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Sintering Control of Ni Internal Electrode for MLCC by using $BaTiO_3$ Resinate and $BaTiO_3$ Ultra fine Powder as Additives

Ryosuke Ueyama, Kiyoshi Kuribayashi*, Kunihito Koumoto**

Daiken Chemical Industry Corporation Limited,2-7-19 Hanaten-nishi, Jyoto-ku Osaka 536-0011
*Environmental&Material Engineering, Teikyo University of Science and Technology, Yatuzawa,Uenohara -machi, Kitatsuru-gun, Yamanashi 409-0193
**Department of Molecular Design and Engineering, Graduate School of Engineering Nagoya University, Fro-cho Chikusa-ku Nagoya City 464-8603

Abstract

We have studied chemical agents, which suppress a sintering of Ni electrode films in multilayer ceramic chip capacitor (MLCC) during the production processes. It is essential that the firing shrinkage of Ni electrode films and dielectric green sheets should show the same shrinkage behaviors for production processes of MLCC. In order to accomplish the objects, we have studied the use of $BaTiO_3$ ultrafine powder and $BaTiO_3$ organometallic acid, which has the same composition as that of ceramics dielectrics. The experimental results showed that a sintering of Ni electrode films added with $BaTiO_3$ resinate and $BaTiO_3$ ultrafine powder was remarkably suppressed especially at high temperatures. And it has been clarified that $BaTiO_3$ resinate play an important role for sintering suppression of Ni electrode films at the low-temperature region and $BaTiO_3$ ultrafine powder worked at the high-temperature region, respectively.

1. Introduction

The demand for multilayer ceramic chip capacitors (MLCCs) has been rapidly increasing, and smaller capacitors with larger capacitance than conventional models 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 the thickness of the dielectric layers. Therefore, to achieve small-size MLCCs with large capacitance, it is necessary to realize a larger number of thinner dielectric layers with higher dielectric constant and a thinner electrode layer. From the view point of production of thinner electrode layer, we have studied monodispersed Ni particles obtained by pulverization of agglomerated particles.[1-3]

Recently, smaller particle size Ni powder has been required to realize thinner electrode films which are essential for production of smaller MLCCs. Our previous studies[4)-6)] revealed that sintering of Ni electrode films was remarkably suppressed for the electrode paste in which additives particles, generally ceramic particles, were occupied between Ni particles and at triangle position (three pockets) of Ni particles. The three pockets of Ni particles are 0.0301 μ m in size for Ni powder with 0.2 μ m in particle size. This is much smaller than currently used $BaTiO_3$ additives which have approximately 0.1 μ m and 0.05 μ m in particle size. Therefore, we have examined the use of barium-titanate organometal resinate ($BaTiO_3$ resinate) as an additive which has a similar composition to dielectric green sheet. The experimental result[7)8)] clarified that $BaTiO_3$ resinate showed a significant effect on suppression of sintering of Ni electrode films at low-temperature region. This is because three pockets of Ni particles might be easily occupied by $BaTiO_3$ resinate. However, a sufficient suppression effect of sintering was not observed on high-temperature sintering of Ni electrode films because of a problem that sufficient amount of $BaTiO_3$ resinate couldn't be used as additives.

In the present study, both $BaTiO_3$ resinate and $BaTiO_3$ ultrafine powders were used as additives. And Effects of the addition on sintering of Ni electrode films were studied in detail.

2. Experimental methods

In this study, we used commercially available 0.2 μ m Ni powder synthesized by the CVD method. The Ni powder was pulverized to obtain monodispersed Ni particles with 0.2 μ m in average particle size. In the pulverization processes, n-hexane was used as a dispersion agent for Ni slurry, and the flow velocity and flow length of Ni slurry were controlled by using a media mill.[2)]

The Ni paste was prepared as follows: approximately 1 mass% (relative to Ni powder) $BaTiO_3$ resinate, as a sintering suppressor, was added to the mixture of ethyl-cellulose (binder) and terpineol (solvent). And $BaTiO_3$ ultrafine powder (BT-01, Sakai Chemical) was added with an amount between 0 and 10 mass%. Then the resultant mixture was kneaded with a conventional kneader. 1 mass% addition of $BaTiO_3$ resinate was determined from previous study,[8)]i.e., the highest green density of electrode films was obtained with 1 mass% addition of $BaTiO_3$ resinate.

