Transactions of the Materials Research Society of Japan 32[4] 851-854 (2007)

Evaluation of Ni-MLCC and Fabrication of Ni Thin Electrode by used Ni Nano powder .

Ryosuke Ueyama, Tomohiro Ando ,Kunihito Koumoto*
Engineering 2 Department, Electronic Material Division, Daiken Chemical Corporation Limited.1-3-6 Imafuku-minami, Joto-ku, Osaka,536-0003 FAX:81-6933-9325 e-mail:ando@daiken-chem.co.jp
*Department of Molecular Design and Engineering, Graduate School of Engineering Nagoya University, Fro-cho Chikusa-ku Nagoya City,464-8603,FAX:81-52-789-3201 e-mail:g44233a@nucc.cc.nagoya-u.ac.jp

Abstract

In order to obtain thinner Ni electrode layers for MLCCs, $BaTiO_3$ organometal resinate was added into Ni paste which consisted of 100nm Ni powders. Ni electrode films were fabricated with the Ni paste added with $BaTiO_3$ organometal resinate, and sintering and electrical characteristics of the film were examined in the present study. The experimental results indicated that addition of $BaTiO_3$ organometal resinate remarkably suppressed the sintering of the Ni electrode films, i.e., no abnormal grain growth was observed on Ni electrode films with $BaTiO_3$ organometal resinate. In addition, MLCCs with 10stacked layers was experimentally fabricated. And the capacitance, the dielectric loss and insulating resistance of MLCCs were measured. The results indicate that even when the of $BaTiO_3$ organometal resinate added is, the electrical characteristics of the MLCCs are not impaired regardless of the nano-size of the Ni particles. An addition of $BaTiO_3$ organometal resinate was found to be extremely effective for obtaining thin electrode layers.

1. INTRODUCTION

The demand for multilayer ceramic chip capacitors (MLCCs) has been rapidly increasing, and smaller capacitors with larger capacitance have been introduced into the market. The capacitance is directly proportional to the dielectric constant and the number of dielectric layers, and inversely proportional to a thickness of dielectric layer. In order to achieve small-size capacitors with larger capacitance, it is required not only materials with larger dielectric constant, and a larger number of thinner dielectric layers, but also thinner electrode layers. From the viewpoint of fabrication of thinner electrode layers, we have studied on the synthesis of monodispersed Ni powder via pulverization of agglomerated particles and other methods.[1)-5)]

Recently, smaller particle size Ni powder has been required to realize thoroughly thinner electrode layers which are essential for production of smaller MLCCs. Our previous studies[6)-8)] revealed that sintering of Ni electrode films was remarkably suppressed for the electrode paste in which additives particles, generally $BaTiO_3$ particles, were occupied between Ni particles and at triangle position (three pockets) of Ni particles. The three pockets of Ni particles are 30nm in size for Ni powder with 100nm in particle size. This is much smaller than currently used $BaTiO_3$ additives which have approximately 0.1 μm or 50nm in particle size.

Therefore, we have used barium-titanate organometal resinate (BT resinate, hereafter) as an additive which has a similar composition to a dielectric green sheet. The experimental result[9) 10)] clarified that the BT resinate showed a significant effect on suppression of sintering of Ni electrode films. In this study, an influence of the Ni particle size on the shrinkage suppression effect of the BT resinate was examined for 100nm Ni powders. Furthermore, a MLCCs was fabricated and the electric characteristics of the MLCCs were evaluated in detail.

2. EXPERIMENTAL METHODS

2.1 Preparation and evaluation of electrode paste

Ni powder was used by sumitomo metal Mining Co. Ltd for the experiment. Figure 1 shows SEM images and a particle size distribution of the Ni powder. The Ni powder was pulverized to obtain monodispersed powder with 100nm in average particle size. In the pulverization process, n-hexane was used as a dispersion agent, and the flow velocity and flow length of Ni slurry were controlled by using a media mill during the wet pulverization.[2)]

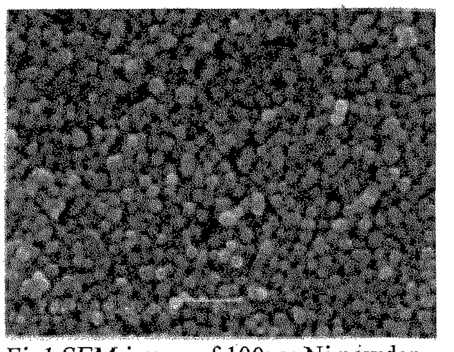

Fig1 SEM image of 100nm Ni powder.

