Mechanical Property and Fracture Behavior of BaTiO₃-Based Nanocomposites

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Dense and fine grained BaTiO₃-based composites with the nano-sized SiC particulate were successfully fabricated by hot-pressing method. Mechanical properties and fracture behavior were investigated. High resolution TEM observation revealed that there were no conspicuous reaction phases in the interface between BaTiO₃ and SiC. The crystal structure was changed from ferroelectric tetragonal to paraelectric cubic phase with increasing SiC, and finally was pseudo-cubic for BaTiO₃ with more than 3vol% SiC. Mechanical properties such as fracture strength, fracture toughness, Young's modulus and so on were markedly improved by the incorporation of nano-sized SiC particulates. The improvement of mechanical properties, particularly, microhardness and Young's modulus might be caused by the crystal structural change as well as SiC addition. Fracture behavior and subcritical crack growth (SCG) phenomenon were also investigated using the indentation induced flaw method (IIF).

1. Introduction

Barium titanate (BaTiO₃) is well-known as a perovskite-type ferroelectrics used for multi-layer capacitors, PTC (positive temperature coefficient) thermistors and other electronic devices. The electrical/dielectric properties have been studied extensively¹⁻³. Recently, electrical devices have been miniaturized and are used under quite severe circumstances. Such environments often lead to the initiation and propagation of cracks due to thermal shock and fatigue, and then the improvement of mechanical properties and reliability is also required as well as good electrical and dielectric properties. Thus, much attentions have been focused on the relation between the dielectric and mechanical properties^{4,5}. However, the research on mechanical properties are limited to the internal stress and the corresponding fracture strength change⁶⁻⁸.

In the previous study⁹, new types of BaTiO₃-based composites with the nano-sized SiC particulates as a secondary phase were successfully fabricated and the influence of SiC particulates on crystal structural variation was investigated. In the present study, effects of the nano-sized SiC particulate addition on mechanical properties for BaTiO₃-based composites were investigated. Especially, the fracture behavior and subcritical crack growth (SCG) phenomenon were also studied using indentation induced flaw (IIF) method.

2. Experimental procedure

Monolithic BaTiO₃ and BaTiO₃-based composites with the nano-sized SiC particulates were prepared using a conventional powder metallurgical method. The material preparation procedures and details of various evaluation methods, such as fracture strength, fracture

toughness by indentation fracture (IF) and controlled surface flow(CSF) method and other mechanical property measurements, have been described elsewhere⁹⁾.

SCG was studied using IIF technique proposed by Mendiratta and Petrovic¹⁰⁾. The sintered specimens were diamond-cut into bars of 3 by 4 by 25 mm in dimension. A controlled surface flaw was induced at room temperature in the center of the tensile surface of each specimen with a Knoop diamond indenter, the flaw being oriented perpendicular to the longitudinal axis of the specimen. Prior to any tests, the indented surfaces were ground and polished to about 50 μm to remove any possible surface-stressed layer caused by the indentation. The induced surface flaw was extended by subjecting the specimen to constant stresses in three-point bending machine for several hours at room temperature. The loading was conducted for about 1-2 s to 1 h to investigate a stress rate effect on the SCG phenomenon, and the unloading was done quickly for less than 1 s. After the constant loading test, the specimen was removed from the loading test and the length of surface trace of the crack was measured with an optical microscope and then catastrophically fractured by three-point bending test with 20 mm span. If a single controlled surface flaw of suitable size is placed on the tensile surface of a three-point bend specimen and accurately aligned perpendicular to the tensile stress direction as shown schematically in Fig. 1, the fracture initiates at the site of this flaw because it is the "worst flaw" in the specimen. For all specimens, the fracture initiated at the site of the extended surface flaw.

Fracture surfaces were observed with an optical microscope and a scanning electron microscope (SEM). Dispersion state of the SiC particulates in matrix and interfaces between BaTiO_3 and SiC were observed by a transmission electron microscope (TEM).

Fig. 1. Indentation induced flaw method for measuring SCG.

- (a) schematic view of bending
- (b) typical fracture surface without SCG
- (c) typical fracture surface with SCG

3. Results and Discussion

3.1 Mechanical property and microstructure

X-ray diffraction profiles show that BaTiO_3 composites with SiC particulates were mainly composed of BaTiO_3 and $\beta\text{-SiC}$ for the specimen sintered at 1300°C. Nearly 100 % of theoretical density was achieved for the monolithic BaTiO_3 . On the other hand, the relative density of BaTiO_3 -based nanocomposites markedly depended on the sintering temperature rather than monolithic BaTiO_3 . As the SiC content increased, the relative density lowered gradually to 98, 97 and 96% for BaTiO_3 -1vol% SiC, 3vol% SiC and 5vol% SiC nanocomposites sintered at 1300°C, respectively.

