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Shrinkage behavior and interfacial diffusion in Ni-based internal electrodes with $BaTiO_3$ additive

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Abstract

The effects of particle size of starting materials and amount of a $BaTiO_3$ additive on the shrinkage behavior and elemental diffusion in Ni-based internal electrodes have been investigated in order to control the shrinkage of the internal electrode in multilayer ceramic capacitors (MLCCs). Two kinds of Ni and $BaTiO_3$ powders were used with different particle sizes. Volume shrinkage over the range of 700–1300 °C at 150 °C intervals and linear shrinkage during sintering were measured for starting materials and composites in a reducing atmosphere. The interfaces of Ni/$BaTiO_3$ composites with 90:10 and 70:30 volume ratios, respectively, were investigated using TEM. Composites with bimodal Ni powder show less shrinkage than those with monomodal Ni powder, showing less shrinkage in monolith Ni of bimodal particle size. The shrinkage behavior is changed during sintering with increasing amounts of $BaTiO_3$ additives in both Ni-based composites. The particle size of the $BaTiO_3$ additive affects the shrinkage behavior of composites, without the additional amount affecting the final shrinkage. A reaction layer of about 300 nm wide is observed at the interface between the Ni and $BaTiO_3$ powders in composites, in which elemental Ni diffuses into the $BaTiO_3$ without counterdiffusion.

Keywords: B. Interfaces; C. Diffusion; E. Capacitors; Internal electrode

1. Introduction

In the fabrication process for multilayer ceramic capacitors (MLCCs), the downsizing of dielectric and internal electrode layers and the reducing of cost are key processing technologies to meet the demand for miniaturization of electric components and to improve properties. For this purpose, smaller-sized powders and cheaper base metals need to be used as dielectric and electrode materials, respectively, and more attention must be given to the sintering process to control the shrinkage mismatch between dielectric and electrode layers in MLCCs, as this is the main reason for residual stress resulting in cracking and delamination during fabrication and service [1–6].

A significant number of residual pores are formed after binder burnout, giving a porosity of 40–50 vol.%. Even though the residual pores disappear during the sequential sintering process, normally the sintering process shows a shrinkage mismatch, larger than a 10% linear shrinkage ratio, between the ceramics and the internal electrode. There have been numerous studies undertaken to avoid the formation of sintering defects or to reduce the mismatch [7–10]. Usually, when the Ni paste used as an internal electrode is printed on the green sheet prepared by the so-called slot-die method used in industry, a dielectric material, $BaTiO_3$, is added into the paste to control the shrinkage mismatch. However, the shrinkage behavior will change as the powder size is reduced to reduce the layer thickness in both the dielectric and internal electrode layers. In addition, the formation of an interdiffusion layer between the dielectric and internal electrode layers has been reported in previous studies [11–14], which plays an important role in the properties of MLCCs such as dielectric constant and Curie temperature. Low sintering temperatures and compositional gradients have been recommended to decrease the interdiffusion [13]. Investigation for the interaction between the matrix, Ni, and the additive, $BaTiO_3$, in the internal electrode, however, has been limited and results here are different to those previously reported [15–17]. Therefore, estimation of shrinkage behavior and investigation of diffusion phenomena with

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respect to the mixing composition ratio of Ni and $BaTiO_3$ powders are essential for improving reliability through the optimized fabrication process of MLCCs.

The aim of this study is to find the optimum-mixing ratio of Ni and $BaTiO_3$ powders and to know the effects of Ni and $BaTiO_3$ particle sizes on shrinkage behavior and composition change. Therefore, the present work describes the influence of the particle size of the starting materials and mixing ratio on the shrinkage behavior and interdiffusion phenomena in $BaTiO_3$-added Ni electrodes. The relationships among the starting materials, shrinkage behavior, mechanical properties, and diffusion phenomena have also been investigated.

2. Experimental procedure

Two kinds of nickel (Ni) and barium titanate ($BaTiO_3$, Sakai Chemical Industry Co. Ltd., Japan, hereinafter referred to as BT) powders were used as the matrix and additive, respectively, to modify the internal electrode in MLCCs. For the Ni powders, one was bimodal with particle sizes of 0.1 and 0.5 μm (nominal particle size of 0.3 ± 0.2 μm, Shoei Chemical Industry Co. Ltd., Japan, hereinafter referred to as Ni-1) and the other was monomodal with a particle size of 0.2 μm (Soho Chemical Industry Co. Ltd., Japan, hereinafter referred to as Ni-2). The $BaTiO_3$ powers had monomodal particle sizes of 0.1 μm (hereinafter referred to as BT-1) and 0.2 μm (hereinafter referred to as BT-2). Images observed with a scanning electron microscope (SEM, S2700, Hitachi, Japan) are shown in Fig. 1. The powders of Ni and BT were mixed in volume ratios of 90:10, 80:20 and 70:30, respectively, considering the particle sizes of Ni and BT, and reference specimens using only Ni and BT were also prepared. The mixed powders were ball-milled over 12 h in isopropyl alcohol without organic binder. Green compacts were uniaxially formed from granulated powders at 5 MPa and then hydrostatically pressed under 200 MPa. The sintering process was carried out in the reducing atmosphere of (97)Ar–(3)H_2 (vol.%) with a wet atmosphere (25 °C, H_2O), $P_{O_2} \approx 10^{-11}$ to 10^{-19}, from 700 to 1300 °C at 5 °C/min with a 150 °C interval. In each case, the dwell time was given as 1 h.

