

Uniform Coating of Organic-Capped Ba-Ti-O Nanolayers on Spherical Ni Particles

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(2007년 1월 20일 받음, 2007년 2월 12일 최종수정본 받음)

Abstract The organic-capped Ba-Ti-O nanolayers were coated uniformly on spherical Ni particles for multilayer ceramic capacitor (MLCC) applications via the formation of Ti-hydroxide nano-coating layers and their subsequent reaction with Ba-stearate at 180°C. The capping of organic shell on oxide coating layer changed the hydrophilic surface structure into hydrophobic one, which significantly improved the dispersion behavior in hydrophobic solvents such as terpineol and butanol. In addition, the uniform coating of Ba-Ti-O layer was advantageous to prevent Ni oxidation. This method provides a useful chemical route to fabricate organic-soluble Ba-Ti-O coated Ni particles for a highly integrated passive component.

Key words Nickel, multilayer ceramic capacitor, coating, oxidation, organo capping, dispersion.

1. Introduction

The multilayer Ceramic Capacitor (MLCC) using a Ni electrode is one of the most representative passive components in the electronic and telecommunication industry.¹⁻³⁾ The higher capacitance within a smaller volume is a key development direction, which is being accomplished by thinning the BaTiO₃ active layers and Ni electrode layers. Two major challenges in fabricating a Ni electrode layer for a highly integrated MLCC are the prevention of Ni oxidation⁴⁾ during the binder-burnout stage and the reduction of shrinkage mismatch between the Ni and BaTiO₃ layers during sintering.⁵⁻⁷⁾

The addition of nano-sized BaTiO₃ particles can prevent low temperature sintering between Ni particles. However, Ni oxidation during the binder-burnout process is inevitable because the surface of the Ni is exposed to the atmosphere. The uniform coating of oxide nanolayers on a Ni powder can prevent not only low temperature sintering between the Ni particles but also the Ni oxidation.⁸⁻¹¹⁾ Because the dielectric properties of a MLCC are quite sensitive to the composition of the active layer, the principal components of a MLCC such as BaTiO₃ is the best materials for coating. Previously, facile routes for coating a Ti-hydroxide layer on

Ni spheres via the controlled hydrolysis of a TiCl₄ butanol solution⁸⁾ followed by converting the coated Ti-hydroxide layer into BaTiO₃ via hydrothermal conversion were suggested.^{9,11)} Indeed, a BaTiO₃ coating inhibited the oxidation and low temperature sintering of Ni particles considerably.

The remaining challenge is a dispersion of BaTiO₃-coated Ni particles in a paste form. Generally, in making a Ni paste, an organic solvent and plasticizer are employed for both homogenization and for attaining a shear thinning behavior, respectively. The organic vehicles are typically hydrophobic while the BaTiO₃ coating layer shows a hydrophilic character. Therefore, a dispersion of BaTiO₃-coated Ni particles within an organic media is a challenging issue. Organic capping on metal or oxide nano particles has been reported to be quite effective in preparing organic-soluble particles¹²⁻¹⁴⁾ and to change the physico-chemical properties of nano particles.^{15,16)} Recently, Wu *et al.*¹⁷⁾ reported that BaTiO₃ particles with an organic shell layer could be prepared by a reaction between tetrabutyl titanium and Ba-stearate at 180-185°C. The key concept is the preparation of organic-soluble BaTiO₃ particles via organic surface modification. Therefore, in this report, Ba-Ti-O nanolayers with an organic shell layer were coated on spherical Ni powder via the following two-step reactions: 1) A Ti-hydroxide coating on Ni particles via the controlled hydrolysis of a TiCl₄ butanol solution and 2) the subsequent reaction of Ti-hydroxide coated particles with Ba-stearate at high temperature. The main focus was placed on the role of the

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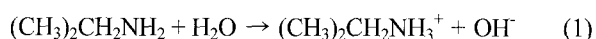
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organic capping layer chemically bonded to the Ba-Ti-O coating layer on the dispersion behavior in hydrophobic solvents.

