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Sintering Properties of MLCC Internal Electrode Made from CVD Ni Powder

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ABSTRACT
The dispersion characteristics of $BaTiO_3$ powder in Ni paste for multilayer ceramic capacitors and effects of $BaTiO_3$ addition on properties of Ni electrode film were studied. The maximum green density of electrode Ni film dried at 100℃ was obtained to be 5.45 g/cm^3 at 10 mass% $BaTiO_3$ addition. Shrinkage of Ni electrode film decreased with increase in amount of $BaTiO_3$ addition. Electrical resistivity of Ni electrode film, however, increased with $BaTiO_3$ addition. The increase was observed markedly when the $BaTiO_3$ addition exceed 30 mass%.

1. Introduction

Inexpensive and larger-capacitance MLCs have been strongly required recently. In order to obtain larger-capacitance MLCs without changing their case size, it is necessary to develop thinner dielectric and internal electrode layers and to increase the number of these layers in MLCs. Therefore, it is essential to use fine primary particles that are homogeneously dispersed in paste without agglomeration. In addition, lower cost electrode materials have been required to increase the number of electrode layers in MLCs. From this point of view, studies on MLCs with nickel (Ni) internal electrode instead of the conventional palladium (Pd) electrode have been actively carried out[1)-8)].

Ni paste contained fine $BaTiO_3$ powders are generally used for electrode in MLCs, because a simultaneous sintering of dielectric and the metal electrodes are required in the sintering process of MLCs. Fine $BaTiO_3$ powders in Ni paste makes the metal electrode having analogous shrinkage characteristics to the dielectric layer (ceramics). Thus $BaTiO_3$ powders in Ni paste plays an important roles in electrode of MLCs. In the production of the electrode paste, properties of the fine metal particles, an amount of additive agent ($BaTiO_3$) and the dispersibility of fine $BaTiO_3$ powders in the paste are thought to be important factors to determine performance of the electrode films, especially to shrinkage characteristics during the sintering. In the previous study, we have reported an influence of the dispensability of $BaTiO_3$ in the paste and properties of wet chemical Ni powders on the sintering characteristics of Ni electrode paste which include various amounts of $BaTiO_3$[9),10)]

In the present study, pulverized Ni powders synthesized by the chemical vapor deposition (CVD) were used to investigate on the influence of $BaTiO_3$ additions on the sintering and electrical properties of the Ni electrode films.

2. Experimental Method

Pulverized Ni powder, which was synthesized by the CVD method(NF-40,TOHO TITANIUM Co.,LTD), was employed in the present study. Ni powder with 0.6 μm in an average grain size (determined by SEM measurement) was obtained by the pulverization process[11)].

Ni paste was prepared by mixing 55 g of the pulverized CVD Ni powder with 0.6 μm in grain size, 2.2 g ethyl cellulose as a binder, and 42.8 g terpineol as a solvent. In order to study an influence of addition of $BaTiO_3$ on characteristics of Ni electrode films, four kinds of Ni pastes added with various amount of $BaTiO_3$ powder (Sakai Chemical Industry Corporation, approximately 0.1 μm in grain size) were prepared. The pastes contained $BaTiO_3$ powder from 0 mass% to 50 mass%. We studied relationship between the dispersibility of $BaTiO_3$ powder and green density of Ni films. Then, packing density of the films was calculated. Green density of Ni films was calculated from the following procedures. First, Ni electrode films with approximately 200 μm in thickness were formed on a polyethylene terephthalate (PET) film with an applicator. After drying at 100°C for 1 hr, the Ni electrode films were peeled from the PET film and punched out into disks with 13 mm ϕ in diameter. Thickness and weight of disks were measured with a micrometer and a precision balance (precision of 1/1000 mg), respectively. The weight/volume ratio of the disks was calculated to determine the green density of the films.

Sintering characteristics of Ni films were evaluated from the sintering shrinkage. A 13 mm φ Ni disk with 200 μm in thickness was heated up to temperatures ranging from 600℃ to 1300℃ with an temperature increasing rate 3°C /minute in a reducing atmosphere (97% N_2 and 3% H_2), and was maintained at each desired temperature for 2 hr. A diameter of the sintered disks was measured with a microscope. Shrinkage of the disks was calculated by dividing a disk diameter measured after sintering into the one before sintering. Fine structures of the surface of electrode films after sintering at various temperatures was observed by scanning electron microscopy (SEM, Nippon Electron's, JSM-6100).

