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Preparation and Evaluation of highly Monodispersed Ni powders use for pulverization and dispersion technique

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Abstract

Highly dispersed Ni powders for base metal electrode (BME) for multilayer ceramic capacitors (MLC), prepared by carbonyl process and wet chemical process, have been realized by means of noble pulverization and dispersion technique. Carbonyl Ni powders have relatively large particle size and strong oxidation-resistance property. Therefore ,they are suitable for BME with small capacitance MLC with low active layer (>50layers). On the other hand ,wet chemical process Ni powders poses fine particles size and they are suitable for large capacitance MLC with high active layers(<50 layers).

It is obvious that a narrow distribution particle size and highly dispersed Ni powders developed by the pulverization and dispersion technique make them ideal to realize thin layer BME for MLC.

Key word: Ni powders, Base metal electrode, Paste, Multilayer ceramic devices, Ceramic Capacitors, Dispersion

1.Introduction

The demand for multilayer ceramic capacitors (MLCs) has rapidly increased, because they are easily miniaturized and their performance can be improved, resulting in a strong demand for price reduction and increasing capacitance value. Therefore, it is essential to use low-cost materials in the fabrication of internal electrodes as they account for most of the cost. In order to realize a large capacitance value of MLCs without changing their shape, the dielectric layer and the internal electrode layer must be thinned and made into a multilayer. The dielectric layer and the internal electrode layer subjected to thinning tend to induce short circuits between layers and connection failure, resulting in structural defects. Accordingly, in order to prevent short circuiting and conduction failure, powder materials used for both the dielectric and the internal electrodes need to be sufficiently dispersed into the primary particles without any agglomerated particles.

Toward this end, Ni instead of the conventionally used Pd, has been intensively studied for cost reduction.[1-8)] However, studies were mainly carried out on ceramics, which were the base material of the capacitor. Only a handful of studies dealt with Ni powder used as the internal electrode.[9-10)] At present, Ni powder obtained by (chemical vapor deposition) CVD is being studied; however, such powders are disadvantageous in that their manufacturing cost is high, nucleus development and particle growth occur simultaneously, and particle size distribution tends to be substantial even though they have excellent dispersibility.

Thus, we focused on the use of carbonyl Ni powders, which exhibit excellent heat and oxidation resistance even though they tend to aggregate, as internal electrodes of low-level MLCs. Meanwhile, for internal electrodes of high-level MLCs, we examined Ni powders synthesized by the wet chemical process, which had strong aggregation forces even though their particle size was homogeneous and suitable for the fabrication of thin-layer electrodes.

In this study, we examined the method of pulverizing agglomerated particles such as the two types of Ni powders. We report the characteristics of pulverized Ni powders with high dispersibility when they exist as powders or as paste for use as an internal electrode.

2.Experimental

In this study, we used carbonyl Ni powder (Daiken chemical Industry, Ni-002325NS) as a metal of internal electrodes in low-level MLCs, Ni powder (Daiken chemical Industry, Ni-001014 DMAX SUPER) synthesized by a wet chemical process (hereafter, WCP-Ni powder) and (commercially available) Ni powder synthesized by CVD (hereafter, CVD-Ni powder).

AS for the pulverization of agglomerated fine particles, using a scanning electron microscope (SEM; Nihon Electron, JSM-6100), the average particle size and the particle size distribution of carbonyl Ni powder mechanically pulverized by a dry method and that of Ni powder synthesized by the wet chemical process when it was mechanically pulverized by the wet method.

We measured the particle size distribution of powders using the laser diffraction method (Nikkisou, Microtrack-HRA100 particle size distribution measuring instrument) to determine the particle aggregation conditions before and after pulverization. On the basis of the change in particle size distribution, the state of particle dispersion was evaluated. The detailed structure of surfaces was observed using a SEM. Fine particles were also characterized by the measurement of tap density and specific surface area using the BET method. Paste characteristics were evaluated by measuring the dry density, the packing rate of fine particles and the surface roughness.

