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Synthesis and characterization of $BaTiO_3$-coated Ni particles

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Abstract

In this study, we proposed the processing of novel Ni powder coated with a major dielectric material $BaTiO_3$ layer to improve the large sintering shrinkage mismatch between Ni electrode and dielectric materials and the resistance to oxidation of Ni electrode in the co-firing process of multilayer ceramic capacitors (MLCCs). The $BaTiO_3$ coated Ni powders were successfully synthesized by the controlled hydrolysis of Ba–Ti complex alkoxide on the surface of Ni particles treated with NH_3. This $BaTiO_3$ coated Ni powder affords the drastically improved resistance to oxidation and sintering matching. In addition, the sintered compact prepared from this powder had sufficient conductivity as an alternative electrode.

Keywords: $BaTiO_3$; Ni–$BaTiO_3$; Coatings; Sintering; Electrodes

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1. Introduction

The improvement of MLCCs has been achieved by the control of the thickness and the lamination number of dielectric layers,[1] leading to an increase in the amount of internal electrode. In addition, the noble metal electrode Pd was, recently, replaced by base metal Ni in MLCCs because of its lower cost and lower resistivity compared with Pd. However, there are two serious problems in using Ni as an electrode material, which are a large sintering mismatch and oxidation of Ni. In the co-sintering process of multilayer dielectric/electrode green sheets, significant defects such as cracks and delamination[2,3] were commonly observed due to the large difference in the sintering temperatures between Ni and dielectric materials. Furthermore, Ni metal is easily oxidized under the oxidative atmosphere during co-firing. For this reason, the development of the process to synthesize MLCCs without any defects under the reductive atmosphere was greatly desired.

The addition of various materials such as sub-micron $BaTiO_3$ powders to Ni powder has been investigated to depress the contacting and sintering of Ni particles at lower temperatures.[4] However, this conventional method did not satisfy the requirements mentioned above, since the fine secondary particles tend to aggregate easily. In the near future, further improvements would be required for the sintering of MLCCs by suppressing the heterogeneous aggregation of the particles through the development of newly composed electrodes.

In this study, we proposed a novel method to improve the sintering and the oxidation resistances of Ni particles for internal electrode of MLCCs by the homogeneous coating of Ni powder with $BaTiO_3$ through the sol-gel method. The $BaTiO_3$ layer plays an important role in preventing both contacting and oxidation of Ni particles during sintering. In addition, the coated layer decreases the surface free energy of Ni particles, resulting in the improvement of dispersibility of the Ni particles. Chemical composition, sintering behavior and microstructure of the $BaTiO_3$ coated Ni particles (Ni–BT) were investigated. In the present work, we applied the sol-gel method[5–8] to coat the Ni particle with $BaTiO_3$ because of advantages such as ease of controlling the chemical composition, low processing temperature and homogeneity of the coating layer.

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2. Experimental

2.1. Surface treatment of Ni particles

The Ni powder (Shoei Chemical Inc., Japan) with the mean particles size of 4.0 μm was selected as a starting material for internal electrode of MLCCs. An aqueous suspension with 5 vol.% Ni powder was prepared at pH 11.5. The pH of the suspension was adjusted by the addition of aqueous ammonium solution. The suspensions were refluxed at 100 °C for 24 h, then the treated Ni particles were ultrafiltrated, washed with 1-PrOH, and finally dried at 100 °C for 12 h. This powder is named as Ni–NH_3.

2.2. Surface coating of Ni particles with $BaTiO_3$ layer

Ba metal (Raremetallic Inc., Japan) and $Ti(O^iPr)_4$ (Ko-jundo Chemical, Japan) were used as starting materials for the $BaTiO_3$ coating layer. Ba metal and $Ti(O^iPr)_4$ corresponding to the composition of $BaTiO_3$ were dissolved in a mixed solvent of 1-PrOH and 2-methoxyethanol (EGMME, Kishida Chemical Co., Japan) with a volume fraction of 5:1. The precursor solution was refluxed for 24 h, and was diluted with 1-PrOH up to 0.01 mol/l. Ni–NH_3 and original Ni powders were added to this $BaTiO_3$ precursor solution, then followed by the hydrolysis with 0.02 mol/l deionized water in 1-PrOH and refluxed for 24 h. The Ni particles coated with Ba–Ti–O (Ni–BT) were separated by an ultrafiltration, washed with 1-PrOH and dried at 100 °C.