Thus prepared Ni pastes were examined as electrode films for MLCCs. The sintering performance of the pastes was evaluated by measuring the shrinkage of disc samples as follows: an approximately 200 μ m-thick film was formed on a PET film using an applicator and dried at 100°C for 1 h. Then it was removed from the PET film and was cut to a 20-mm disk sample by a punch. The disk sample was heated with a temperature raising rate 3°C per min. under a reduction atmosphere of 97%N_2 + 3%H_2, and was maintained at a temperature ranging from 600 to 1300°C for 1 h. Shrinkage of a disk sample after firing was measured. In addition, the surface microstructure of samples after firing at various firing temperatures was observed using a scanning electron microscope (SEM: JSM-6199, Nihon Denshi).

3. Results and discussion

3.1 Effects of addition of $BaTiO_3$ ultrafine powder on the green density of Ni electrode films

The green density of Ni electrode films is generally correlative with the dispersibility of Ni powders and additives in the film. Figure 1 shows an effect of addition of $BaTiO_3$ ultrafine powder (varied from 0 to 10 mass%) on the green density of the electrode films included 1 mass% $BaTiO_3$ resinate. The maximum green density of the film was obtained at 5 mass% addition of $BaTiO_3$ ultrafine powder. Further increase in the amount of the additive resulted in a decrease in the green density.

This optimum amount (i.e., 5 mass%) of addition of $BaTiO_3$ ultrafine powder is almost the half of the case when only 0.1 μm $BaTiO_3$ Ultrafine powder (BT-01, Sakai Chemical) was used as an additive.[4] This is considered to be due to the packing configuration of Ni and $BaTiO_3$ particles as shown in Fig. 2. Namely, since the $BaTiO_3$ resinate completely dissolved in terpineol as solvent of Ni paste, Ni particles might be covered with nano-meter size $BaTiO_3$ resinate particles. And 0.1 μm-size $BaTiO_3$ ultrafine powder might be thoroughly placed between the Ni particles and at three pockets of Ni particles, which resulted in the increase in green density of Ni films. As the addition of $BaTiO_3$ ultrafine powder is further increased, $BaTiO_3$ particles might enlarge the three pockets of Ni particles and a space between Ni particles, which leads a decrease in the green density.

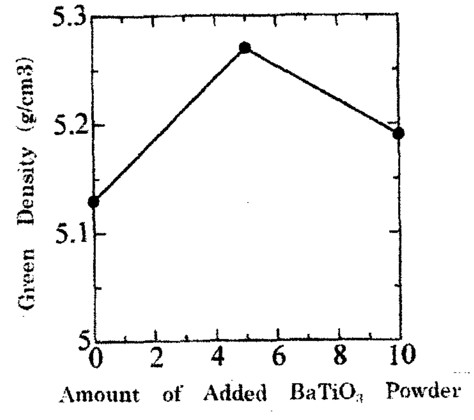

Fig. 1 Relationship between green density of Ni electrode films and amount of $BaTiO_3$ powder added.

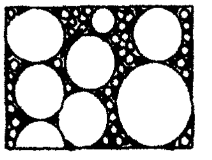

Fig. 2 Typical Packing model of Ni Electrode Films
○ : Ni Particles ● : $BaTiO_3$ Particles
▲ : $BaTiO_3$ resinate