We evaluated the oxidation behavior and heat resistance of three powders, Ni powder synthesized by the wet chemical process, Ni powder synthesized by CVD and carbonyl Ni powder, by thermogravimetry and differential thermal analysis (TG-DTA; Rigakudenki, Thermoflex).

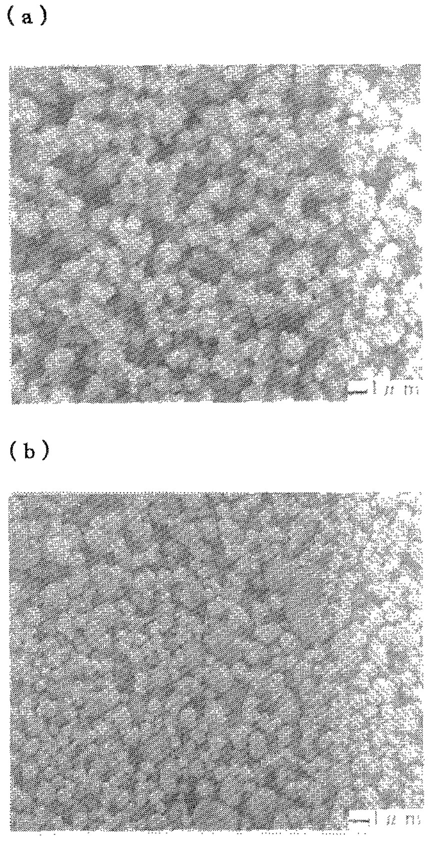
3. Results and Discussion

3.1 Pulverization of agglomerated particles

3.1.1 Synthesis of Ni powder with high dispersibility

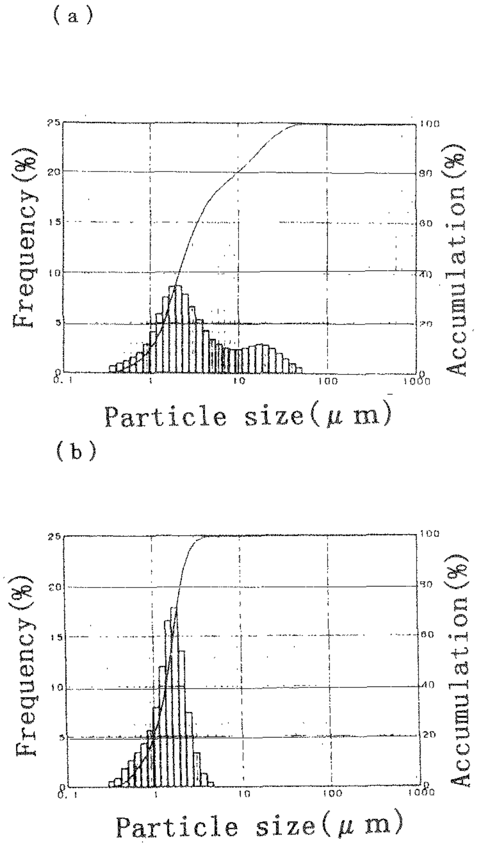
Agglomerated particles explain the dry and wet method in experimental were pulverized into primary particles by applying mechanical force in the dry and the wet method.

Metal powders usually form rigid, agglomerated particles when they are reduced to fine particles around 1 μm in size and behave as if they were rough particles. When metal powders dispersed in a liquid, they are pulverized again after extraction and drying to form remarkably rigid reagglomerated particles. In this study, we controlled the reaggregation of pulverized particles using the following methods. Organic compounds that form bonds with metal powders were added to the metal powders. Then, agglomerated particles were pulverized by applying a mechanical strong shear force on them.



(1)

Fig. 1. (1) SEM photograph of carbonyl Ni powders.
(a) Non-pulverized carbonyl Ni powders.
(b) Pulverized carbonyl Ni powders.



(2)

Fig. 1. (2) A particle size distribution measured by Microtrac laser particle size analyzer.
(a) Non-pulverized carbonyl Ni powders.
(b) Pulverized carbonyl Ni powders.