2.3. Characterization

Ni–NH_3 and original Ni powders were characterized by X-ray diffraction (XRD; Rigaku, RAD-2B) using CuKα radiation with a monochrometor, electron spectroscopy for chemical analysis (ESCA; JEOL JPS-9000MC), scanning electron microscopy (SEM; JEOL, JSM-6100), and transmission electron microscopy (TEM) with an energy dispersive X-ray analysis (EDX). The oxidation resistance of Ni powders was evaluated by differential thermal analysis and thermogravimetric analysis (DTA and TG; Rigaku, TAS-300) in an O_2 flow. The composition of Ni–BT powder was investigated by ICP spectrometry (ICP-AES, Jarrell Ash, Plasma AtomComp. MK II).

3. Results and discussion

3.1. Surface treatment of Ni particles with ammonia solution

The effect of NH_3 treatment on the surface structure of Ni particles was first investigated, since hydroxide groups existing on the Ni surface were considered to be the nucleation sites of $BaTiO_3$ in the sol-gel coating process if the surface of Ni particles was successfully hydrolyzed.[5] Fig. 1 shows the spectra of O 1s and Ni $2p_{3/2}$ electrons of original Ni, Ni–NH_3, nickel oxide, and nickel hydroxide as references. Both spectra of O 1s and Ni $2p_{3/2}$ of Ni–NH_3 powder were similar to those of $Ni(OH)_2$, while the original Ni powder had almost the same surface structure as NiO. The treatment of Ni surface with NH_3, therefore, resulted in hydration of the Ni surface.

3.2. Homogeneous coating of Ni particle with $BaTiO_3$

It is known that the crystalline $BaTiO_3$ is synthesized by the hydrolysis of Ba–Ti complex alkoxides, which have the characteristic chemical bonds of Ba–O–Ti in its structure.[9] A mixed solvent of 1-PrOH and EGMME was used to prepare a stable and homogeneous $BaTiO_3$ precursor solution. The crystalline $BaTiO_3$ phase could successfully be synthesized by the hydrolysis of the alkoxide solution in the mixed solvent.

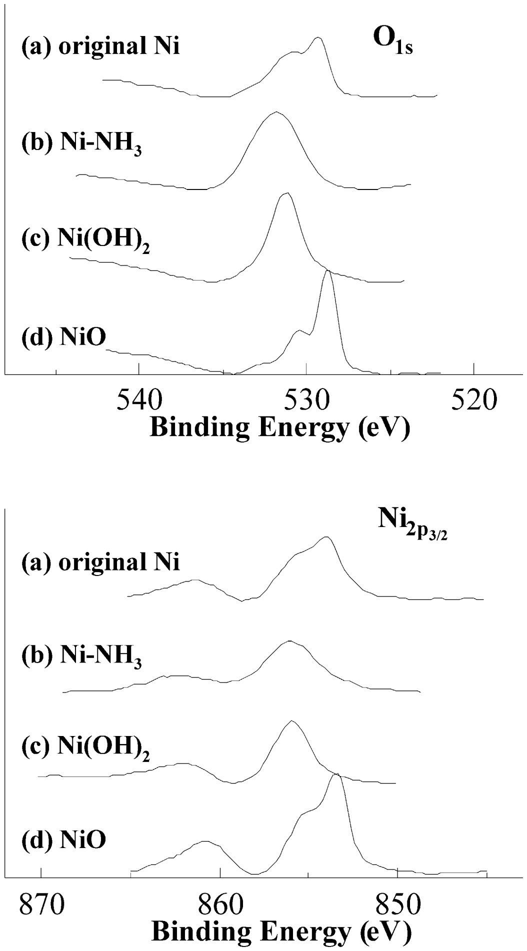

Fig. 1. ESCA profiles of (a) original Ni, (b) Ni–NH_3, (c) $Ni(OH)_2$ and (d) NiO.

The surface structure of Ni–BT powder was characterized as follows. Fig. 2 shows the SEM and TEM micrographs of Ni–BT. Their images [Fig. 2(b) and (c)] indicate that Ni–NH_3 was uniformly coated with the Ba–Ti–O layer of 30 nm in thickness. In addition, EDX analysis on the cross section of Ni-BT reveals that Ba, Ti, and O are homogeneously observed on the Ni particles as shown in Fig. 3. ICP analysis indicates that the ratios of Ba/Ti and (Ba or Ti)/Ni in Ni–BT powder were 1.0 and 3.0×10^{-3}, respectively, which reveals that Ni–NH_3 was successfully coated with an ideal $BaTiO_3$ layer.