2. Experimental

Reagent grade chemicals, TiCl_4 (99.9% Aldrich Co., Milwaukee, WI), $(\text{CH}_3)_2\text{CH}_2\text{NH}_2$ (IPA, isopropylamine, Alrich Co., Ltd.), and $\text{C}_4\text{H}_9\text{OH}$ (99.9%, Junsei, Chemical Co., Tokyo, Japan), were used as the Ti-source, precipitant and solvent, respectively, to coat Ti-hydroxide on the spherical Ni powder (NF2A, Toho Titanium Co. Ltd., Chigasaki, Japan, experimentally determined average diameter = 200 nm). 6.8 g of $(\text{CH}_3)_2\text{CH}_2\text{NH}_2$ was dissolved in butanol and the Ni particles were subsequently dispersed. 1-3 ml of a 5.6 M TiCl_4 aqueous solution was diluted with butanol and dropped slowly to the Ni-particle-dispersed IPA solution. The total amount of butanol in solution was 576 ml. In the stock solution, the controlled hydrolysis reaction proceeded via the slow release of $(\text{OH})^-$ ion according to the following reaction:



As can be found in the reaction (1), the water content in the stock solution plays an important role in the reaction rate. Therefore, 1.5 g of distilled water was added to tune the rate of the hydrolysis reaction, and the total stock solution was hydrolyzed by stirring the solution at 23°C for 12 h. The resultant powder was washed 5 times with ethanol to remove the Cl^- ions and dried at 70°C for 12 h. The coating amount was controlled by the TiCl_4 concentration in solution and the reaction time for hydrolysis. The Ti contents of the Ti-hydroxide-coated Ni powders prepared using 1 and 3 ml of 5.6 M TiCl_4 solution were found to be 0.5 and 1.8 wt%, respectively, by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy, JY70PLUS, Jobin YVON, Cedex, France), which correspond to 54.5 and 64.1% Ti in the source solution, respectively. For simplicity, the Ti-hydroxide coated Ni powders with 0.5 wt% Ti and 1.8 wt% Ti will be denoted as '05Ti-Ni' and '18Ti-Ni', respectively. 20 g of the Ti-hydroxide-coated powder was added to 300 g of 2-ethyl hexanol ($\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$, Aldrich Co., Milwaukee, WI) and 1.82 g of Ba-stearate (99%, $\text{C}_{36}\text{H}_{70}\text{BaO}_4$, Song-won Chemical Co., Ltd.) was then added. The stock solution was heated to 180°C and the reaction was begun at 180°C for 6 h using a refluxer.

After cooling, the powder was washed with butanol and dried at 80°C for 24 h. The powders after the reaction with Ba-stearate are referred to as '05Bst-Ni' and '18Bst-Ni', respectively. BaTiO_3 -coated powder without an organic capping layer was also prepared by the hydrothermal conversion of a Ti-hydroxide coated (05Ti-Ni) powder at 200°C for 4 h for comparison. This powder is '05BT-Ni'.

3. Results and Discussion

Fig. 1(a) shows a SEM image of the Ti-hydroxide-coated Ni powders (05Ti-Ni: Ti content 0.5 wt%). The powders were mainly composed of spherical particles and no significant changes were observed in the morphologies before and after Ti-hydroxide coating. The substantial Ti content of the coated powder, as determined by ICP-AES analysis, suggests that the Ni powders are uniformly coated with a Ti-hydroxide layer. The detailed analysis and experimental procedures reported elsewhere. Shell-like morphologies were frequently found after the reaction with Ba-stearate at

