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Effect of polarization treatment on bending strength of barium titanate/zirconia composite

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Abstract

The change in strength of barium titanate/zirconia composite on polarization treatment is evaluated, and the mechanism of this phenomenon is discussed. We have already reported that the bending strength of this composite has increased on longitudinal poling. In this paper, poling time and applied electric field intensity are varied in order to elucidate the strengthening mechanism. Moreover, it is found out that the polarization strengthened specimen can be weakened to the almost original state by heating above T_c of barium titanate. Then, the crack propagation after polarization treatment is observed by SEM, and the detour of cracks around barium titanate grains is found in the cracks going along the poling direction. The detour of crack probably has close connection with the increase in strength in the poling direction.

Keywords: $BaTiO_3$; $BaTiO_2$-ZrO_2; Composite; Mechanical properties; Strength ZrO_2

1. Introduction

Ceramic materials have the advantage to demonstrate their function under severe conditions such as high temperature or corrosive environment. Furthermore, some of the ceramics exhibit excellent wear resistance. Such advantages, however, turn to be a drawback from the view point of recycling. This is a serious problem in environmental conscious days.

In order to break down and recycle structural ceramic materials, strength degradation is desired. Recently, recycling of zirconia ceramics is proposed as follows. The strength of zirconia is drastically degraded on heating at 200–500°C due to phase transformation from tetragonal to monoclinic accompanied by specific volume change.[1,2]

As a result, the strength can be controlled using such strength degradation property in connection with heat treatment. As another example of controllable mechanical strength, PZT ceramics has been reported to show a change in tensile or compressive strength on polarization treatment.[3,4] These changes are considered to be due to the internal stress generated. The problem is that the former is useful only in the case of zirconia, and the latter, a monolithic ferroelectric material, is too weak to use for a structural material.

Ceramic materials are often tried to be toughened or strengthened by dispersing another material to form composites.[5] The particle dispersed composite sometimes incorporates nonlinear effects such as crack deflection and residual internal stress, since the internal compressive stress is derived from the difference in thermal expansion coefficients among the components. If the internal residual stress is the predominant strengthening factor, the final strength is determined by the difference of thermal expansion coefficients between matrix and dispersoid, and it is not possible for this method to control the strength of composites once fabricated.

Therefore, it is necessary for structural materials to maintain the improved mechanical properties during the operation period and to be abandoned easily when they become unnecessary. We have already reported that the strength of dielectric material (8 mol% yttria stabilized zirconia, 8YSZ) dispersed with piezoelectric particles ($BaTiO_3$) is controllable, namely, weakened or strengthened by polarization treatment.[6] The origin of the change in strength in this system is supposed to be the generation of internal stress at the interface between matrix and dispersoid, but details are still unknown. In

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this paper, we attempt to elucidate the mechanism of the electric control of strength from the experiment of dependence on poling time and on applied electric field, and from the observation of unisotropic crack propagation in connection with the poling direction.

2. Experimental procedure

Commercial yttria stabilized zirconia, 8YSZ (Toso Co., Ltd, TZ-8Y) and barium titantate, BT (Central Glass Co., Ltd) powders were used as the starting materials. They were mixed in a preditermined ratio (BT/(BT + 8YSZ) = 5 or 10 mol%, corresponding to 8.5 and 16.4 vol.%, respectively) by ball-milling with ethanol for 2 h, and calcined at 700°C for 1 h. After the calcination, powder mixture was sieved under 75 μm mesh, then, uniaxially pressed into rectangular bars with the dimension of $5\times8\times15$ mm^3 under 100 MPa followed by CIP under 140 MPa. The pressed powder compacts were sintered at 1400°C for 4 h in an alumina boat in air. The characterization of sintered specimens was assessed by XRD.

In order to evaluate the strength by means of the three point bending test, the specimens were cut into thin plates with the width of 2.5 mm and the thickness of 0.5 mm. Regarding the specimens which were treated with poling before bending test, silver electrodes were vapor-deposited on both sides of the thin plate, and polarization treatments were performed in silicone oil at 80°C. The schematic sample setup is shown in Fig. 1(a). Change in strength due to polarization treatment was evaluated by comparing the bending strength of poling-treated specimens with that of untreated one. In this paper, in order to discuss the mechanism of strengthening by poling, poling time and applied electric field intensity were varied.

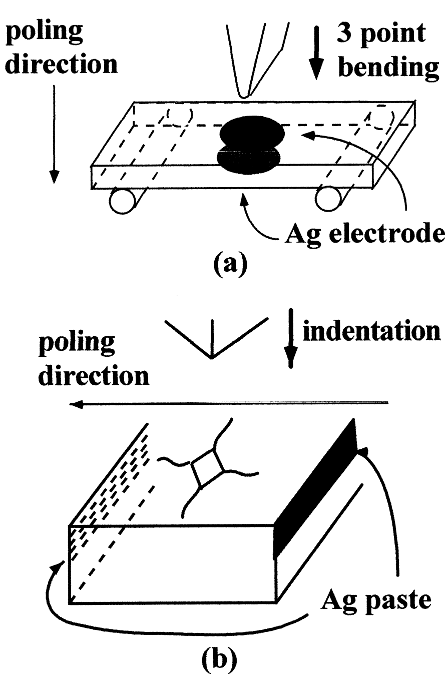

Fig. 1. Schematic view of sample setup: (a) bending test after poling and (b) Vickers' indentation after poling.