In addition, Ni–BT particles had almost the same zeta potential as that of $BaTiO_3$ in contrast to the original Ni particles, as shown in Fig. 4. It turns out from these results that the chemical modification was suitable for the preparation of homogeneously coated Ni powder.

3.3. Oxidation and sintering behaviors of Ni–BT

Fig. 5 shows DTA and TG curves of the Ni–BT and the original Ni powders monitored in an O_2 flow. The oxidation of the Ni–BT powders was observed at 900 °C, which is 200 °C higher than that of the original Ni. The improvement of the oxidation resistance of the original Ni powder for internal electrode material was successfully achieved by the surface coating with $BaTiO_3$ layer.

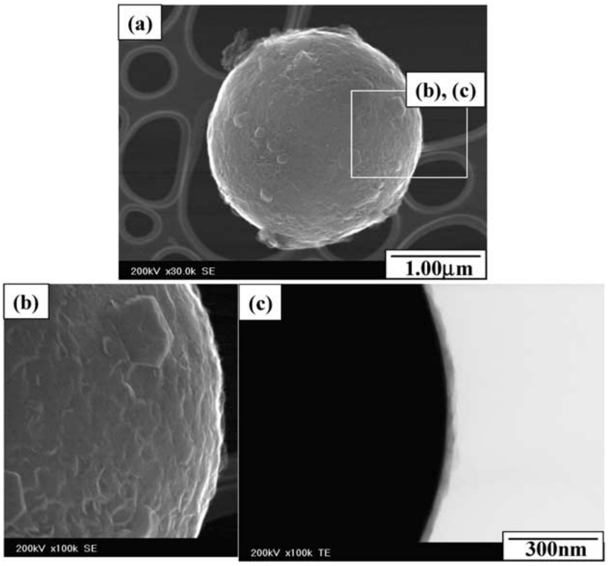

Fig. 2. SEM and TEM micrographs of Ni–BT.

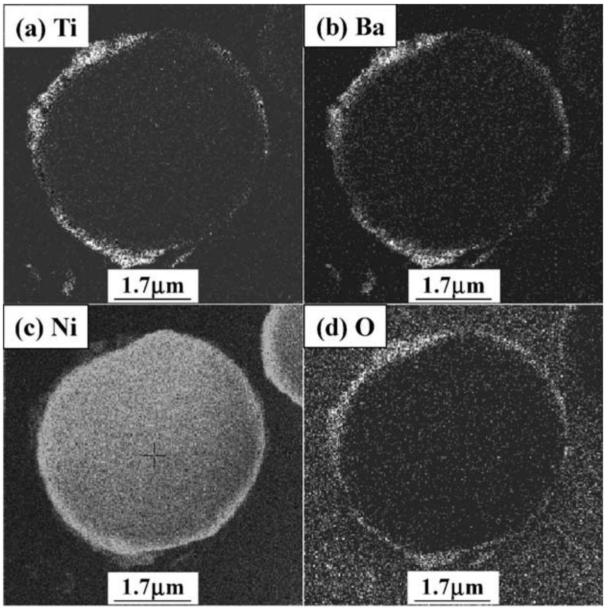

Fig. 3. EDX mapping on cross section of Ni–BT (a) Ti, (b) Ba, (c) Ni and (d) O.

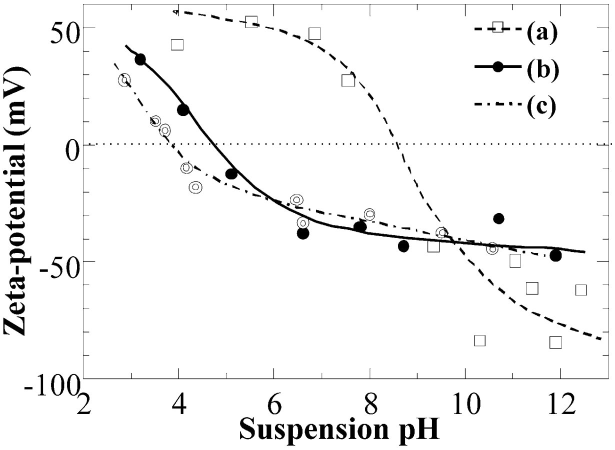

Fig. 4. Zeta-potential of aqueous suspensions of (a) original Ni, (b) Ni–BT and (c) $BaTiO_3$ particles.