In order to measure an electrical resistivity of Ni electrode films, a comb pattern electrode was screen-printed on the alumina ceramic substrate and was sintered at 1000°C in 97% N_2 and 3% H_2 reducing atmosphere. The maximum sintering temperature was set at 1000°C in this study because the Ni powder fused above 1200°C, which resulted in the abnormal deformation and variable resistivity of the electrode films.

3. Results and Discussion

3.1. Influence of $BaTiO_3$ addition on the green density of electrode films

The green density of electrode films is an important factor to evaluate the dispersibility of $BaTiO_3$ powder in the paste. In general, it is essential that the paste for internal electrode in MLCs has no agglomerates and has to be prepared from primary particles with uniform particle size. The degree of dispersibility of $BaTiO_3$ is evaluated from the packing density of electrode film.[12] The packing density of electrode film ρ is given by the following equation:

$$\rho = \rho_g \cdot X_d / \rho_d \quad (1)$$

where ρ_g is the green density of electrode films, ρ_d is the dry density of the powders, and X_d is the mass percentage of the powders in paste.

Figure 1 showed the calculated green density of electrode films prepared from precursor powder with various packing densities and measured green density of the films as a function of an amount of added $BaTiO_3$. It is generally considered that screen-printed films are formed by non-pressure condition. The packing of particles in the films formed by screen-printing are a single staggered arrangements with 8 coordination number.[13),14] The highest packing density of a single staggered arrangement with 8 coordination number is 60.45% and a residual 39.55% was considered to be void existed in films. Here, the corners of triangle (three pockets) surrounded by three Ni particles with 0.6 μm in grain size were considered as void in the films.

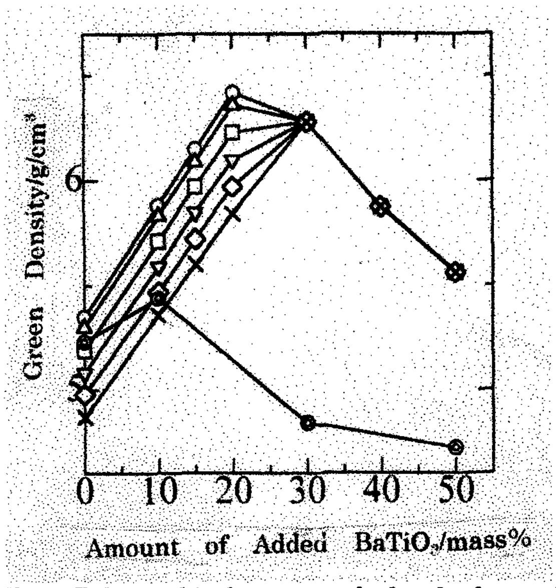

Fig.1 Relationship between calculated ,observed green density of CVD Ni electrode film and amount of added $BaTiO_3$.
○:Packing density 60.45%,
△:Packing density 59.85%,
□:Packing density 58.64%,
▽:Packing density 57.43%
◇:Packing density 56.23%,
×:Packing density 55.01%,
◎:Observed.

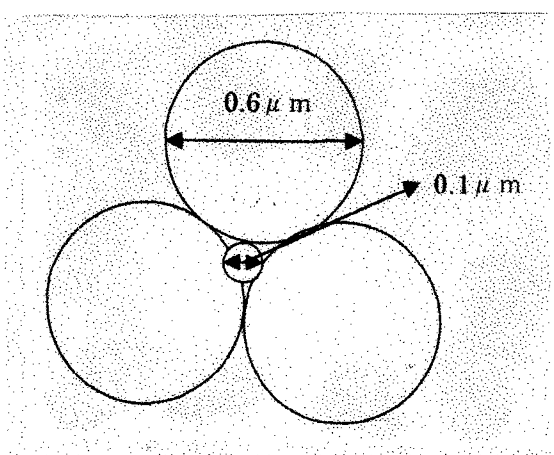

Fig.2 Typical packing model of Ni and $BaTiO_3$ powder.