BT resinate was added as a sintering inhibitor into pulverized Ni powders. And ethyl-cellulose (binder) and terpineol (solvent) were added to the mixture. The resultant mixture was kneaded to paste with a conventional kneader. In order to characterize a sintering property of the paste, shrinkage of Ni electrode films after firing was measured via the following procedure. A film of approximately 200 μm in thickness was formed on a polyethylene terephthalate (PET) film using an applicator and then dried for 1 h at 100°C. The dried film was peeled from the PET film and was cut into 20 mm diameter disks with a punch. The disks were fired with temperature increasing speed 3°C/min and maintained at temperatures ranging from 600 to 1300°C for 1 h in a reducing atmosphere consisted of 97% N_2 + 3% H_2. Shrinkage of the disks after firing was measured. A surface microstructure of the electrode films fired at various temperatures was observed by using a scanning electron microscope (SEM, JSM-6100, Nippon Denshi).

2.2 Fabrication of MLCCs

A dielectric paste was prepared from dielectrics with X7R characteristics. MLCCs were obtained from the dielectric paste by the doctor blade method, i.e., Ni electrode was printed on the dielectric green sheet. These processes were repeated 10 times. A Green sheet of the MLCCs with 10 stacked layers was fired under applied pressure and cut into 3.2 x 1.6 x 2.0 mm^3 (3216 type) in size.

The green MLCCs chips were degreased by heat treatment at 280°C for 8 h in air and then fired at 1315°C for 2 h in a strong reducing atmosphere (oxygen partial pressure $Po_2 = 10^{-13}$ MPa). The MLCCs chips were thoroughly heat-treated at 1000°C for 3 h under the oxygen partial pressure 10^{-6} - 10^{-7} MPa to re-oxidize the dielectrics in the MLCCs. The oxygen partial pressure was controlled with varying the H_2 to H_2O ratio in the N_2-H_2-H_2O gas mixture.

2.3 Evaluation of the electrical characteristics of MLCC

An evaluation of the electrical characteristics of the MLCCs was carried out as follows. A Cu terminal electrode (TCu-24G, Daiken Chemical Industry) was coated on the exposed surface of the internal electrode. The capacitance (Cp) and the dielectric loss (Tan δ) of the MLCC at 1 kHz under 1 V were measured by using a LCR meter (4263B, Agilent Technologies). An insulation resistance was measured for 30 sec at AC 50 V, 500 μA by using an insulator resistance tester (4339B, Agilent Technologies).

2.4 Preparation of specimen for observation of microstructure and its evaluation

The MLCC was polished in the direction perpendicular to the electrode and dielectric layers so that the microstructures of both the electrode and dielectric could be simultaneously observed. The polished sample was observed by a metallurgical microscope to examine continuity of the electrode and other factors.

3 RESULT AND DISCUSSION

3.1 Effect of $BaTiO_3$ resinate and 100nm Ni powder on firing shrinkage of Ni electrode films

Figure 2 shows the relationship between a firing temperature and a shrinkage curve of electrode films consisted of 100nm Ni powder without an addition of $BaTiO_3$ and with the BT resinate fired at temperatures ranging from 600 to 1300°C, respectively. A shrinkage curve of the generally used dielectric green sheet is also plotted by a mark "X" in Fig. 2, because the aim of the present study is to obtain Ni electrode films with similar shrinkage to that of the dielectric green sheet. As is obvious from the figure, shrinkage of $BaTiO_3$-free Ni electrode film is large. This is because the sintering generally proceeds more easily as decrease in particle size. Green density of the electrode film decreases as decrease in Ni particle size. A thickness of the resin covered Ni particles, which causes a decrease of the packing density of the electrode films as clarified in our previous study,[3] directly influences on the shrinkage of the electrode films. Since a percentage of the resin covered Ni particles increases as decrease in particle size of Ni, the shrinkage of electrode films may increase because of burn away of the resin.

On the other hand, the shrinkage of the Ni electrode with addition of BT resinate is close to that of the dielectric green sheet. It is indicating that the shrinkage of the electrode films was fairly suppressed by an addition of the BT resinate. It was clarified that an addition of the BT resinate is extremely effective for the Ni paste used for an even thinner electrode layer. However, the shrinkage of the Ni films with the BT resinate did not completely correspond to that of the dielectric green sheet. Further investigations on the amount of addition of the BT resinate should be performed in the future.