From TEM observations, most of SiC particles were uniformly distributed within the matrix grains, with some bigger particle located at the BaTiO_3 grain boundaries. In addition, it could be found that there were no reaction phases between BaTiO_3 matrix and SiC incorporated within BaTiO_3 matrix grains, as well as at matrix grain boundaries and/or three grain junctions, as can be seen in Fig. 2.

Fig. 2. TEM photographs of BaTiO₃-5vol% SiC nanocomposite. Arrows indicate the SiC particulate. (b) is a high magnification TEM photograph of a part of (a).

The polarization domain structure with a large quantity of 90° twins can be clearly seen for the monolithic BaTiO₃⁹⁾. With increasing the SiC particulate, the domain structure gradually disappeared. Consequently, there was no domain structure for BaTiO₃-5vol% SiC nanocomposite, as shown in Fig. 2 (a). This must be caused by the crystal structural variation with increasing the SiC particulate, as will be mentioned later.

Some physical and mechanical properties of BaTiO₃ and BaTiO₃-SiC nanocomposites sintered at 1300°C are summarized in Table 1. Monolithic BaTiO₃ remained in the ferroelectric tetragonal phase regardless of sintering temperature. However, the crystal structure gradually changed from tetragonal to cubic phase with an increase in SiC content. It was

Table 1. Characteristic and mechanical properties of BaTiO₃ and BaTiO₃-based composites with nano-sized SiC particulates.

SiC content (vol %)	Crystal structure [#]	Grain size (μm)	σ_f (MPa)	$K_{IC}^\dagger$ (MPa m ^{1/2})
0	Tet	1.35	145	0.86
1	Tet	0.84	301	0.99
3	P-Cub	0.48	350	1.22 [§]
5	P-Cub	0.35	315	1.19
10	P-Cub	0.31	303	--

[#] Tet:tetragonal, P-Cub:pseudo-cubic

[†] CSF(Controlled Surface Flaw) method

[§] Indentation fracture(IF) method

found that the crystal structure of BaTiO₃-3 vol% SiC and 5vol% SiC nanocomposites was cubic, rather than tetragonal phase, that is, pseudo-cubic phase. These crystal structural changes were found to be caused by the decrease in the grain size of BaTiO₃ matrix. The domain structure disappearance seen in Fig. 2 (a) also must to be due to these crystal structural variation. Moreover, the crystal structural variation also influenced upon the mechanical properties, especially, Young's modulus and microhardness. Figs. 3 and 4 show Young's modulus and microhardness change with the SiC content. In Figs. 3 and 4, two dashed lines represent the upper and lower limits, calculated by Boigt model and Reuss model¹¹⁾, respectively. The measured values are higher than those expected from the rule's of mixture. In particular, Young's modulus of BaTiO₃ markedly increased with small amount of SiC, exhibiting even higher values than the upper limit values. It seems that mechanical properties of BaTiO₃ were strongly influenced largely by the crystal structural variation.

Fracture strength also increased with the increase in the particulate SiC content. This is mainly caused by the reduction in grain size as can be seen in Table 1. And it is also suggested that the increases in fracture toughness and Young's modulus will be other factors for the

Fig. 3. Young's modulus change with the SiC content for monolithic BaTiO₃ and BaTiO₃-SiC nanocomposites.

fracture strength improvement. In fact, the fracture toughness and Young's modulus values increased by a small amount of SiC addition, as can be shown in Table 1 and Fig. 3. The fracture toughness increase may be caused by the crack deflection by SiC particulates, as reported by many researchers¹²⁻¹⁴). In the present study, the obtained specimens are composed of very small grains below 1 to 2 μm , so that toughening mechanism such as micro-cracking and domain switching¹⁵), which is well observed for BaTiO₃ ceramics with large grain size (10 to 50 μm) can be rarely taken into consideration. From TEM observation, the monolithic BaTiO₃ has many 90° twins, therefore, domain switching at crack tip can be likely taken place. On the other hand, the grain size of composite decreased with the SiC content. Thus, it is expected that the toughening mechanism owing to domain switching decreased reversely. Consequently, fracture toughness increase in Table 1 was not so conspicuous by the incorporation of SiC.