The green and sintered densities were measured for each mixing ratio, using the dimensions and Archimedes' methods after preparing the green body and at final sintering temperature, respectively. The volume shrinkage of each monolith material, the Ni and BT reference specimens, and each composite was measured in the range of 700–1300 °C at 150 °C intervals using the dimension method. The linear shrinkage of reference specimens and composites was measured with a heating rate of 5 °C/min to 1300 °C, using a dilatometer (Dilatometer, 5000S, Mac Science, Japan). Nanoindentation tests were conducted on each component: Ni matrix, BT additive, and Ni/BT interface regions in a composite, with a volume ratio of 70:30 of Ni and BT, respectively, to determine the values of elastic modulus (*E*) and hardness (*H*), using a nanoindentor (Nanoinstruments, MTS

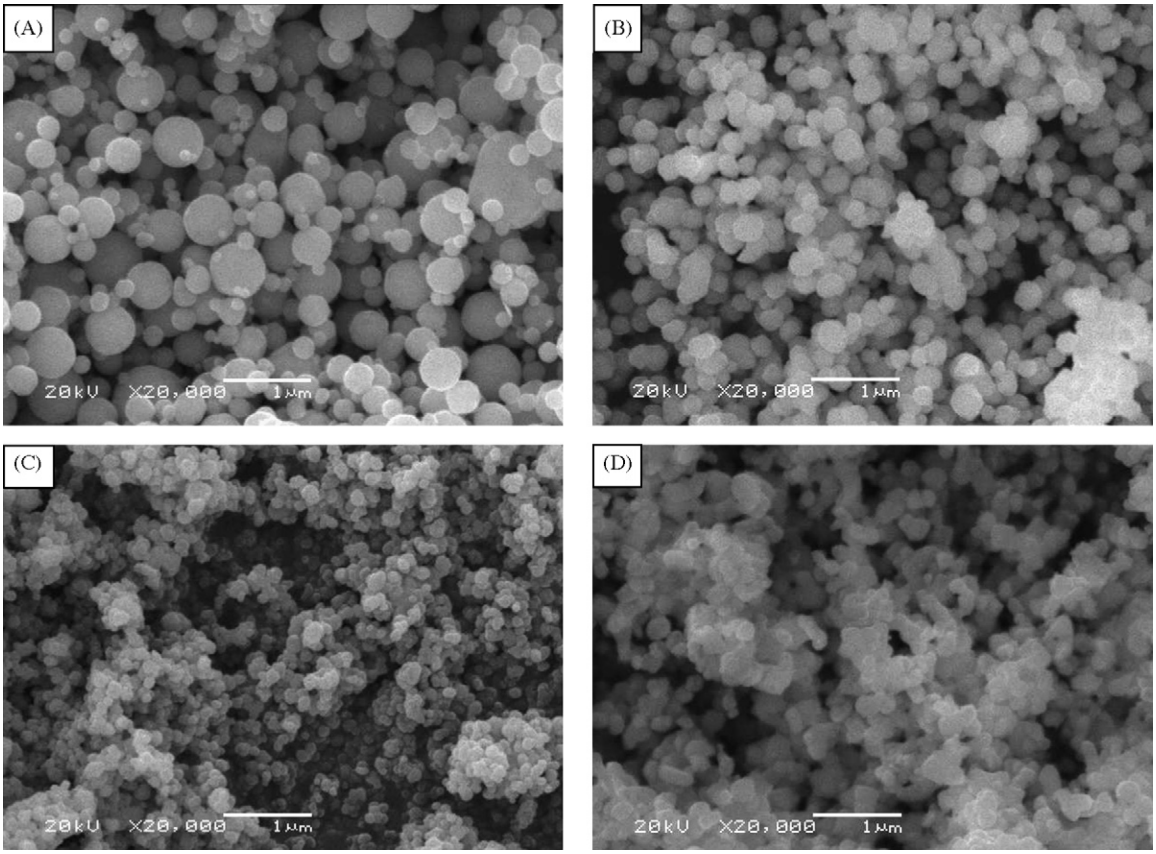

Fig. 1. SEM images of starting materials: (A and B) Ni powders of 0.3 ± 0.2 and 0.2 μm, respectively, and (C and D) $BaTiO_3$ powders of 0.1 and 0.2 μm, respectively.