Improved Nickel Powder for Small Case Size MLCC with High Capacitance

1. Introduction

JEF Mineral manufactures nickel ultrafine powder having advantageous characteristics such as high crystallinity, sharp particle size distribution, and high purity. This nickel ultrafine powder is mainly used for internal electrodes of multi-layer ceramic capacitors (MLCC) as shown in Fig. 1. The internal electrode of MLCC is fabricated by turning nickel ultrafine powder into a paste using an organic solvent, by printing the prepared paste to a thin layer, and then by firing the printed paste. Owing to these advantageous characteristics, the nickel ultrafine powder of JEF Mineral easily forms an electrically continuous and homogeneous thin film electrode after firing, and the drop in capacitance of MLCC with the reduction of nickel weight per layer is small. With these merits, JFE Mineral has captured 60% of the global market for nickel ultrafine powder for internal electrodes of MLCC (as of Sep. 2004).

In recent years, the development and commercialization of small case size and high capacitance MLCC has progressed rapidly with the reduction of layer thickness and increase of the number of layers. As a result, the demand for fewer coarse particles in the nickel ultrafine powder as an electrode material has grown, because the coarse particles penetrate the dielectric layer and induce short-circuits between electrodes. Each year, even



Fig.1 Cut-away view of multilayer ceramic capacitor





smaller coarse particles must be removed as the dielectric layer is made thinner, as shown in **Fig. 2^{1}**.

JFE Mineral has developed a technology for classifying metal powder of sub-micron particle size, and in 2001 commercialized nickel ultrafine powder products from which coarse particles had been removed. Regarding these commercialized products, this paper describes the product grades NFP201S, NFP301S, and NFP401S, in which coarse particles are removed, and also the new product grade NFP201X.

2. Classified Grades of Nickel Ultrafine Powder

2.1 Manufacturing Process and Product Line-up

Figure 3 shows the manufacturing process of nickel ultrafine powder and the average particle size of each



Fig.3 Manufacturing process of Ni powder

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product grade. JEF Mineral manufactures the main product grades (NFP201, NFP301, and NFP401) by the CVD process in which vaporized nickel chloride is reduced by hydrogen. The average particle size and the particle size distribution of products are controlled mainly by adjusting the operating conditions of CVD reactions. Nevertheless, since coarse particles of $1 \,\mu m$ or larger still exist at ppm order in number, it is difficult to further decrease the quantity of coarse particles by CVD reaction control alone. MLCC has grades of layering several hundred dielectric layers and electrode layers, thus the rejection rate of MLCC products is seriously affected by the existence of coarse particles of even ppm order. With this background, JFE Mineral has established a process flow to remove coarse particles from the nickel ultrafine powder manufactured by the CVD process by applying classification after refinement. Grades of NFP201S, NFP301S, and NFP401S are manufactured by classifying the conventional product grades of NFP201, NFP301, and NFP401, respectively, by wet-centrifugal separation, thereby removing coarse particles of 3 μ m or larger.

Furthermore, JFE Mineral has developed a more precise classification process, and has successfully removed coarse particles of $0.8 \,\mu\text{m}$ or larger. This new product grade is NFP201X.

2.2 Characteristics of Classified Products

Photo 1 shows SEM images of NFP201S, NFP301S, NFP401S, and the new product grade NFP201X in which coarse particles are removed. As seen in Photo 1, reduction in the average particle size makes the particle size distribution sharper. **Figure 4** compares the number of coarse particles measured by SEM. For NFP201S, NFP301S, and NFP401S, the counted number of coarse



Photo 1 SEM images of classified products



Fig.4 Number of coarse particles measured by SEM

Table 1 Powder characteristics of classified products

Average diameter of primary particle (µm)		NFP401S	NFP301S	NFP201S	NFP201X
		0.4	0.3	0.2	0.2
BET specific area (m²/g)		1.78	2.56	3.30	3.76
0	(mass%)	0.4	0.5	0.6	1.0
Cl	(mass%)	< 0.003	< 0.003	< 0.003	< 0.003
Tap density	(g/cm ³)	4.0	3.7	3.4	3.8

particles of 3 μ m or larger is zero, and the number of coarse particles of 1 μ m or larger is also decreased compared with standard particles. For NFP201X, the number of coarse particles of 0.8 μ m or larger is significantly decreased.

Table 1 shows the powder characteristics of each classified product grade. The BET specific surface area is stabilized by minimizing the thickness of the surface oxide layer and by decreasing the irregularity of the particle surface.

3. Present State and Future Developments

NFP201S, NFP301S, and NFP401S, in which coarse particles of 3 μ m or larger are eliminated by classification after CVD process, are popular in the market as nickel ultrafine powder for the internal electrodes of MLCC. In particular, NFP201S contains less coarse particles of 1 μ m or larger, causing demand for this grade to increase rapidly as the electrode material for mass-produced small case size MLCC with high capacitance. In the mass-production and classification process of JFE Mineral, the percentage of coarse particles and the thickness of the surface oxide layer on the nickel ultrafine powder are strictly controlled, thereby assuring high reliability when using the powder for small case size MLCC with high capacitance. As a result, JFE Mineral has captured 90% of the market for nickel ultrafine powder for MLCC high performance products (3 μ m or smaller layer thickness). NFP201X, in which coarse particles of 0.8 μ m or larger are eliminated, is an effective electrode material for small case size MLCC with high capacitance having 1 μ m or smaller layer thickness, which will enter the mass-production line.

Since the layer of MLCC is expected to become thinner (to 0.5 μ m thickness), JFE Mineral has developed NFP101 having an average particle size of 0.1 μ m by adjusting the CVD reaction conditions (**Photo 2**). The issues for commercializing this product grade as an internal electrode material for reduced layer thickness are (1) improvement of accuracy of classification, (2) improvement of dispersibility, and (3) increase of starting temperature of sintering.

Regarding the improvement of accuracy of classification, the classification method used in the NFP201X manufacturing is being applied to the manufacturing process of NFP101, and a technology to remove coarse particles of 0.6 μ m or larger, or 0.3 μ m or larger, is being developed. To improve dispersibility, a wet-type product is being developed by supplying the product to users in



Photo 2 SEM images of 0.1 µm product "NFP101"

the form of the nickel ultrafine powder dispersed in an organic solvent, while preventing coagulation. In parallel with these developments, delayed sintering technology is being developed to raise the starting temperature of sintering of nickel ultrafine powder by coating the nickel with another element which effectively prevents delamination caused by shrinkage mismatch between the dielectric layer and electrode layer while firing MLCC. Studies on commercializing NFP101 are now underway.

References

1) Sakabe, Yukio. Center for Dielectric Studies Fall Meeting Penn. State Univ. 2004.

For Further Information, Please Contact to:

Advanced Materials Sales Dept., Advanced Materials Div., JFE Mineral Phone: (81) 3-5288-6849