Effect of a BaTiO₃ nanoparticle additive on the quality of thin-film Ni electrodes in MLCC

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To increase the film quality of the nickel electrode in a multi-layer ceramic capacitor (MLCC), the BaTiO₃ particles are usually used as an additive material in the electrode paste. In this report, we investigated the effects of particle size (30–100 nm) and the amount (10–20% mass ratio to Ni) of BaTiO₃ nanoparticle additives on the quality of thin-film Ni electrodes, stated by a dry film density and Ni film coverage after a firing process. The use of 30 nm BaTiO₃ particles resulted in a high Ni film coverage larger than 75% using only 10 mass% of BaTiO₃ additive in the paste. Using larger particle sizes, a greater amount of BaTiO₃ additive was needed in order to obtain the same Ni film coverage. The use of a smaller particle size of BaTiO₃ nanoparticles leads to the increase of particle numbers for the same mass, resulting in effective BaTiO₃ nanoparticles surrounded on Ni particles. In addition, by decreasing the amount of BaTiO₃ additives, the BaTiO₃ absorbance by the dielectric layer was reduced, and, consequently, the increasing of dielectric layer thickness could also be minimized.

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1. Introduction

Following a trend in the miniaturization of electronic components, the demand for multi-layer ceramic capacitors (MLCCs) has grown because of a large capacitance despite the small size.¹⁾ MLCCs achieve their performance with an increased number of layers, which is made possible by decreasing the layer thickness.^{1),2)} To achieve thinner electrode layers, it is necessary to reduce the electrode paste attachment during the printing process. However, a reduction in the paste attachment resulted in a decreased coverage rate of the metal electrode following the firing process. Moreover, in order to prevent defects in the electrode layers, it is necessary to control the resin combustion and the shrinkage mismatch between the dielectric and electrode layers.^{3),4)}

Several studies have reported that in order to avoid the formation of sintering defects and to reduce the shrinkage mismatch, a proper amount of ceramic powders such BaTiO₃ must be added to the metallic paste. Ueyama et al.^{5)–7)} reported that the largest particle size ratio of ceramic (BaTiO₃) particles/metallic (Ni) particles is 0.155, since it is a requirement that the smaller ceramic particles enter triple bond spots (three spots) among the Ni particles. We previously reported that the dry film density could be improved to as high as 115% by the use of a 20 mass% amount of BaTiO₃ additive to Ni mass ratio and with a particle size lowered from 200 nm to 100 nm (0.225 to the Ni particle size in ratio).⁸⁾ From the commercial production point of view, it is desired to decrease the amount of BaTiO₃ additives. However, it is still difficult to control the shrinkage rate of the Ni electrode by simply reducing the amount of BaTiO₃ additives to lower than 20 mass%. In addition, to the best of our knowledge, there has been no detailed study on the effect of particle size especially in nanometer scale and the amount of BaTiO₃ particle additives on

the quality of a Ni electrode layer.

This paper outlines the detailed study of the effects of particle size (30–100 nm) and amount (10–20% mass ratio to Ni) of BaTiO₃ nanoparticle additives on the quality of a thin-film Ni electrode—the density of dried film and film coverage after the firing process. High Ni film coverage (> 75%) was formed using a small amount (10 mass%) and a small size (30 nm) of BaTiO₃ additives in the paste. The sintering of the Ni particle was restrained when a smaller BaTiO₃ particle size was used even when the additional amounts were reduced. Thus, a thinner layer of Ni electrode was accomplished.

2. Experimental procedure

2.1 Preparation of the Ni-based electrode paste

To investigate the effect of particle size and the amount of BaTiO₃ nanoparticle additive, different types of paste were prepared by mixing Ni powder (JFE Mineral Co., Ltd., NFP-201S, particle diameter of 200 nm) and various amounts (10 to 20 mass% of Ni) of BaTiO₃ nanoparticles with varying particle diameters, 30, 50 and 100 nm, hereafter referred to as BT30, BT50 and BT100, respectively, as shown in **Table 1**. Ni powder (specific gravity: 8.9 g/cm³) and BaTiO₃ nanoparticles (specific gravity: 6.0 g/cm³) were mixed with a vehicle-solved ethyl cellulose (DOW Chemical Company: EC45 and EC100) in terpineol (The Nippon Koryo Yakuhin Kaisya, Ltd., Terpineol), which was selected to obtain an appropriate viscosity (10 Pa·s at 25°C, 40 s⁻¹) for screen printing. A surfactant (San Nopco Ltd., SN2180) also was added to insure an appropriate viscosity.