Since the maximum size of the three pocket is calculated to be 0.093 μm, $BaTiO_3$ particle with 0.1 μm in diameter is preferentially placed in the three pockets, which lead to a increase in the green density of films(Figure 2). If the excess amount of $BaTiO_3$ powder were added into the Ni powder, $BaTiO_3$ particles are placed both in the three pockets and between Ni particles, which contribute to increase a distance between Ni

particles, and consequently the green density of electrode film is decreased. The green density of film without $BaTiO_3$ addition was measured to be 5.23 g/cm^3. Accordingly, the packing density of a single staggered arrangement with 8 coordination number was calculated to be 59.09% from equation (1).
This value is 97.8% to the theoretical value (60.45% of packing density) of a single staggered arrangement with 8 coordination number.
The calculated packing density indicated □ in Fig.1 corresponded to the measured value. The experimental values indicated ◎ in Fig. 1 showed the maximum green density to be 5.45 g/cm^3 at 10 mass% of $BaTiO_3$ addition. In other words, the experimental data showed different tendency from the calculated values(represented by □ in Fig. 1). The calculated values showed the maximum green density at 20 and 30 mass% of $BaTiO_3$ addition. This result suggested that $BaTiO_3$ particles were placed in not only three pockets but also between Ni particles even above 10 mass% of $BaTiO_3$ addition. When BaTiO3 addition was less than 10 mass%, almost all $BaTiO_3$ particles might be preferentially placed in the three pockets, which lead to the increase in the green density of Ni electrode films. And when the $BaTiO_3$ addition was 10 mass% or higher, the percentage of $BaTiO_3$ particles plased between Ni particles increased compared to $BaTiO_3$ particles sit on the three pockets. As the result, distance between Ni particles was increased and the packing density of the films decreased, which lead to the decrease in the green density of Ni films.

3.2. Effect of $BaTiO_3$ addition on the shrinkage of electrode films

In the manufacture of MLCs, difference in sintering shrinkage between the ceramic dielectric and the electrode films significantly affects on delamination of the layers and thermal shock resistance of capacitors. For the above reason, it is important for fabrication of electrode paste to control and stabilize a sintering shrinkage of electrode films. If there is a big difference between a sintering shrinkage of the electrode films and that of the ceramic dielectrics, delamination or cracks may occur between the electrode and the ceramic dielectric. These are called structural defects of capacitor. From a stand point of yield, we should first overcome these problems for the mass production of MLCs.

Figure 3 shows shrinkage of Ni electrode films added with various amounts of $BaTiO_3$ after firing at the temperature ranges from 600°C to 1300°C. The film without $BaTiO_3$ addition (●in Fig. 3) exhibited a large shrinkage, which is big difference from those of the samples with $BaTiO_3$. On the other hand, a sintering shrinkage decreased considerably for the films with 30 mass% and 50 mass% of $BaTiO_3$. In other words, as an increase in amount of $BaTiO_3$ addition, the electrode films exhibited the resemble properties as the ceramics dielectric(× in Fig.3) in the sintering shrinkage. Thus, it is important to add an appropriate amount (30 mass% in this study) of $BaTiO_3$ into Ni powder for elimination of delamination between the electrode and the ceramic dielectric and for the maintenance of the thermal shock resistance of the capacitors.

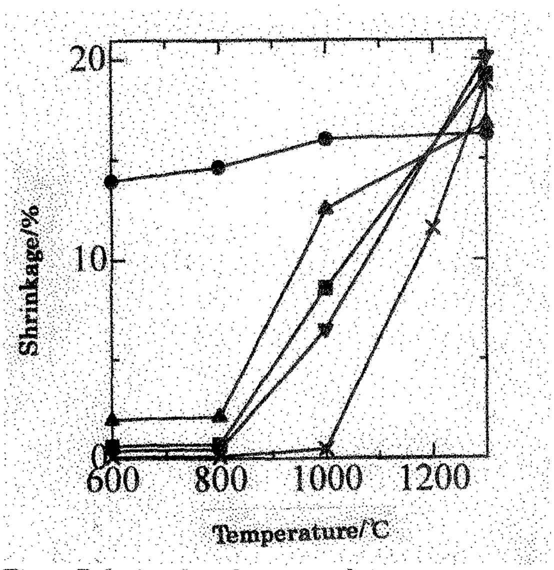

Fig.3 Relationship between firing temperature and shrinkage of electrode films.
● : $BaTiO_3$ 0 mass%, ▲ : $BaTiO_3$ 10 mass%
■ : $BaTiO_3$ 30 mass% ▼ : $BaTiO_3$ 50 mass%
× : Dielectric Green Sheet.