Simultaneously, mechanochemical reactions were induced on the newly formed particle surface. Reaggregation was suppressed by the formation of an organic self-organizing film on the particle surface.

Figure 1(1) shows SEM images of carbonyl Ni powder before and after pulverization by mechanical dispersion. Figure 1(2) shows the particle size distribution of carbonyl Ni powder. As shown in Figs. 1(1) and (2) the agglomerated particles shaped like a bunch of grapes of size about 10 μm or more, were pulverized into primary particles after pulverization. It seems that the pulverized slurry suppressed reagglomeration due to drying by the formation of an organic self-organizing film on the particle surface. Although it is not shown in the figures, this hypothesis was confirmed by the particle size distribution after drying.

Meanwhile, similar to carbonyl Ni powder, Fig. 2 shows an SEM image of Ni powder synthesized by the wet chemical process after pulverization, and Figs. 3(1) and (2) show the particle size distribution of Ni powder before and after pulverization. Based on these, we determined that Ni powder synthesized by the wet chemical process was transformed into primary particles by pulverization.

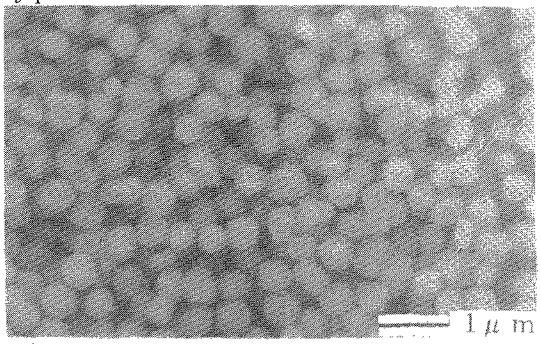


Fig2.SEM photograph of pulverized Ni powders synthesized by WCP.

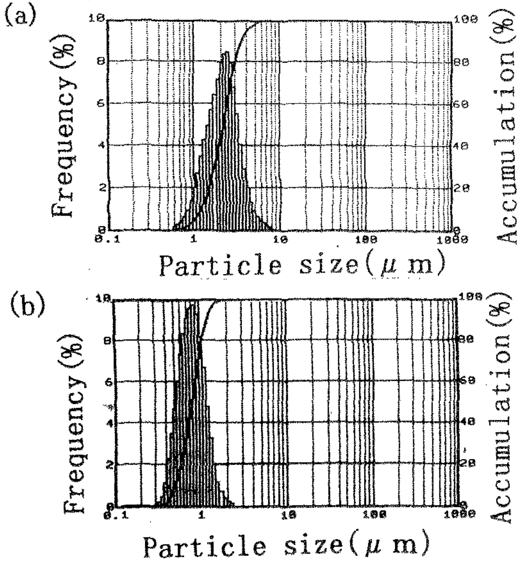


Fig3.A particle size distribution measured by microtrac laser particle size analyzer.
(a) Non pulverrized WCP-Ni powders.
(b) Pulverrized WCP-Ni powders.

3.2 Fine particle characteristics of Ni powder

3.2.1 Influence of agglomerated particles on specific surface area and tap density

Table I shows the specific surface area and tap density measured by the BET method before and after the pulverization of carbonyl Ni powder and Ni powder produced by the wet chemical process. Pulverized Ni powder has a smaller surface area and a higher tap density than nonpulverized Ni powder. These differences are considered to be due to the transformation of agglomerated particles into monodispersed particles by pulverization.

Table I. Densities of carbonyl Ni powders.
(a)Non-pulverized carbonyl Ni powders. (b)Pulverized carbonyl Ni powders.

Sample name	Average particle size (μ m)	Specific surface area (m^2g^{-1})	Tap density (gcm^{-3})
(a)	2.61	1.36	2.93
(b)	1.54	1.11	3.19

Table II. Densities of wet chemical process Ni powders.
(a)Non-pulverized wet chemical process Ni powders. (b)Pulverized wet chemical process Ni powders.

