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Thermal Shock Behavior of Barium Titanate Ceramics

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Post-firing process of electronic ceramics, such as electroding and encapsulation with resin, often causes damage by thermal shock. The thermal shock behavior of $BaTiO_3$ ceramics was investigated by the down-quench test, where the relative strength retained is determined after the sample is quenched from an elevated temperature into a fixed temperature bath The critical temperature drop, ΔT_C, was evaluated for three kinds of sintered $BaTiO_3$ ceramics, which were formed by extrusion, uniaxial pressing using granules, and uniaxial pressing using powders. A drastic loss in strength caused by microcracking was observed for the specimens quenched with $\Delta T \geq 150°C$. This concept can be adopted as a method of the quality control by monitoring the sudden drop of the strength of capacitor products after each exposure to heat.

Key words : Barium titanate, Thermal shock behavior, Strength degradation, Microcracking

I. Introduction

Barium titanate ($BaTiO_3$) is a well-known material for multilayer ceramic capacitors of high-dielectric constant, thermistors with positive temperature coefficient (PTC), gas sensors, and other electronic devices.[1,2] A prime requirement in the manufacture of electronic ceramics is its reproducibility showing the required properties at every run. For satisfactory and reproducible properties of electronic ceramics, the control of specified microstructure is essential, which depends on the characteristics of starting powders and the forming and sintering processes.[3-6] However, $BaTiO_3$ devices often show the lack of reproducibility in properties even though they have the specified microstructure, due to the thermal shock damages during post-firing processes.

In this study, thermal shock behavior of three kinds of sintered $BaTiO_3$ ceramics, which were formed by extrusion (designated as material A), uniaxial pressing using granules (designated as material B), and uniaxial pressing using powders (designated as material C), was investigated by the down-quench method and their critical temperature drops, ΔT_C, were evaluated.

II. Experimental Procedure

Three kinds of $BaTiO_3$ specimens were provided from Dongil Electronics (Seoul, Korea) and their characteristics are listed in Table 1. Only limited details are available concerning these materials such as forming method and composition. Materials A and C were disk-shaped and material B was a doughnut-shaped. The state of samples were as-fired for materials A and B and silver-faced, which has experienced one of post-firing process, for material C. The diameter and thickness of the as-received specimens were measured and the specimens having the dimensions of within $\pm 0.2\%$ of the average value were selected for the experiment. The as-received specimens were heated to the desired temperature (ΔT= 50~300°C) in a box-type furnace in air, annealed for 1 h for thermal equilibrium, and quenched into water bath (20°C). The relative strength of the quenched specimen was measured at room temperature on 8 specimens at each condition using 3-point bending with a 10 mm span. The relative strength was calculated as follows:

$$\text{Relative strength}(\%) = \frac{\text{Load of quenched specimen in bending}}{\text{Load of as-received specimen in bending}} \times 100$$

Densities were measured using the Archimedes method. For material C, the silver layer was removed by polishing for measuring the density. The microstructure was observed by scanning electron microscopy (SEM) for fractured specimens. Some specimens were polished for observing the microcracks.

III. Results and Discussion

Fig. 1 shows typical microstructures of materials A, B, and C. Material B has coarser microstructure (average grain size ≈ 5 μm) and larger pores than the others. Microstructure of material A was similar with that of ma-

Table 1. Characteristics of Specimens Tested

Specimen		A	B	C
Forming method		Extrusion	Uniaxial pressing with granule	Uniaxial pressing with powder
State		As-fired	As-fired	Silver-faced
Shape		Disk (Dia. 17.7×0.8 mm)	Doughnut (O.D. 20.1, I.D 8.9×1.8 mm)	Disk (Dia. 19.5×1.6 mm)
Composition (wt%)	$BaTiO_3$	97.75	98.01	-
	Al_2O_3	0.41	0.26	-
	SnO_2	0.85	1.62	-
	SrO_2	0.99	0.11	-
Bulk density (g/cm^3)		5.77	5.88	5.48

terial C.