3.2 SCG phenomenon

The propagation of surface and subsurface flaws under subcritical load (any load less than

Fig. 4. Microhardness change with the SiC content for monolithic BaTiO₃ and BaTiO₃-SiC nanocomposite.

that necessary to catastrophically propagate the flaw) is called as slow or subcritical crack growth. This SCG in glass and oxide ceramics is supposed to be caused mainly by a chemical reaction between solid and corrosion species in the atmosphere (especially, water) at crack tip, because it is rarely observed in liquid nitrogen, dried air or vacuum. This SCG phenomenon is the origin of catastrophic fracture and reduces the lifetime at operating conditions. Thus, it is very important to investigate the SCG phenomenon in electronic ceramics.

Fig. 5 (a) shows an optical photograph of a Knoop indentation trace made with 9.8 N load on a polished surface of monolithic BaTiO₃ specimen, while Fig. 5 (b) shows the crack extension of the initial crack during a constant loading of 32 MPa for 10 hrs. The fracture surface of the specimens in Fig. 5 are shown in Fig. 6. As can be seen from Fig. 5, it was found that the initial surface flaw grew subcritically during a constant stress loading test. In addition, as can be seen in fracture surfaces of Fig. 6, the dark region was clearly observed between the initial surface flaw and catastrophic fracture region. This dark region is thought to be SCG region. It was suggested

Fig. 5. Crack extension by IIF method. (a) a Knoop indented trace by 9.8 N load, and (b) crack extension by a constant loading test (a stress of 32 MPa for 10 hrs).

that the surface crack grew during a constant loading test as well as before the catastrophic fracture occurred. The further observation of fracture surfaces revealed that both the surface flaw produced by a Knoop indenter and the subsequent brittle (catastrophic) fracture were the intragranular, as shown in Fig. 7 (a). While, Fig. 7 (b) shows the typical SEM photograph of the dark region observed in Fig. 6. In the dark region the intergranular fracture appeared together with the intragranular fracture and became predominant. Thus, it is concluded that the SCG was occurred during the constant bending test, and the fracture mode is intergranular.

Table 2 summarizes the results of the constant stress test and the dependence of the stress rate (crosshead speed in the present study) on the surface flaw extension rate for monolithic BaTiO₃. The extension of initial surface flaw, that, dark region was also confirmed not only during the constant stress testing for 10 h with the stress of 32 MPa, but

Fig. 6. Fracture surfaces, (a) and (b) from the initial surface flaw in Fig. 5 (a) and the extended surface flaw in Fig. 5 (b), respectively.

also just before the catastrophic failure occurs. In addition, the extension of surface flaw depended largely upon the stress rate during the bending test. In particular, the crack extension rate increased tremendously in di-ionized water, as shown in Table 2. This suggests that SCG phenomenon in BaTiO₃ is caused by the chemical reaction between matrix and water molecule at crack tip. Moreover, the fracture strength, as shown in Table 2, decreased with the crack extension rate. Therefore, the

Fig.7 typical fracture surface of the initial surface flaw and subsequent catastrophic fracture region (a) and the SCG region (b)

Table 2. Test conditions and some results of SCG measurement by indentation induced flaw method.

Test condition			Fracture strength	Crack extension [#]
Atmosphere	Crosshead speed	Etc [†]		
Air	5×10^{-1} mm/min	--	44.8 MPa	0.47
Air	5×10^{-3} mm/min	--	46.0 MPa	1.12
Air	5×10^{-3} mm/min	32MPa(10h)	40.4 MPa	1.78
Di-ionized water	5×10^{-3} mm/min	--	37.2 MPa	3.30

[†] Constant stress test for 10 hours with the stress of 32 MPa

[#] Crack extension = $(2c' - 2c) / 2c = \Delta 2c / 2c$ in Fig. 1

SCG seems to be detrimental to mechanical property of BaTiO₃ ceramics. The influence of the SiC particulates on SCG phenomenon is now under investigation.

4. Conclusion

Mechanical property and fracture behavior of monolithic BaTiO₃ and BaTiO₃-SiC nanocomposites were investigated. The subcritical crack growth (SCG) phenomenon was also studied using the IIF method. The following conclusions was obtained from the present study.

- (1) Fracture strength increased markedly by the incorporation of nano-sized SiC particulates. This is due to be the reduction in grain size of BaTiO₃ matrix and the improvement of fracture toughness by the incorporation of SiC.
- (2) Young's modulus and microhardness were strongly improved by both the nano-sized SiC incorporation and the resultant crystal structural variation.
- (3) SCG phenomenon was observed for the monolithic BaTiO₃ before the catastrophic fracture occurred. The intergranular fracture appeared together with intragranular in the SCG region.
- (4) The crack extension rate was depended on the stress rate and the test atmospheres. Therefore, SCG may be due to the chemical reaction between the matrix and the atmosphere.

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