2.2 Measurement of dry film density, Ni density and porosity

In order to evaluate the dry film density, the pastes were attached to a PET (polyethylene terephthalate) film using an applicator. The film thicknesses were 20 to 30 μm after drying at 100°C for 15 min. The film was then cut into a circular disc

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Table 1. Material Properties and Experimental Conditions

Ni mean particle size (nm)	200														
Ni concentration in paste (mass%)	50														
BaTiO ₃ mean particle size (nm)	30 (BT30)					50 (BT50)					100 (BT100)				
BaTiO ₃ concentration in paste (mass%)	5.0	6.25	7.5	8.75	10.0	5.0	6.25	7.5	8.75	10.0	5.0	6.25	7.5	8.75	10.0
The addition amount of BaTiO ₃ (mass%)	10.0	12.5	15.0	17.5	20.0	10.0	12.5	15.0	17.5	20.0	10.0	12.5	15.0	17.5	20.0
Surfactant concentration (mass%)	2.2	2.6	3.2	3.6	4.0	1.4	1.6	1.9	2.1	2.3	1.1	1.2	1.4	1.5	1.6
Ethyl cellulose concentration (mass%)	2.0														

with a diameter of 20 mm, and its weight, thickness and diameter was measured to evaluate its dry film density. Ni density was evaluated by measuring the dry film density and the mass ratio of the solid contents (mixing ratio) of the dry film using the following equation:

$$\rho_{\text{Ni}} = \rho_{\text{dry film}} \times \frac{\phi_{\text{Ni}}}{\phi_{\text{Ni}} + \phi_{\text{BaTiO}_3} + \phi_{\text{Rsn}} + \phi_{\text{Surf}}} \quad (1)$$

where ρ_{Ni} , $\rho_{\text{dry film}}$, ϕ_{Ni} , ϕ_{BaTiO_3} , ϕ_{Rsn} and ϕ_{Surf} are Ni density, dry film density, Ni content, BaTiO₃ content, resin content, and surfactant content, respectively.

Furthermore, porosity of the films was calculated by considering dry film density and theoretical material density using the following equation:

$$\varepsilon = 100 - \frac{\rho_{\text{dry film}}}{\rho_{\text{theory}}} \times 100 \quad (2)$$

where ε and ρ_{theory} are porosity and theoretical material density, respectively.

2.3 Shrinkage rate measurement of Ni-based electrode film

The shrinkage-rate measurement of the Ni-based electrode film was determined by measuring the diameter of the samples before and after the firing process at different temperatures. The samples were fired under the conditions shown in **Table 2**.

2.4 Coverage-rate measurement of Ni electrode film on the dielectric sheet

First, a dielectric green sheet was prepared using a doctor-blade method from a paste consisting of polyvinyl butyral (Sekisui Chemical Co., Ltd., BM-1) and BaTiO₃ powder (particle size of 250 nm). Then, various electrode pastes were printed on the dielectric green sheet using a screen-printing method, followed by the firing process under the conditions shown in **Table 3**. The quantity of the Ni film was maintained at 0.5 mg/cm². The coverage rate of Ni electrode film on the provided dielectric sheet was measured from SEM images using image software (Adobe Photoshop, Adobe System Inc.). The similar measurement method has also been reported elsewhere.⁹⁾

3. Results and discussion

3.1 Dry film density, Ni density and porosity

To investigate the compactness of the film, the dry film density, Ni density and porosity were evaluated by methods as explained in the experimental procedure. **Figures 1–3** show the effects of particle size and amount of the BaTiO₃ additive on dry film density, Ni porosity and density, respectively. As shown in Fig. 1, the use of BT50 shows the highest dry film density, followed by BT30 and BT100, respectively. To achieve optimal fill-

Table 2. Experimental Conditions for the Shrinkage Rates of Ni Film

	Surrounding gas	Heating rate (°C/h)	Temperature (°C)	Retention time (min)
Binder removal	Air	300	300	20
Firing	95%N ₂ -5%H ₂	200	600 to 1300	10

Table 3. Experimental Conditions for the Coverage of Ni Electrode with a BaTiO₃ Dielectric Layer

	Surrounding gas	Heating rate (°C/h)	Temperature (°C)	Retention time (min)
Binder removal	Air	25	280	600
Firing	95%N ₂ -5%H ₂	600	1250	60

Fig. 1. Dry film density as a function of the amounts of BaTiO₃ for various particle sizes of BaTiO₃. Fig. 2. Porosity as a function of the amounts of BaTiO₃ for various particle sizes of BaTiO₃.

Fig. 3. Ni density as a function of the amounts of BaTiO₃ for various particle sizes of BaTiO₃.

ing of Ni with particles of 200 nm, a previous study reports that BaTiO₃ additives should be smaller than 45 nm (200×0.225).⁸⁾ For the present study, we predicted that the use of BT30 (the smallest particle size) would exhibit the highest value of dry film density. However, our results showed that the highest value of dry film density was obtained using BT50. This behavior can be explained as follows. In the case of BT30, more surfactant addition was necessary to obtain an appropriate viscosity for screen-printing Table 1. We concluded that the distance between Ni and BaTiO₃ particles in dry film was extended by adding more surfactant, which resulted in a decrease in dry film density. Also, with a high amount of BaTiO₃ additive (20 mass%), the dry density of BT30 was lower than BT100 due to the increasing surfactant concentration.