The results of the water quench tests are summarized in Table 2. The relative strength as a function of temperature difference (ΔT) is shown in Fig. 2. The material A shows a typical thermal shock behavior of ceramics on rapid cooling. The strength was constant up to ΔT=100°C and it decreases catastrophically in a narrow temperature range (100°C < ΔT < 150°C). A gradual decrease in relative strength was observed with increasing ΔT when ΔT ≥ 150°C. This behavior indicates that the thermal tensile stress introduced in the surface region as a result of the temperature gradient is sufficient to initiate growth of surface cracks or defects when ΔT ≥ 150°C. Because of the steep thermal gradient, the surface tensile stress diminishes with distance into the sample reaching a zero level and then becoming compressive in nature.[7] This stress profile may act to arrest the surface cracks

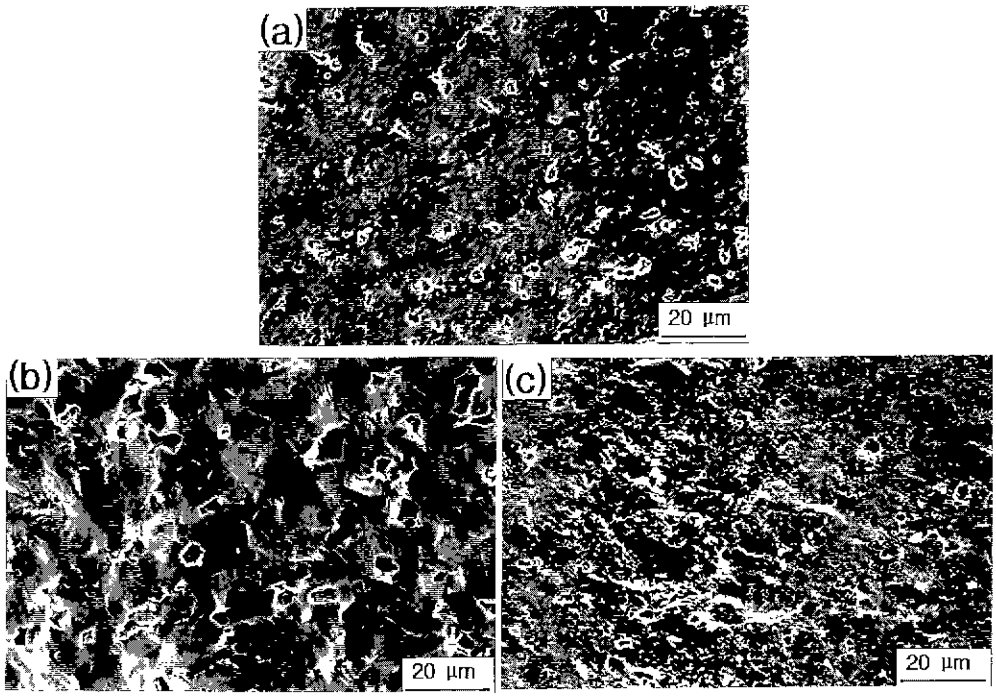

Fig. 1. SEM micrographs of fracture surfaces: (a) A, (b) B and (c) C (Refer to Table 1).

Table 2. Relative Strength of As-Received and Quenched Specimens

Specimen / ΔT (°C)	A Load (kg)	A Relative strength (%)	B Load (kg)	B Relative strength (%)	C Load (kg)	C Relative strength (%)
0*	3.74±1.59	100	24.07±0 02	100	21.74±7.83	100
50	3 83±0.79	102	34.69±0.50	144	14.22±5.49	65
100	3.85±0.93	103	25.10±3.67	104	13.65±5.77	63
150	2.71±1.65	72	7.67±1.49	32	8.55±4.42	39
200	2.31±1.07	62	6.20±1.20	26	8.14±1.21	37
250	1.64±0.43	44	5.36±1.27	22	7.78±0.79	36
300	1.56±0.19	42	4.98±0.75	21	7.26±0.70	33

*As-received specimen.

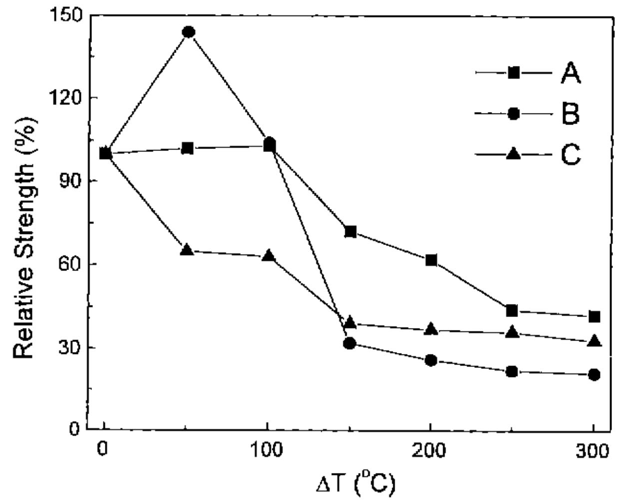

Fig. 2. Relative strength as a function of temperature difference (ΔT) for various $BaTiO_3$ ceramics.

at some point below the surface depending on the temperature profile and the fracture resistance of the material.