Sample name	Average particle size (μ m)	Specific surface area (m^2g^{-1})	Tap density (gcm^{-3})
(a)	2.14	1.88	2.86
(b)	0.79	1.54	2.88

3.2.2 Thermal characteristics of Ni powder

As is already well known, the sintering of ceramic capacitors which use a Ni electrode consists of the following three steps: the debinding process in which the binder (general term for organic binder used for forming and multilayering of ceramic materials) is subjected to an acidic atmosphere; the sintering process of Ni electrodes and dielectric ceramics in a reducing atmosphere; and the cooling process. Accordingly, in order to study the thermal oxidation behavior of the Ni electrode, it is necessary to compare the thermal oxidation behaviors at temperatures ranging from room temperature to around 700°C in air.

For the three kinds of Ni powders, Ni powder synthesized by the wet chemical process with fine particle characteristics(table2), Ni powder synthesized by CVD and carbonyl Ni powder (Table 1), Their thermal oxidation behaviors were investigated by subjecting them to increasing temperatures from room temperature to 1000°C centering at 500°C in air, by TG-DTA analysis. Then, we compared and heat evaluation and oxidation resistance of the three kinds of Ni powders.

The TG curves in Fig. 4(1) indicate that the three powders began to oxidize gradually from 300°C; the oxidation was accelerated when the temperature exceeded 400°C. In particular, a sharp weight increase due to oxidation was observed at around 550°C in Ni powder synthesized by the wet chemical process and Ni powder synthesized by CVD, while that of carbonyl Ni powder was observed at around 600°C. Afterwards, the extremely slow oxidation of Ni powder synthesized by the wet chemical process and the CVD derived Ni powder was observed. The TG-DTA curve of Ni powder synthesized by CVD was saturated at around 600°C due to rapid oxidation; in contrast, the TG-DTA curve of carbonyl Ni powder was saturated at around 700°C. Accordingly, it became clear that the thermal oxidation saturation temperature of carbonyl Ni powder was approximately 100°C higher than that of Ni powder synthesized by CVD. Ni powder synthesized by the wet chemical process had comparable heat and oxidation resistance to Ni powder synthesized by CVD. Meanwhile, the differences in the exothermic and endothermic peaks among the three kinds of Ni powders, as shown in Fig. 4(2), indicate that carbonyl Ni powder excelled in terms of oxidation resistance and that Ni powder synthesized by the wet chemical process exhibited a comparable oxidation resistance to Ni powder synthesized by CVD. The tendency of weight increase by oxidation, which occurs after 600°C, was slightly different among the three kinds of Ni powders. We assume that the difference occurred because the shape of the powders differed depending on the atmosphere in which the powders were manufactured and due to the difference in the manufacturing equipment used. However, details should be clarified in future studies.

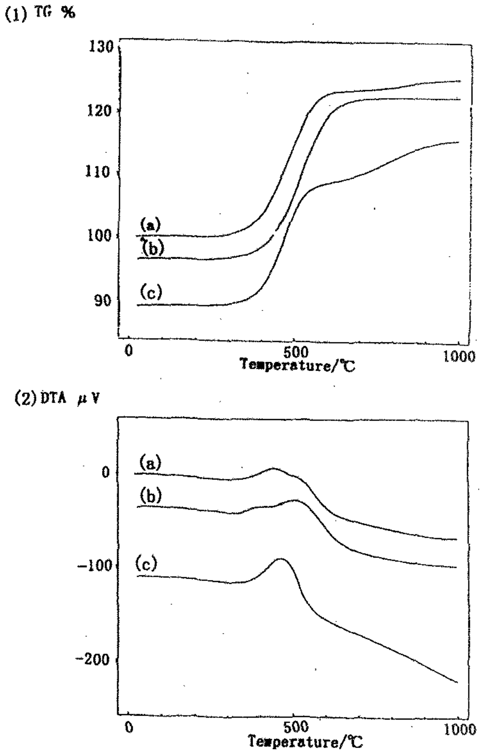


Fig4.TG-DTA curve of Ni powders.

(1) TG curve (2)DTA curve

(a) CVD Ni powders. (b) Carbonyl Ni powders. (c)WCP-Ni powders.