Figure 2 shows the relationship between the porosity of film and the amount of BaTiO₃ additive under various sizes of BT particles. The porosity of the paste of BT30 was smaller than that of BT100, while the dry film density of BT30 was similar to, or slightly higher than, BT100. Obviously, obtaining an appropriate viscosity necessitated adding more surfactant to the paste with the smaller particle size.

The value of the Ni density as a function of the amount of BaTiO₃ additive for various BT particle sizes is shown in Fig. 3. As a result, the Ni density of the paste of BT30 was smaller than that of BT100, while the dry film density of BT30 was similar, or slightly higher, than that of BT100. Similar results were reported in our previous work, whereby Ni density decreased linearly as the amount of BaTiO₃ additive was increased.⁸⁾

3.2 Shrinkage rates of Ni-based electrode film

Figure 4 shows the shrinkage of Ni-based electrode film as a function of temperature for different particle sizes and amounts of BaTiO₃ additives. As temperature increased, the shrinkage volume also increased, and the rate of shrinkage was larger for BT30 than it was for either BT50 or BT100. As the amounts of BaTiO₃ additive decreased (from 20 mass% to 10 mass%), the shrinkage rate increased. However, this behavior was observed more strongly with BT50 and BT100 than with BT30, which had only a small change in the shrinkage rate.

Figure 5 shows the theoretical particle number ratio of BaTiO₃/Ni by composition as a function of the amount of BaTiO₃ additive. The specific gravities of Ni and BaTiO₃ were 8.9 and 6.0 g/cm³, respectively, and it was supposed that each material was a single spherical particle for each particle size. The number of BaTiO₃ particles for one Ni particle increased remarkably

Fig. 4. Shrinkage of various particle sizes and amounts of BaTiO₃ as a function of firing temperature.

Fig. 5. Number of BaTiO₃/Ni as a function of the amounts of BaTiO₃.

Fig. 6. Typical packing and existence ratio model of Ni and BaTiO₃ particles for particle sizes of (a) 100, (b) 50 and (c) 30 nm.

kably for smaller-sized BaTiO₃ particles. For a similar amount of BaTiO₃ additive, the number ratio is a function of the cube of the reciprocal number of the particle size ratio. For example, the particle number ratios of similar amounts of BT100, BT50 and BT30 are 1, 8 and 37, respectively. Therefore, in the case of BT30, although the particle number largely decreases as the amount of BaTiO₃ additive decreases, the number ratio of BT30 to Ni particles in 10 mass% of additive would be higher than it would be in 20 mass% of additive using either BT50 or BT100 (illustrated in Fig. 6). A pin stopper for the sintering between the Ni particles was enabled by an increase in the BaTiO₃ particles,

Fig. 7. SEM images of dry film for 10 mass% of BaTiO₃ and particle sizes of (a) 30, (b) 50 and (c) 100 nm. SEM images of dry film for 20 mass% of BaTiO₃ and particle sizes of (d) 30, (e) 50 and (f) 100 nm.

which was expected in the case of BT30. This was the reason the shrinkage change rate was small, although the additional amount was decreased Fig. 4. A small particle size for BaTiO₃ could lead to an increase in the particle number and could maintain heat resistance even when amounts of BaTiO₃ additive were reduced. However, the shrinkage rate of the BT30 film was larger than that of the BT50 film. At least two factors caused this observation: heat resistance of one particle deteriorated according to the small BaTiO₃ particle size, and the influence of Ni density of the dry film decreased as the amount of surfactant addition increased Fig. 3. In order to control the shrinkage rate of the Ni-based electrode film, the control of over-sintering between Ni particles by BaTiO₃ particles became very important, as did the improvement of dry film and Ni density.

3.3 Coverage rate of the Ni electrode on the dielectric sheet

Figure 7 shows the SEM images of screen-printed dry film on the dielectric green sheet for various particle sizes and amounts of BaTiO₃ additives. The BaTiO₃ particles among Ni particles decreased as the amount of BaTiO₃ additive also decreased. However, the electrode paste containing smaller-sized BaTiO₃, experienced the most BaTiO₃ particles filling among the Ni particles to reflect the existence of number ratios shown in Figs. 5 and 6. Furthermore, for BT30, many BaTiO₃ particles remained among the Ni particles even with the additional amount of 10 mass%.