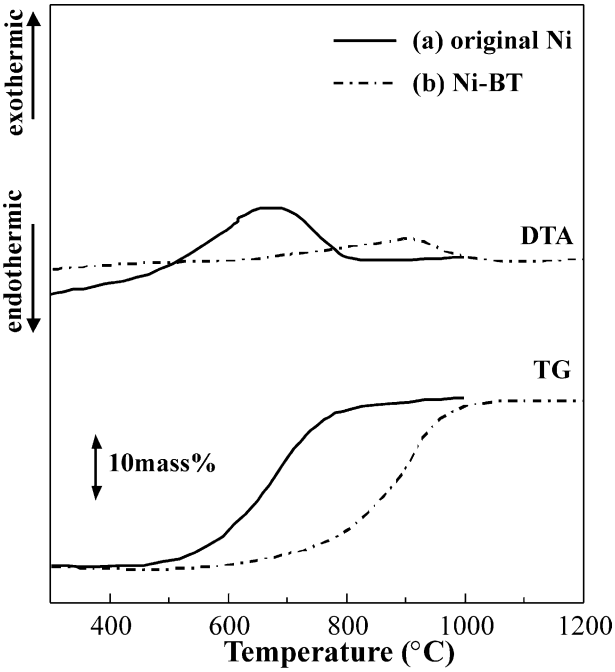

Fig. 5. DTA and TG curves of (a) original Ni and (b) Ni–BT.

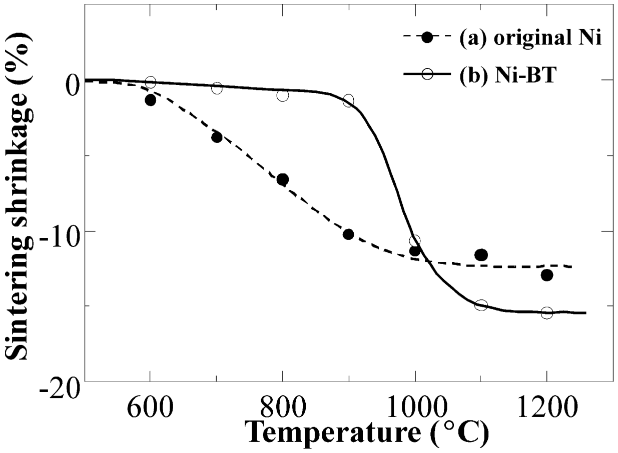

Fig. 6. Sintering shrinkage curves of (a) original Ni and (b) Ni–BT.

Fig. 6 shows the sintering behaviors of the original Ni and the Ni–BT powders up to 1200 °C. The Ni–BT powders began to shrink at higher temperature than the original Ni by 300 °C, since the $BaTiO_3$ layer interfered with the direct contact among Ni particles and prevented their sintering at lower temperatures, leading to the suitable matching of the sintering feature between Ni electrode and dielectric powders.

3.4. Electrical property of the sintered compact of Ni–BT

The resistivity of Ni–BT compact sintered at 1200 °C was confirmed to be 8.9×10^{-6} Ωcm, which was slightly higher than that of Ni metal (6.84×10^{-6} Ωcm). This value was low enough for the internal electrode of MLCCs.

4. Conclusion

The novel electrode layer material was developed by the homogeneous coating of Ni particles through controlled chemical processing. The effects of the surface coating of Ni powders with $BaTiO_3$ layer were investigated on the sintering and the oxidation of Ni powders, and the results are summarized as follows:

1. $BaTiO_3$ coated Ni particles could successfully be synthesized by the hydrolysis of Ba–Ti complex alkoxide on the surface of Ni particles treated beforehand with NH_3.
2. The resistance to the oxidation and sintering of Ni powder was drastically improved by the surface coating with $BaTiO_3$ layer.
3. The sintered compact prepared from $BaTiO_3$ coated Ni particles had sufficient conductivity as an alternative electrode material for Pd.

Acknowledgements

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