3.3. Influence of $BaTiO_3$ addition on the fine surface structures of the electrode films

Electrode films heated at 600-1300°C were subjected to the SEM measurement to analyze a fine surface structures. Photographs of SEM images are presented in Fig.4. Ni particles in the films without $BaTiO_3$ addition began neck growth at 600°C and grew enormously above 1000°C. On the other hand, an addition of $BaTiO_3$ into Ni powder seems to suppress the Ni particles from sintering. With an increase in the amount of $BaTiO_3$ addition, it was observed a segregation of $BaTiO_3$ on the sintered surface of the film and this segregated area was increased gradually. The sintered $BaTiO_3$ became a dominant over the surface of the film. The surface of the sintered Ni electrode film without $BaTiO_3$ addition differs greatly from that of the film with $BaTiO_3$ in terms of surface microstructures. These results suggested that with the increase in the amount of $BaTiO_3$ addition, the particle growth of Ni observed in electrode films was prevented even for high temperature sintering. Thus we can appropriately control particle growth of the Ni in electrode film. SEM observation gave the similar results as those obtained from sintering shrinkage curves.

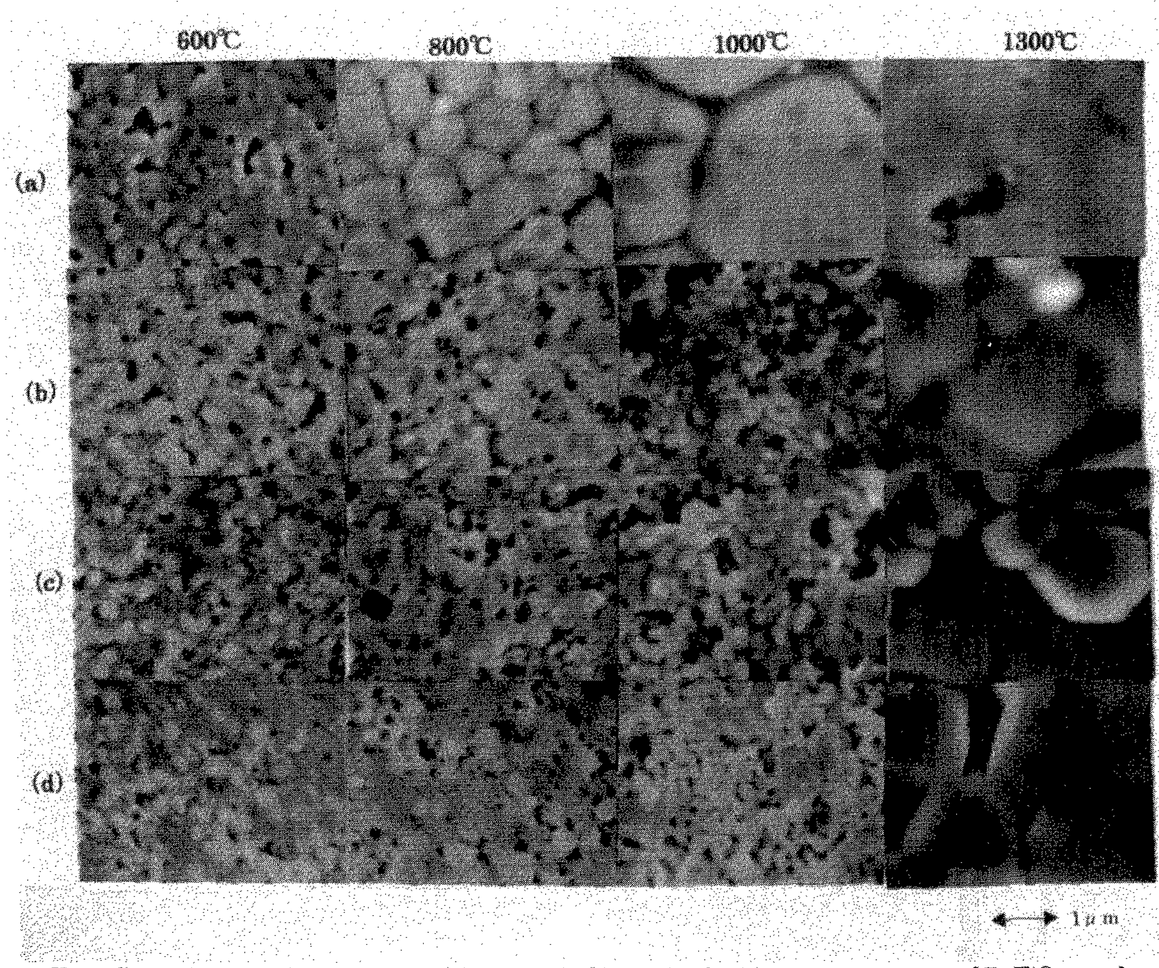

Fig.4 SEM photographs of sintered Ni electrode films added with various amount of $BaTiO_3$ powder.
(a) $BaTiO_3$ 0 mass%(b)$BaTiO_3$ 10 mass%(c) $BaTiO_3$ 30 mass%(d) $BaTiO_3$ 50 mass%