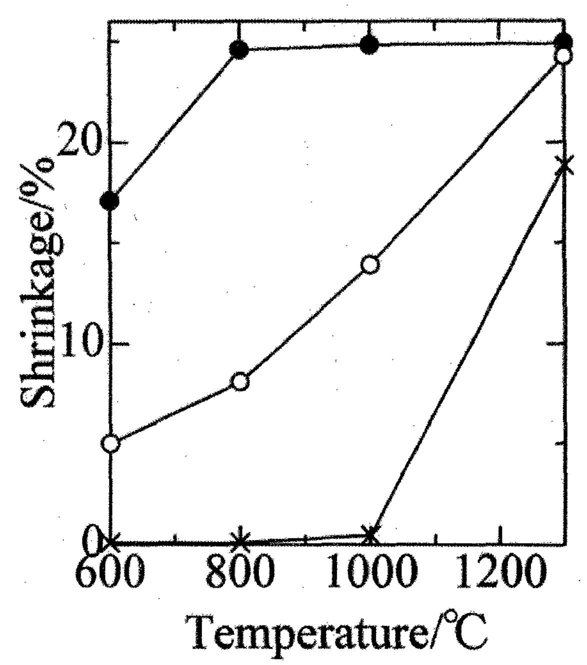

Fig2. relationship between a firing temperature and a shrinkage ● : with no addition of BT resinate ○ : addition of BT resinate × : Dielectric green sheet

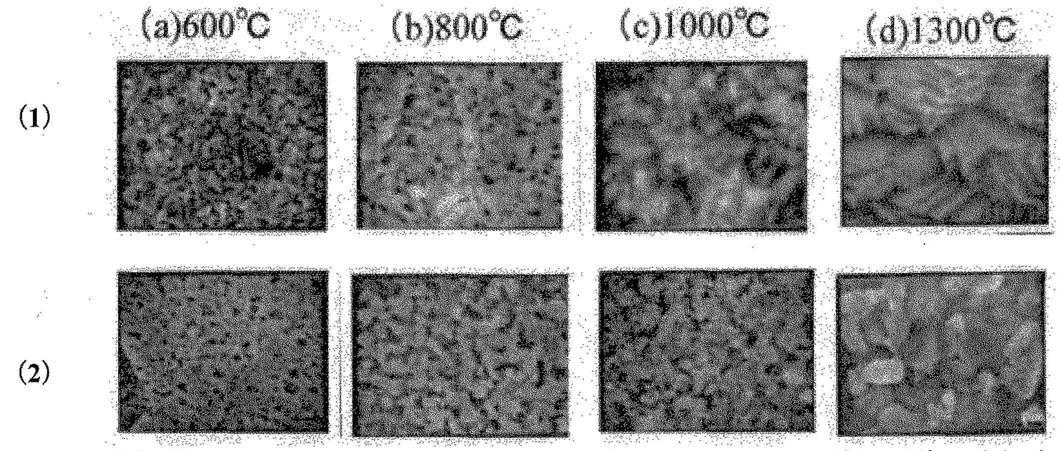

Fig3. SEM photograph of sintered Ni electrode films prepared from 100nm Ni particle size at various temperature (1) without an addition and (2)with an addition of the BT resinate.

3.2 Effect of BT resinate and 100nm Ni powder on microstructure of the sintered electrode surface

In order to confirm the effect of an addition of the BT resinate, the change in the microstructure of the surface of the sintered Ni films with 100nm in particle size was examined. Figures 3 show SEM images of a surface of the sintered Ni films without an addition (1) and with an addition of the BT resinate (2), respectively. As observed from the microstructures in Figs. 3(1) , a particle growth started approximately at 600°C and marked at 800°C.The particles growth was observed significantly at 1000°C or the higher. In the other words, a sintering proceeds at lower temperatures as decrease in particle size. Therefore, it is impossible for the currently adopted firing process of MLCCs to use Ni paste without an addition of the BT resinate.

Consequently, in order to apply Ni electrode paste for the currently adopted MLCCs firing process, the BT resinate was added to the Ni paste. The change in the microstructure of the fired Ni films is shown in Figs. 3(2) . No neck growth of Ni particles was observed at 600°C for the Ni pastes prepared from 100nm Ni powders. Growth of Ni particles was observed at 800°C. Abnormal particle growth, which was observed for the Ni paste without an addition of the BT resinate, was not observed. For the films fired at 1000°C, a size of the grown particles was approximately half of that for Ni paste without the BT resinate. A particle size of the films with the BT resinate sintered at 1300 °C was similar to that for the Ni paste without the BT resinate sintered at 1000°C.