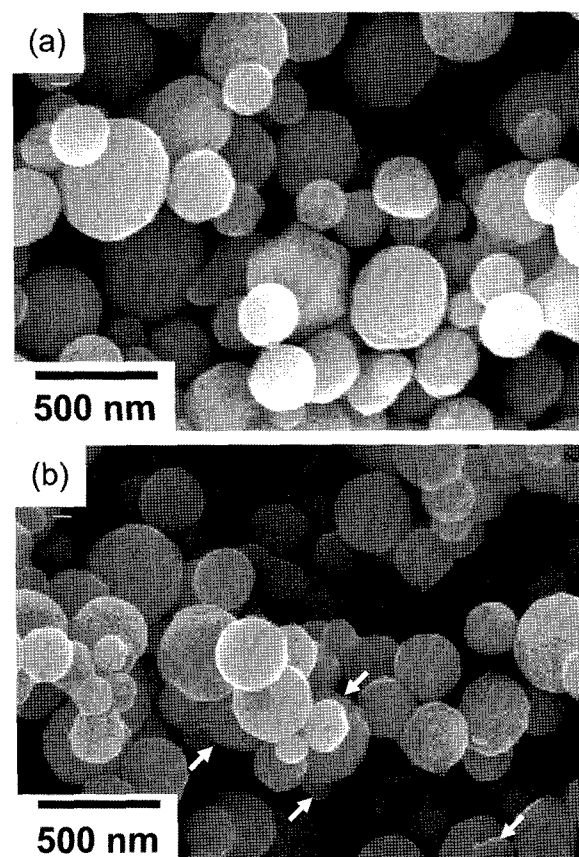


Fig. 1. Scanning electron micrographs of (a) Ti-hydroxide coated Ni (05Ti-Ni) powder and (b) Ba-Ti-O coated Ni (05BsT-Ni) powder with an organic shell.

180°C for 6 h (white arrows Fig. 1(b)). This confirms the presence of coating layer.

The phase of the coating layer was analyzed by X-ray diffraction (Fig. 2). Note that the 18Bst-Ni powder was used for XRD analysis. After the reaction between Ti-hydroxide coated Ni (18Ti-Ni) powder and Ba-stearate at 180°C for 6 h, Ba-stearate and Ni peaks with a few unknown minor peaks were observed (Fig. 2(a)). The coated powders were heat-treated at 400°C for 1 h in order to examine the oxidation behavior. (Fig. 2(b1)) No BaTiO₃ was formed despite the presence of Ti-hydroxide coating layer. BaCO₃ was formed instead. According to the calculation by Lencka and Riman,¹⁸⁾ BaCO₃ is inherently more stable than BaTiO₃. Therefore, BaCO₃ rather than BaTiO₃ can be formed at 400°C considering the carbon component in the stearate radical. However, this will be converted eventually into BaTiO₃ during high temperature sintering (for example, at 1200-1400°C).^{19,20)} The X-ray intensity ratio between the

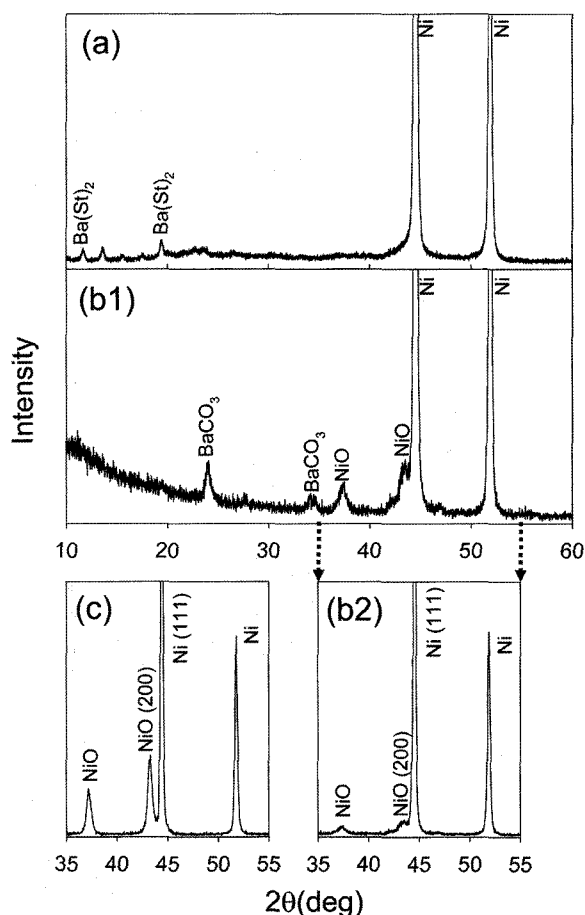


Fig. 2. X-ray diffraction patterns of the Ba-Ti-O coated Ni (18Bst-Ni) powder with an organic shell. (a) as-prepared powder (b1), (b2) powder heat-treated at 400°C for 1h, (c) untreated Ni powder heat-treated at 400°C for 1h.

NiO (200) and Ni (111) peaks after heat-treatment at 400°C were 0.02 for the 18Bst-Ni powder, which is much lower than 0.16 for the untreated powder. (Fig. 2(c)) This suggests that the coating of an organic-capped Ba-Ti-O layer prevents the oxidation of Ni particle effectively.