3.3 Paste characteristics of Ni powder with high dispersibility

3.3.1 Influence of agglomerated particles on green density

(In the internal electrode paste) , it is essential that primary particles exist in the form of homogeneous monodispersed particles without agglomeration . The level of monodispersity could be evaluated from their packing density.[17]

The packing density (P) is given as follows:

$$P=\rho_g\cdot X_d/\rho_d\cdot \qquad (1)$$

Where the green density is (ρ_g), the dry density of powder is (ρ_d) and the percentage content of powder weight is (X_d).

The results of the packing density using equation (1) show that the packing rate of non pulverized carbonyl Ni powder was approximately 39.8% while that of pulverized Ni powder was greatly increased to approximately 54.5%. The packing rate of Ni powder synthesized by the wet chemical process was greatly increased from 37.5% before pulverization to 60.2% after it. However, on the basis of theoretical density, when the packing density was set under an eight-coordination packing condition (60.45%) obtained by pressure-free forming, the residual void rate was approximately 9.8% for carbonyl Ni powder, and 0.3% for Ni powder synthesized by the wet chemical process. Thus, it seems unlikely that the complete pulverization of agglomerated particles of carbonyl Ni powder occurred, and further investigation on pulverization is required.

Figure 5 shows the difference in the dependence of green density on the mixing time between Ni paste synthesized by CVD and that synthesized by the wet chemical process, when they were simply mixed in an agitator. Figure 5 reveals that the pulverized Ni paste synthesized by the wet chemical process had a higher average green density than Ni paste synthesized by CVD. Therefore, it became clear that Ni powder synthesized by the wet chemical process exhibited high dispersibility and was very dense even after dispersion and pulverization.

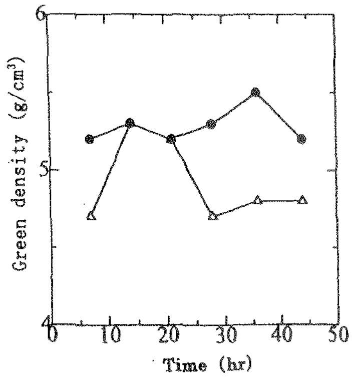


Fig5.Relationship between mixing time and paste green density of pulverized WCP Ni powder paste and CVD Ni powder paste.

● ; Paste of pulverized Ni powders synthesized by WCP.

△ : Paste of Ni powders synthesized by CVD.

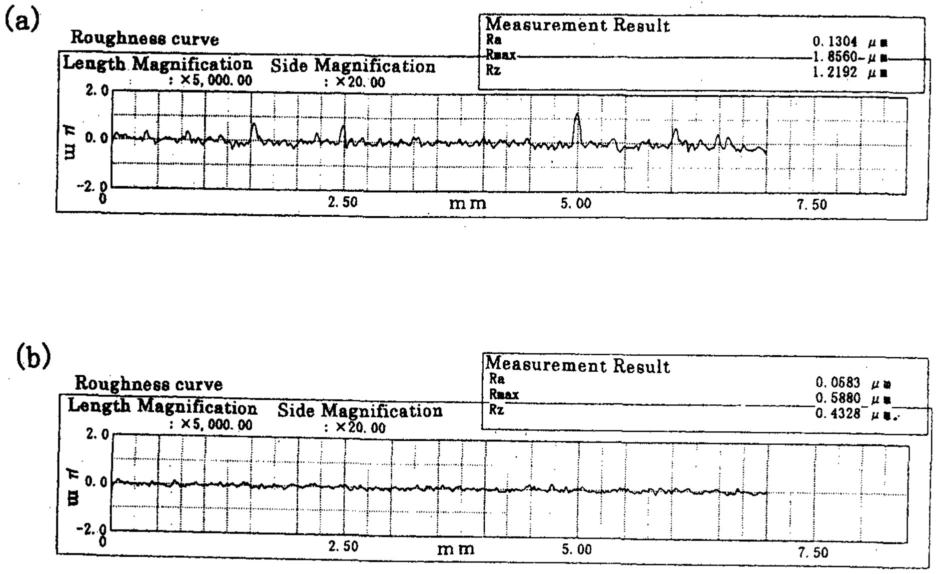


Fig6.Surface roughness of Ni paste synthesized by WCP Ni powders.