3.2 Effects of addition of $BaTiO_3$ ultrafine powder on the firing shrinkage of Ni electrode films

In a fabrication of MLCCs, a difference in the firing shrinkage between ceramic dielectric layers and electrode layers causes delaminations between them and decreases in thermal shock resistance of MLCCs. Delaminations and cracks occurred between dielectric layers and the electrode films is called structural defects. Techniques to prevent such structural defects are extremely important for the mass production of MLCCs. Therefore, a shrinkage control of both dielectric layers and electrode films must be achieved. In the present study, an amount of $BaTiO_3$ ultrafine powder included in the electrode films is varied from 0 to 10 mass %, while an amount of $BaTiO_3$ resinate in the films is constant at 1 mass%. Figure 3 shows a firing shrinkage of electrode films sintered at temperatures from 600°C to 1300°C. A shrinkage of electrode films with 1 mass% $BaTiO_3$ resinate (solid circles) increases as the temperature increases. However, as an addition of $BaTiO_3$ ultrafine powder increases from 5 mass% to 10 mass%, the shrinkage of electrode films remarkably decreases at sintering temperatures ranging from 800°C to 1300°C.

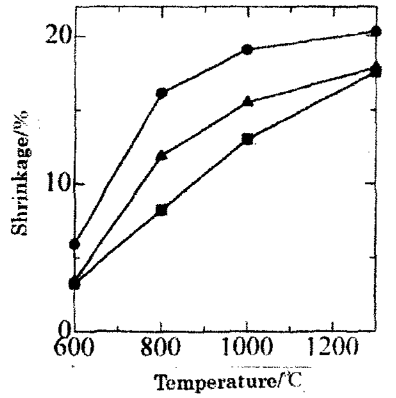

Fig. 3 Relationship between firing temperature and shrinkage of Ni electrode films.
● : $BaTiO_3$ resinate with 1mass%,
▲ : $BaTiO_3$ resinate with 1mass%and BT powder 5mass%,
■ : $BaTiO_3$ resinate with 1mass%and BT powder 10mass%,

3.3 Effects of addition of $BaTiO_3$ fine powder on the surface microstructure of Ni electrode paste films

Electrode films were prepared with an addition of 1 mass% $BaTiO_3$ resinate and various amounts of $BaTiO_3$ ultrafine powder at firing temperatures between 600°C and 1300°C.

Then their surface microstructures were observed by using SEM. Figure 4 shows the SEM images. As is obvious from the sintering shrinkage curves shown in Fig. 3, a neck growth of Ni grains began at a firing temperature of 800°C for the electrode film added with 1 mass% $BaTiO_3$ resinate. A grain growth began at 1000°C and a significant grain growth was observed at the firing temperature of 1300°C.

For the electrode film added with 1 mass% $BaTiO_3$ resinate and 5 mass% $BaTiO_3$ ultrafine powder, Ni particles were covered with $BaTiO_3$ resinate and were suppressed the sintering at 600°C. The same phenomenon was observed for the electrode film added with 1 mass% $BaTiO_3$ resinate and 10 mass% $BaTiO_3$ fine powder, which shows that an effect of $BaTiO_3$ resinate was not eliminated by an addition of the $BaTiO_3$ ultrafine powder.

When the firing temperature increased from 800°C to 1000°C, it was observed that the $BaTiO_3$ ultrafine powders suppressed the sintering of the Ni electrode. Sintering and grain growth of $BaTiO_3$ ultrafine powder in electrode films were observed at 1300°C. $BaTiO_3$ powder were homogeneously dispersed between Ni particles. In other words, a microstructure observation of sintered surface of electrodes demonstrated that the $BaTiO_3$ resinate suppresses sintering of electrode films at the lower temperature region and $BaTiO_3$ ultrafine powder suppresses one at the higher temperature region.