The coating morphology of powders was observed by transmission electron microscopy. (Fig. 3) An approximately 10 nm thick Ti-hydroxide layer was coated uniformly on the surface of the Ni spheres. (Fig. 3(a)) After the reaction with Ba-stearate at 180°C, the Ba-Ti-O-coated Ni powder was immersed in a dilute HCl (pH=2) solution for 10 days in order to dissolve the core Ni.²¹⁾ However, the dissolution of the core Ni sphere was quite difficult, which is probably due to the impermeable character of the coated layer. This shows that the oxide shell layer is effective in retarding Ni oxidation. The core Ni part could be removed using dilute HCl (pH=2) for 4 days after the coated powder had been heat-treated at 400°C for 1 h. Considering the report showing that Ni oxidation accompanies a 70% increase in volume,

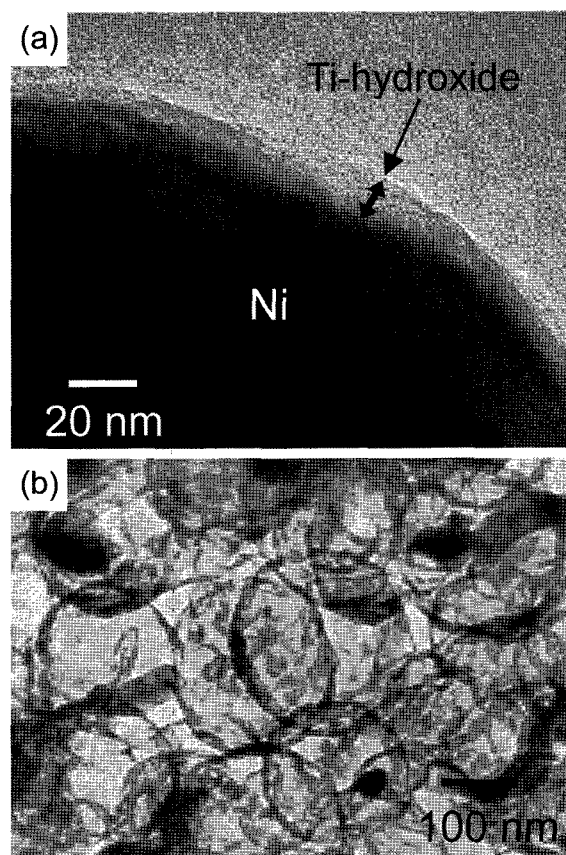


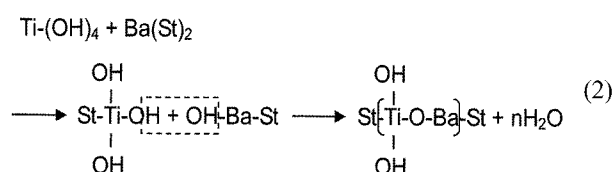
Fig. 3. Transmission electron micrographs of (a) Ti-hydroxide coated Ni (05Ti-Ni) powder and (b) Ba-Ti-O hollow spheres prepared by removing the core Ni part. The core Ni sphere was dissolved in dilute HCl (pH=2) over a 2 day period after heat-treatment of the 05Bst-Ni powder at 400°C for 1h.

successful Ni dissolution after heat treatment can be attributed to the ballooning effect of the core Ni part as a result of weak oxidation. Fig. 3(b) shows the hollow BaTiO₃ sphere after the removal of the Ni core. The BaTiO₃ shell layers were typically 5-7 nm thick. A uniform shell thickness of the hollow spheres clearly shows that a well-defined Ba-Ti-O layer can be coated reproducibly.

In the fabrication of a MLCC, BaTiO₃-coated Ni powders are generally prepared in the form of a paste mainly using a hydrophobic terpeneol-based solvent along with organic additives for achieving the shear-thinning behavior. Sedimentation is a convenient way to determine the dispersion of the particles in the solvent. Therefore, 05BsT-Ni and 05BT-Ni powders were mixed with terpeneol and the sedimentation behaviors were compared. The 05BT-Ni powder settled down after 7 days, while the 05BsT-Ni powder did not sediment even after 30 days. Butanol also shows a hydrophobic nature with a low viscosity. Therefore, butanol solvent was employed as another dispersing medium for confirming the sedimentation behavior. (Fig. 4(a)) After 30 minutes of sedimentation from a complete dispersion produced by ultrasonic treatment, the 05Bst-Ni powder remained the same while the 05BT-Ni Ni powder settled down significantly. The dispersion of the 05Bst-coated Ni powder in butanol did not show notable changes even after

3 days. This demonstrates that the Ba-Ti-O coating layer capped with an organic shell is compatible with an organic solvent. In addition, Steric stabilization due to the organic capping layer can play a role in preventing the agglomeration of Ba-Ti-O coated Ni particles.