Moreover, the polarization treated specimens were heated at 200°C which is over the T_c (~120°C) of barium titanate transforming from ferroelectrics to paraelectrics, because the residual polarization, namely, the deformation of barium titanate after poling is expected to be released by heat treatment over T_c.

In order to investigate the difference in the crack propagation parallel or perpendicular to the poling direction, Vickers' indentation was performed after poling and generated cracks in the parallel or perpendicular direction to poling were observed. The relation between crack propagation and poling direction is drawn in Fig. 1(b). The crack length was measured by an optical microscope, and the behavior of crack propagation was observed by SEM.

3. Results and discussion

In our previous work, we reported that the obtained sintered specimens have relative densities of about 95%, and they are composites consisting of two phases, zirconia and barium titanate according to the XRD analysis.[6] We have also reported that these specimens show a ferroelectric property confirmed by D-E hysteresis. These results indicate that the ferroelectricity is derived from the tetragonal phase of barium titanate in this composite. Therefore, it is reasonable to think that the applied electric field would cause a distortion of barium titanate accompanied by the generation of internal stress.

At first, change in strength depending on the prolonged poling time is measured in both composites incorporated with 5 or 10 mol% of barium titanate. Results are shown in Fig. 2 where minimum and maximum data are shown in each measurement point as error bars at which approximately 10 specimens were tested. With a few minutes poling, the mechanical strength of both composites rises abruptly compared with those untreated. After such a sudden increase in strength immediately after the poling starts, the strength increase ratio against the poling time drastically decreases. Furthermore, as the poling time becomes long, the bottom of error bars is gradually rising and the distribution width of strength tends to become small.

It is considered that such a sudden increase in strength within a few minutes is based on the fast ferroelectric domain switching in barium titanate in this composite, since the dipoles in the barium titanate crystal would be immediately aligned in the poling direction on polarization treatment. If polarization treatment is performed on this composite, the internal stress would be generated in the zirconia matrix to the poling direction, because

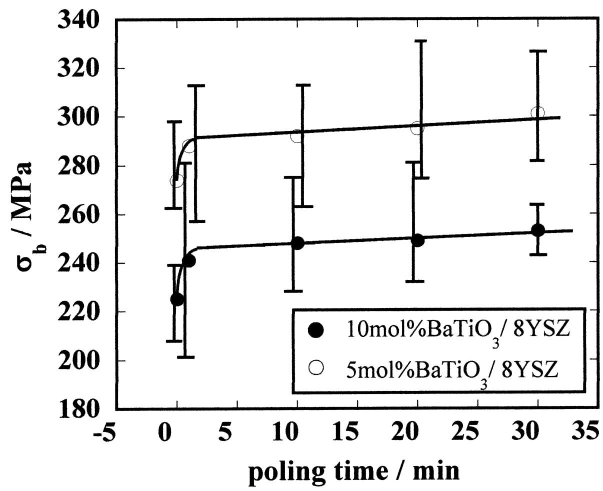

Fig. 2. Poling-time dependence of bending strength in $BaTiO_3$/8YSZ. The applied electric field is 80 kV/cm.

barium titanate extends in the poling direction while zirconia should maintain its crystal structure and orientation. This reversible internal stress should cause the strength change. However, this hypothesis alone cannot explain the tendency that distribution width of strength becomes small with poling time. It is probable that the microstructural change would occur with several 10 min poling, but it is difficult to prove due to the small strength increase ratio.

Secondly, change in strength depending on the applied electric field intensity is measured in the composite incorporated with 5 mol% barium titanate. Results are shown in Fig. 3 in which open figures represent raw data and the filled circle represents mean values at each poling time. The change ratio of mechanical strength first increases with applied field, then saturates around 40–60 kV/cm, that is, change in strength is not affected by applying an electric field larger than 40–60 kV/cm. When an electric field is removed after polarization treatment, a distortion comparable to the final one retains.[7] Therefore, the result of Fig. 3 indicates that the residual stress influences the increase in strength.

If the increase in strength is really due to the distortion of barium titanate accompanied by the generation of internal stress on electric field application, the strength is thought to return to the original state by removing the distortion. When barium titanate is transformed from ferroelectric phase to the paraelectric one on heat treatment, spontaneous polarization disappears. Then, if it returns to ferroelectric phase again, spontaneous polarization orients at random and apparent residual polarization does not exist. Therefore, if the residual distortion affects the increase in strength in this system, the strengthened specimen could return to the original state by means of phase transformation of barium titanate from a ferroelctric phase to a paraelectric one. Then, further experiment was performed as follows.