The material B, which has the largest grain size, shows an initial increase in relative strength at ΔT=50°C, returns to the as-received value at ΔT=100°C, and shows catastrophic strength loss in a narrow temperature range (100°C < ΔT < 150°C). A gradual decrease in relative strength was observed with increasing in ΔT when ΔT≥150°C. The cause of the initial increase in relative strength was not clear at present. This kind of behavior was also observed in Si_3N_4 ceramics with controlled flaw.[8]

The material C shows an initial decrease in relative strength at ΔT=50°C, retains its strength up to ΔT=100°C, and decreases again in a narrow temperature range (100°C < ΔT < 150°C). A gradual decrease in relative strength was observed with increasing ΔT when ΔT≥150°C as the other materials. The initial drop in relative strength was believed due to the tensile stress formed in silver-printing process, which experiences thermal shock from room temperature to the temperature of the melt of silver-paste.

The above results indicate that the critical temperature drop (ΔT_C) of $BaTiO_3$ ceramics is in the range of 100~150°C, irrespective of the forming process. It also suggests that post-firing process, such as electroding and encapsulation with resin, of $BaTiO_3$ ceramics should be controlled within ΔT=100°C

SEM micrographs of polished cross sections for both the as-received and quenched specimens (ΔT=200°C) of material B are shown in Fig. 3. The quenched specimen shows the presence of microcracks, as indicated by arrows in Fig. 3(b). Therefore, the observed decrease in relative strength of specimens quenched from the temperatures above ΔT_C was due to the microcracking in the specimen. The amount of cracking may increase with increasing ΔT, which explains the gradual decrease in relative strength observed with increasing ΔT when ΔT≥150°C.

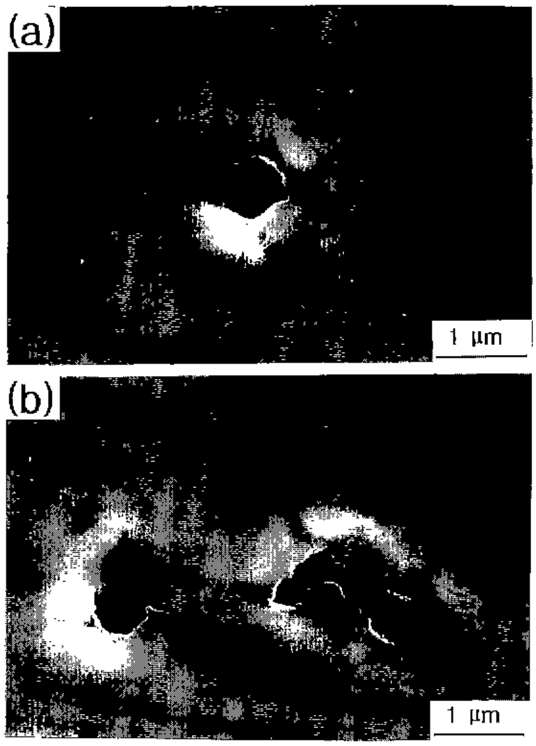

Fig. 3. SEM micrographs of polished cross sections: (a) as-received specimen (B) and (b) quenched specimen (B, ΔT=200°C). The arrows in (b) indicate the microcracks induced by quenching.

This concept of fracture mechanics can be utilized into the manufacturing plant as an easy way of quality control, by monitoring the strength of capacitors at each steps. The sudden strength drop below the average value can be interpreted as an indication of mechanical damage done by the previous heat exposure.

IV. Conclusions

1. The critical temperature drop (ΔT_C) of $BaTiO_3$ ceramics was observed in the range of 100~150°C.
2. The observed loss in relative strength for the specimen quenched from the temperatures above ΔT_C was due to the microcracking in the specimen.
3. The results of this research suggests that post-firing process, such as electroding and encapsulation with resin, of $BaTiO_3$ ceramics should be controlled within ΔT=100°C.

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