Wu *et al.*¹⁷⁾ prepared BaTiO₃ particles with an organic shell by a reaction between Tetrabutyl titanium and barium stearate (Ba(St)₂) in the presence of a small amount of water. The substitution of stearate and hydroxyl radicals with the butoxyl group and subsequent polymerization was the suggested reaction mechanism. In this study, a nanometer-scale Ti-hydroxide layer was already formed on the Ni surface. Accordingly, no water was added to promote the formation of a Ti-OH bond. The following reaction can be considered for the formation of a Ba-Ti-O layer with an organic shell.



The formation of a Ti-St bond by the partial substitution of OH⁻ by stearate radicals and the subsequent condensation reaction between Ti-OH and Ba-OH are shown in

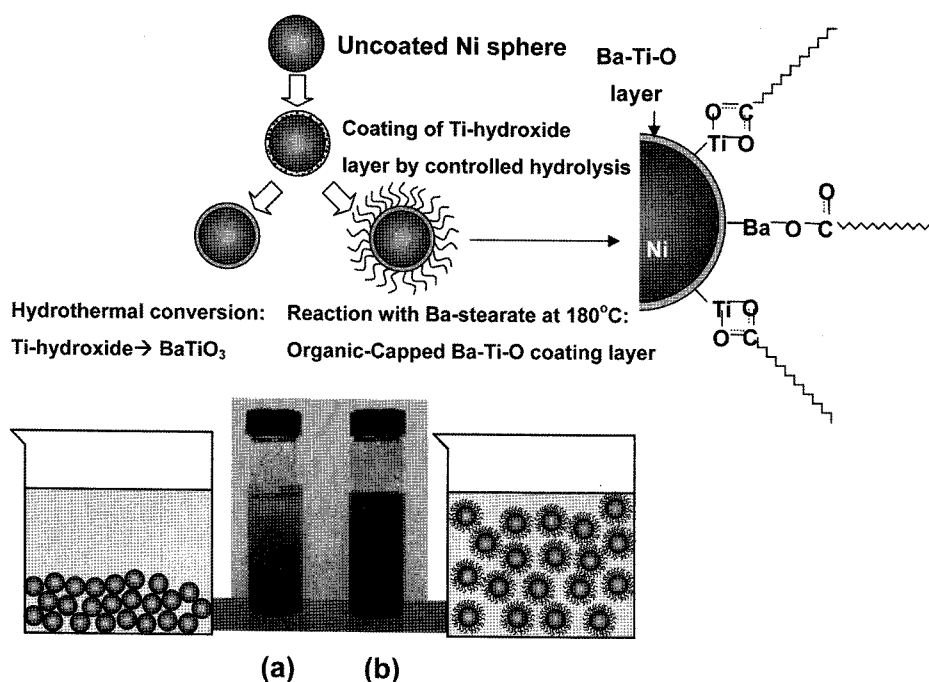


Fig. 4. Schematic coating mechanism of the Ba-Ti-O layer with and without the organic capping shell and their sedimentation behaviors in butanol. (a) 30 minutes after complete dispersion of the BaTiO₃ coated Ni (05BT-Ni) powder in butanol and (b) 30 minutes after complete dispersion of Ba-Ti-O coated Ni (05Bst-Ni) powder in butanol.

the reaction scheme.

4. Conclusions

Ba-Ti-O nanolayers with an organic capping shell were coated uniformly on spherical Ni particles via the formation of Ti-hydroxide nanolayers on the Ni spheres and a subsequent reaction with Ba-stearate at 180°C for 6 h. The uniform coating morphology of the Ti-hydroxide shell did not change even after a hydrothermal reaction with Ba-stearate. Ba-Ti-O-coated Ni particles with an organic shell did not sediment in butanol solvent after 6 days while the BaTiO₃-coated Ni particles settled within 30 minutes. The organic capping was effective in the dispersion of the Ba-Ti-O-coated Ni particles in organic vehicles, which can be used to fabricate the electrode layer of a highly integrated MLCC.

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