It is considered that an addition of the BT resinate suppresses the sintering of Ni electrode films since the BT resinate occupied at the grain boundaries and at three pockets of the Ni particles. However, the mechanism associated with this suppression of sintering has not been clarified yet, and will be examined in the future.

3.3 Electrical characteristics of the MLCCs prepared from Ni paste with BT resinate and 100nm Ni Powder an observation of a microstructure

A metallographic microscope observation was carried out on the cross section of MLCCs in which Ni electrode layer include of the BT resinate. Figures 4 show the photographs of the observation. No electrode breaking was observed in the MLCCs, showing good continuity of electrodes. And Ni Electrode formation very thinner was about 0.6 μm after sintered.

In order to evaluate electrical characteristics of MLCCs, the capacitance (Cp), the dielectric loss (Tan δ) and insulation resistance were measured. The capacitance, the dielectric loss and insulation resistance were 44.0 nF(average), 2.52% and 7.7 x $10^9\ \Omega$ for 100nm Ni powder, The above results indicated that an addition of the BT resinate to the Ni electrode paste caused no significant harmful influence on the electrical characteristics of the MLCCs.

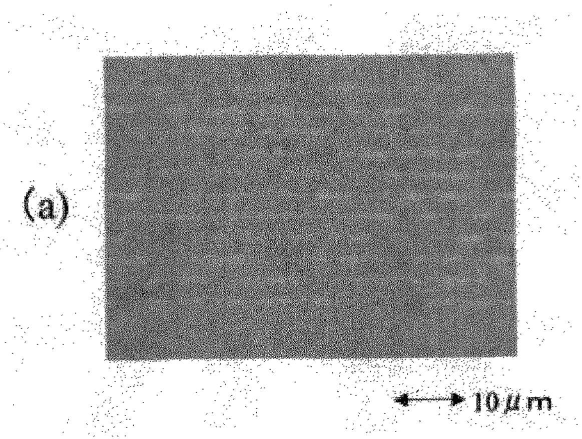

Fig4. Cross-section view of MLCCs observed by metallographic microscope

4 CONCLUSIONS

Aiming at obtaining a thinner electrode layers, the influences of an addition of the BT resinate to 100nm Ni powders on the sintering suppression effect and electrical characteristics of the MLCC were examined. We obtained the following conclusions.
(1) An addition of the BT resinate to Ni paste showed a significant influence on the sintering suppression effect of the Ni electrode films in MLCCs .
(2) Ni electrodes with an addition of BT resinate in MLCCs were fabricated with good continuity, i.e., no electrode breaking was observed.
(3) An addition of the BT resinate to the Ni electrode paste caused no significant harmful influence on the electrical characteristics of the MLCCs.

Reference

1) R.Ueyama,N.Seki,M.Harada,K.Kamada,T.Ueyama, J.Ceram.Soc.Japan.,107,(1999)652-656.
2) R.Ueyama,N.Seki,T.Ueyama,K.Koumoto,K.Kuribayashi,J.Ceram.Soc.Japan.,108,(2000)661-665.
3) R.Ueyama,T.Ueyama,K.Koumoto, J.Ceram.Soc.Japan.,108(2000)769-773.
4) R.Ueyama,T.Ueyama,K.Koumoto, K.Kuribayashi, J.Ceram.Soc.Japan.,109(2001)661-666.
5) R.Ueyama,M.Harada,T.Ueyama,A.Harada, T.Yamamoto,T.Shiosaki,K.Kuribayashi,J.Ceram.Soc.Japan., 107(1999) 60-65.
6) R.Ueyama,T.Ueyama,K.Koumoto,K.Kuribayashi, J.Ceram.Soc.Japan.,109(2001)351-354.
7) R.Ueyama,T.Ueyama,K.Koumoto,K.Kuribayashi, T.Yamamoto,J.Jpn. Soc. Powder and Powder Metall.,48 (2001) 392-396.
8) R.Ueyama, T.Ueyama, K.Koumoto, K.Kuribayashi,Trans.Mater.Res.Soc.Japan.,27 (2002) 13-17.
9) R.Ueyama,K.Koumoto,J.Ceram.Soc.Japan., 110(2002) 870-873.
10) R.Ueyama,T.Ueyama,K.Koumoto,J.Ceram.Soc. Japan.,110(2002)329-332.

(Received August 13, 2006;Accepted October 10, 2007)