(a) Paste of nonpulverized Ni powders.(b)Paste of pulverized Ni powders.

3.3.2 Influence of agglomerated particles on surface roughness

The surface of the pastes formed by screen printing needs to be smooth without pin-holes. With increasing demand for further high-level multilayering, the thickness of the electrode film per layer tends to be reduced. In particular, excellent smoothness is required for Ni paste used in high-level MLCs. We compared the surface roughness of the paste synthesized from pulverized and nonpulverized Ni powders for a high-level MLCs.

After preliminary mixing of ethylene glycol mono-n-butyl ether solution in which non pulverized Ni powder was dissolved to binder in advance using a high-speed oscillation mixer (Daiken chemical Industry, MKR-300), simple mixing in an agitator was performed to produce Ni powder pastes.

Figure 6 shows that this Ni powder paste had an Ra of 0.13 μm and an Rmax of 1.85 μm, and had a rough surface. On the other hand, the paste of pulverized Ni powder, which was prepared by the same process as the non pulverized Ni powders, had an extremely smooth surface with an Ra of 0.05 μm and an Rmax of 0.58 μm. Therefore, pulverized Ni powder can form a smooth and homogeneous film that mainly consists of primary particles on which pinholes are difficult to generate. This is a desirable condition for producing high-level MLCs.

Figure 7 shows the difference in the dependence of surface roughness on mixing time in an agitator between the paste of Ni powders synthesized by CVD and the paste of pulverized Ni powder synthesized by the wet chemical process. Figure 7 also shows that paste of pulverized Ni powder synthesized by the wet chemical process had excellent smoothness compared to the paste of Ni powder synthesized by CVD. Therefore, it became clear that dispersed and pulverized Ni powders exhibit high dispersibility in the case of simple mixing using an agitator; therefore, they are suitable for use as internal electrodes of high-level MLCs which require a thin layer of electrode film.

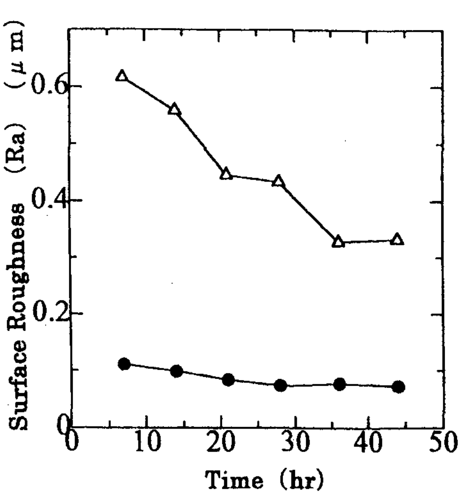


Fig7.Relationship between mixing time and paste surface roughness of pulverized WCP Ni powder paste and CVD Ni powder paste.

● ; **Paste of pulverized Ni powders synthesized by WCP.**

△ : **Paste of Ni powders synthesized by CVD.**

4. Conclusions

The fine particle characteristics and paste characteristics of aggregated and pulverized Ni powders which are to be used as internal electrodes of MLCs was studied. The following results were obtained:

(1)Carbonyl Ni powder, and Ni powder synthesized by the wet chemical process into primary particles were pulverized when they were subjected to pulverization.

(2)Carbonyl Ni powder excelled in terms of heat and oxidation resistance compared to Ni powder synthesized by the wet chemical process and Ni powder synthesized by CVD.

(3)Based on the results of paste green density, carbonyl Ni powder and pulverized Ni powder synthesized by the wet chemical process were found to exhibit excellent dispersibility.

(4)After paste printing, the surface roughness Ra was 0.05 μm and Rmax was 0.58 μm, satisfying the level of smoothness required for use as high-level MLC electrodes.

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