3.4 Influence of $BaTiO_3$ addition on resistivity of the electrode films

The equivalent series resistance (ESR), which is one of the most important properties of MLCs, is increased as increase in amount of added $BaTiO_3$ which is insulator in the Ni electrode films. It is important to study an influence of BaTiO3 addition on the electrical properties of electrode films. The electrode film was printed comb-pattern on an alumina substrate and was sintered in N_2 and 3% H_2 atmosphere at 1000°C. Resistivity of this sintered film was measured. Figure 5 presents the relationship between the amount of added $BaTiO_3$ and resistivity of electrode films heated at 1000°C. Resistivity of electrode films with 10 mass% and 30 mass% $BaTiO_3$ showed the almost same values (approximately 20μΩcm and 40 μΩcm). And that of the film with 50 mass% $BaTiO_3$ was measured to be 260 μΩcm. Significant increase in resistivity was observed for the film with 50 mass% $BaTiO_3$. Comparing with the bulk resistivity of the Ni film sintered at 1445°C (7 μΩcm), resistivity obtained in this experiment had a higher value as 30 μΩcm even when an effect of the sintering temperature is taken into account. The difference in resistivity of electrode film could be explained by the minute change in film thickness caused by the irregularity of surface of alumina substrate. Thus, it is desirable that the smaller amount of BaTiO3 powder is added into Ni paste from the point of view of higher conductivity of electrode film, ie., $BaTiO_3$ addition must be less than 30 mass%. It is a matter of concern that an increase in resistivity of electrode film due to the addition of $BaTiO_3$ may affect on the production of thinner electrode films as 1 μm or less.

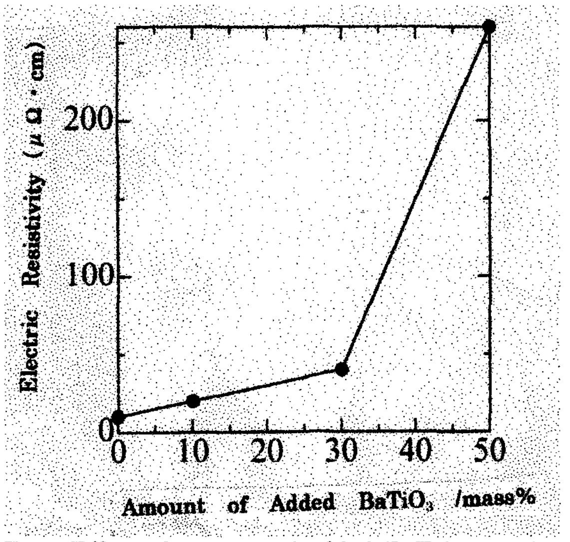

Fig.5 Effect of amount of added $BaTiO_3$ powder on resistivity of Ni electrode sintered temperature at 1000℃.

4. Conclusion

We studied on influences of $BaTiO_3$ addition to Ni powder produced by CVD and pulverization methods on the sintering and electrical properties of the Ni electrode films. The following results were obtained.

(1) The green density of Ni electrode films increased up to 10 mass% of $BaTiO_3$ addition and decreased with increase in an amount of $BaTiO_3$. We found that the most appropriate amount of $BaTiO_3$ addition was 10 mass%.

2) The shrinkage of electrode films decreased with an increase in the amount of $BaTiO_3$ addition and approached to that of the ceramics, which was in good agreement with the SEM observation. It was also demonstrated that sintering of Ni particles in electrode films was prevented with an increase in the amount of $BaTiO_3$ addition.

3) Resistivity of the electrode films increased remarkablly when the amount of $BaTiO_3$ addition exceed 30 mass% or more. This result indicated that the maximum amount of $BaTiO_3$ addition should not exceed 30 mass% from the stand point of the problems related to the ESR of the MLCs.

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