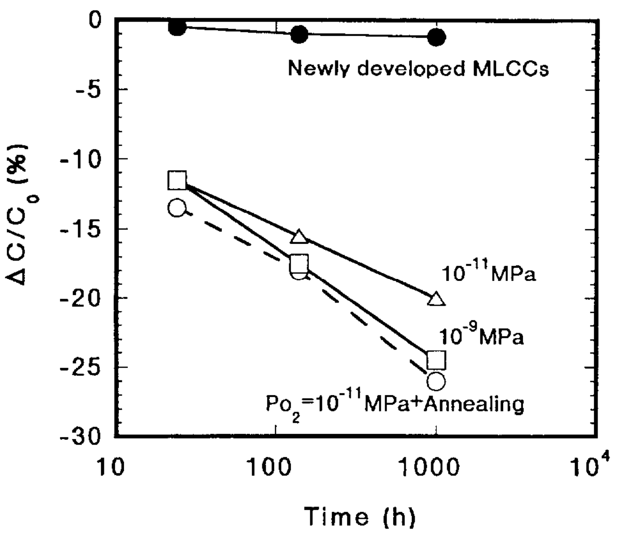

Fig. 5. Effect of oxygen partial pressure during firing on the aging behaviors of capacitance at 40 °C, 1.8 V/μm.

induced crystallographic anisotropy, and then the mobility of the domain wall decreases.

Although not shown here, capacitance aging was a strong function of MnO content [6]. Manganese ions, which are indispensable constituents for $BaTiO_3$-based dielectrics, are considered to induce a residual bias electric field. Based on the results mentioned above, we have newly developed highly reliable and high capacitance MLCCs with X7R characteristics of 4.7 μF in the C3216 form, as is shown in Table 3.

4. Conclusions

The reliability of MLCCs with Ni electrodes was studied from the viewpoint of the P_{O_2} during firing. Firing under a low P_{O_2} is effective in prolonging the load lifetime in the accelerated IR life test because the impurities in the grain boundary are concentrated at the surface of the electrode. This supports the grain boundary model. Annealing with some oxygen pressure after firing is also effective to prolong the life of the capacitor because it restricts the generation of oxygen vacancies. This supports the reduction model.

The generation of cation vacancies increases the dielectric aging in the capacitance. This seems to be attributable to the fact that cation vacancies migrate under an electric field, thus causing induced crystallographic anisotropy and stabilizing polarization.

MLCCs with Ni electrodes had been less reliable than MLCCs with precious metals such as Pd as the internal electrode. We also found, however, that the MLCCs could be made virtually reliable as MLCCs with Pd electrodes by controlling the P_{O_2} during firing and by appropriately designing the dielectric composition. Using these techniques, we have developed the MLCCs that feature a high reliability and a large capacitance of 10 μF with an Y5V characteristic and 4.7 μF with an X7R characteristic in the case of the C3216 form (3.2 mm × 1.6 mm × 1.4 mm).

Table 3
Representative characteristics of the newly developed MLCCs with X7R characteristics

Type	C3216 (3.2 mm × 1.6 mm × 1.4 mm)
Rated voltage (V)	6.3
Number of layers	270
Thickness of layer (μm)	3.9
Capacitance (μF)	4.7
Dissipation factor (%)	2.3
Insulation resistance at 25 V d.c. (Ω)	2.7×10^{8}
Breakdown voltage (V)	190
Life time at 200 °C, 64 V d.c. (h)	> 120
Capacitance aging after 1000 h at 40 °C, 6.3 V (%)	−9.0

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