High coverage rate of Ni electrode on the dielectric sheet is very important for obtaining high performance of MLCC. Typically for industrial applications, coverage of around 70–75% is required. The coverage was estimated from the SEM images after sintering shown in Fig. 8. Figure 9 shows the effect of particle size and amounts of BaTiO₃ additives on the coverage rate of Ni electrodes on the dielectric sheet after the sintering process. The coverage rate of the Ni electrode with similar particle sizes of BaTiO₃ decreased as the amount of BaTiO₃ additive decreased. Moreover, the rate of decreasing coverage became lower for smaller sizes of BaTiO₃. It was found that high Ni film cov-

Fig. 8. SEM image of interconnected Ni particles or neck formation among Ni particles of Ni electrode film on Dielectric (BaTiO₃) sheet caused by sintering process.

Fig. 9. Coverage of Ni electrodes on BaTiO₃ sheets as a function of amounts of BaTiO₃.

erage larger than 75% could be achieved by only 10 mass% of BT30 additives in the paste. The high Ni film coverage larger than 75% cannot be obtained by the use of BT50 and BT100 in

10 mass% BaTiO₃ additives. This may be due to the influence of the number of BaTiO₃ particles among the Ni particles, which controlled the sintering of the Ni particles. The smaller particle size of BaTiO₃ nanoparticles leads to an increase of the particle number, and results in the effective existence of BaTiO₃ nanoparticles among Ni particles. Furthermore, a decreasing amount of BaTiO₃ additive decreased the amount of BaTiO₃ that was absorbed by the dielectric layer in the sintering process, and the increase of dielectric layer thickness could also be minimized.

Figure 10 shows the correlation of the theoretical number ratio of BaTiO₃/Ni against the function of the coverage rate of Ni electrodes. The decreasing coverage rate of Ni electrodes was influenced by the decreasing number of BaTiO₃ particles and the influence was stronger as the number ratio of BaTiO₃ particles to Ni particles decreased. The Ni density as well as dry film density was important for the improvement of the coverage rate of the Ni electrode as it allowed to add more Ni particles to the thinner portions of the printed film, and allowed more BaTiO₃ particles between the Ni particles to control the sintering. As depicted in the Fig. 10, the percentages of coverage of Ni electrode greater than 75% were obtained using at least 17.5, 15.0 and 10 mass% BaTiO₃ particle additive with sizes of 100, 50 and 30 nm, respectively. It was likely the number of BaTiO₃ particle additive played a role in increasing the coverage percentage of the Ni electrode. The calculation of the number of BaTiO₃ particle additive to Ni indicated that around 44 particles of 30 nm BaTiO₃ additive was obtained and well surrounded the Ni particles as illustrated by the figure. For the sizes of 50 and 100 nm BaTiO₃ particle additives, even using higher mass percentage (17.5 and 15 mass%, respectively), they have only around 14 and 3 particles, respectively, surrounding a Ni particle. Therefore, the amount of BaTiO₃ particle additive can be reduced and the increase of dielectric layer thickness can be minimized by using a smaller particle (BT30).

When the thickness of the Ni electrode after the sintering process was at 800 nm, the coverage rate of the Ni electrode was

Fig. 10. Coverage of Ni electrodes on BaTiO₃ sheets with various particle sizes of BaTiO₃ as a function of the number of BaTiO₃/Ni.

80%, the BaTiO₃ at 20 mass% paste was added and it was assumed that all BaTiO₃ particles included in the Ni-based electrode film were absorbed by the layer of dielectrics. Then, the thickness of the dielectric layer could be calculated theoretically to an increase of 190 nm by the absorption of the BaTiO₃ in the electrode paste. Therefore, the decreasing amount of BaTiO₃ additive in the paste was caused not only by the thinner Ni electrode layers but also by the thinner dielectric layers, which were important for the small size, thin layer, and higher capacity of MLCC development.

As a final note, the dispersion of the electrode paste using BT30 was not easy due to nanoparticle agglomeration. Further efforts to improve the dry film density using a surfactant with effective addition and dispersion capabilities, as well as further heat-resistance improvements for small particle sizes of BaTiO₃, are needed, and these two points will be our focus in the near future.

4. Conclusions

The effects of particles size and the amount of BaTiO₃ nanoparticle additives in the development of high-performance, thin-film Ni electrodes were studied. Using 30 nm BaTiO₃, the dry film density is still lower than of the use of 50 nm BaTiO₃ particles. This is caused by more surfactants being needed in the preparation of well-dispersed 30 nm BaTiO₃ additives in the paste. However, after the firing process, it was found that a high Ni film coverage larger than 75% could be achieved by only 10 mass% of 30 nm BaTiO₃ additives in the paste. Using larger particle size, a greater amount of BaTiO₃ additive was needed in order to obtain the same Ni film coverage. The small amount of BaTiO₃ additive in the electrode paste leads to minimize the increase of dielectric layer thickness from the BaTiO₃ additive absorbance after the firing process.

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