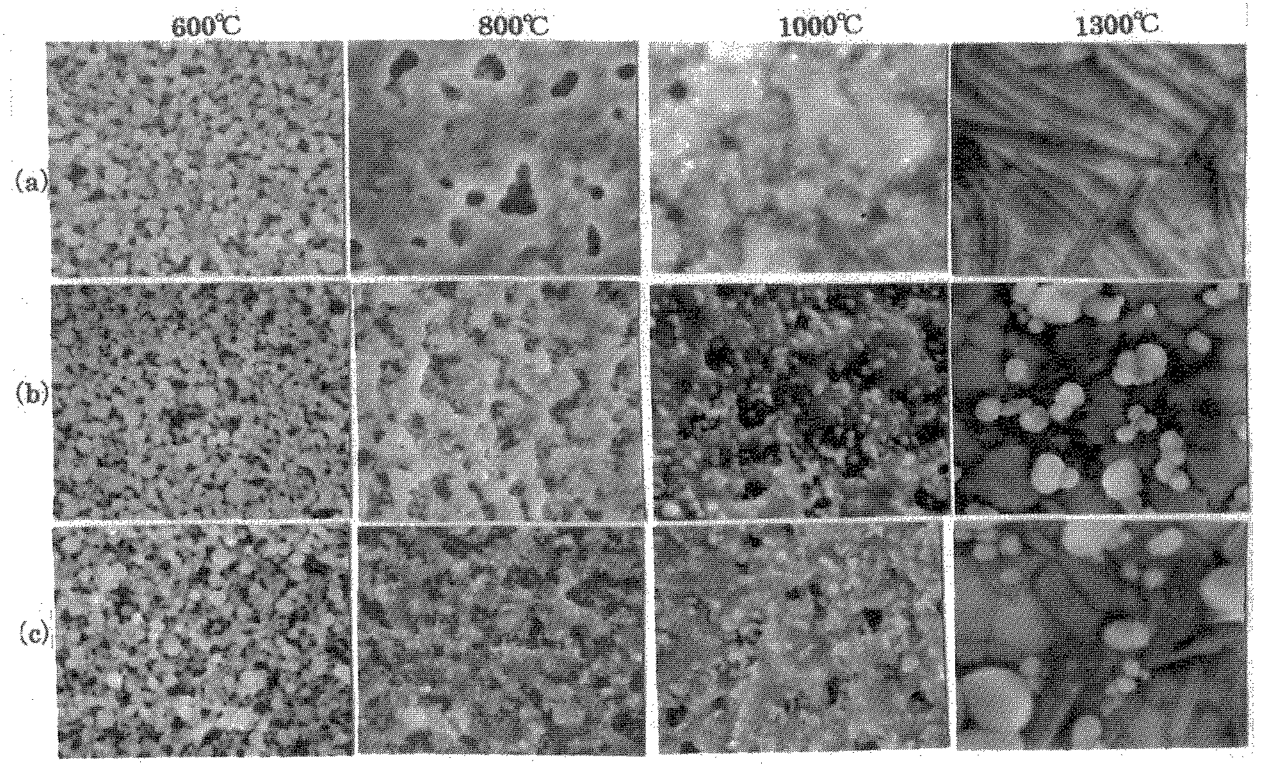

Fig. 4 SEM images of sintered CVD Ni electrode films containing various amounts of $BaTiO_3$ powder.
(a) $BaTiO_3$ resinate with 1mass%, (b) $BaTiO_3$ resinate with 1mass% and BT powder 5mass%, (c) $BaTiO_3$ resinate with 1mass% and BT powder 10mass%

4. Conclusions

We investigated on sintering suppression effect by using conventional $BaTiO_3$ ultrafine powder and $BaTiO_3$ resinate as additives for 0.2-□m Ni powder which was used in the preparation of thin electrode films for MLCCs. The following points were clarified.

(1) An addition of both $BaTiO_3$ resinate and $BaTiO_3$ ultrafine powder enables a suppression of sintering of Ni electrode films at lower temperature region (by $BaTiO_3$ resinate) and at higher temperature region (by $BaTiO_3$ ultrafine powder). Furthermore, the degree of sintering suppression can be controlled by changing an amounts of $BaTiO_3$ resinate and $BaTiO_3$ ultrafine powder.

(2) From respect to microstructures of sintered surfaces of Ni electrode films, the $BaTiO_3$ resinate is effective in achieving sintering suppression at lower temperature region, and an increase in an addition of $BaTiO_3$ ultrafine powder increases the degree of suppression of sintering of the Ni electrode films.

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