The strengthened specimens by poling were heated at 200°C, above the transition temperature ~120°C, to remove the spontaneous polarization, and they were cooled down to room temperature. Such treated specimens were compared with the original and strengthened specimens. The results are shown in Fig. 4. The strengthened specimens tend to return to the almost original strength by heating over T_c of barium titanate. This result strongly indicates that the residual distortion accompanied by residual polarization would be the origin of the increase in strength. However, Fig. 4 also shows that the strength does not perfectly return to the original state by simply removing the residual polarization. Considering the small increase in strength with several ten minute periods of poling in Fig. 2, it is probable that the irreversible change, such as a microstructural change,

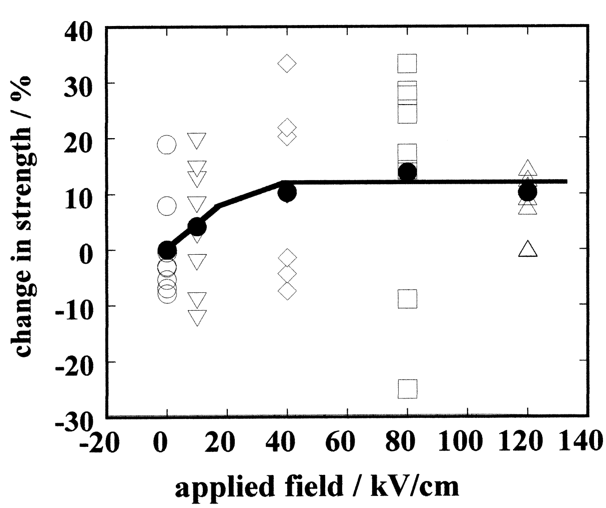

Fig. 3. Dependence of the strength on applied electric field. The open symbols are the raw data, and the closed ones are the averages.

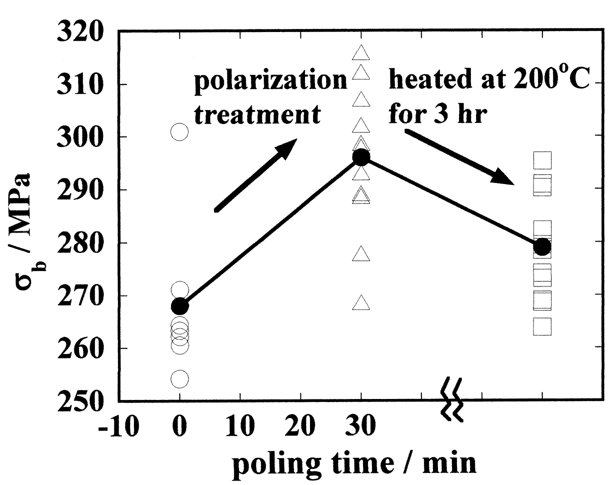

Fig. 4. Change in the strength on polarization treatment and on heat-treatment after poling. The open symbols are the raw data, and the closed ones are the averages.

would occur on long-term polarization treatment and the strength does not perfectly return to the original state in Fig. 4. But it is that the orientation of polarization is the dominant factor in the increase in strength, because the irreversible increase in strength is extremely small.

Next, in order to investigate the effect of the generated internal compressive stress on crack propagation, Vickers' indentation was performed with a load of 1 kgf (=9.8 N) after polarization treatment as shown in Fig. 1(b), and the generated crack length was measured in both parallel and perpendicular directions to the applied field. As to monolithic ferroelectric materials, it is reported that the indentation crack propagates anisotropically affected by the direction of the applied field.[8,9] Regarding the composite in this paper, however, the apparent difference of crack length between the parallel and perpendicular to poling direction was not observed. Then, the distributions of crack length in relation to both directions were investigated by measuring the crack length on 80 samples poled in the same way. The results are shown in Fig. 5(a) and (b). As shown in Fig. 5(a), two sets of histograms of crack length, the peak of the distribution of crack length in the poling direction (X crack) locates at the left of that in the perpendicular to the poling direction (Y crack). Fig. 5(b) shows the statistical difference of the averages of X and Y crack length by using standard error (S.E.). The error bar (=average±1.96×S.E.) indicates the 95% confidence limit of the average of crack length, and the width of box (=average±S.E.) does the 70% one. It is certain that the crack length statistically differs between X and Y crack, because the bottom of the error bar of the Y crack is significantly larger than the top of the error bar of the X one. This is probably because the crack propagation along the poling direction is obstructed and the perpendicular to the poling direction is facilitated by the residual stress, taking into account the difference in bending strengths for anisotropic poled composite.[6] Then, the behavior of crack propagation was investigated by SEM as follows.

The crack of polarization untreated specimens (a), the crack parallel to the poling direction (b), and that perpendicular to the poling direction (c) were observed. The SEM micrographs of these cracks are shown in Fig. 6(a)–(c). In any case, it is commonly seen that cracks mainly propagate in grains of zirconia matrix. However, the crack in the poling direction [Fig. 6(b)] is different from the others. The difference is that the crack in Fig. 6(b) detours around barium titanate grains which have lower strength than the zirconia matrix. In the other two SEM micrographs, to the contrary, the cracks propagate mainly in the zirconia matrix and penetrate into the barium titanate grains. Not all cracks along the poling direction detour around barium titanate grains, however, in relation to the cracks polarization untreated or treated in the perpendicular direction, detour of cracks around barium titanate grains can not be observed.

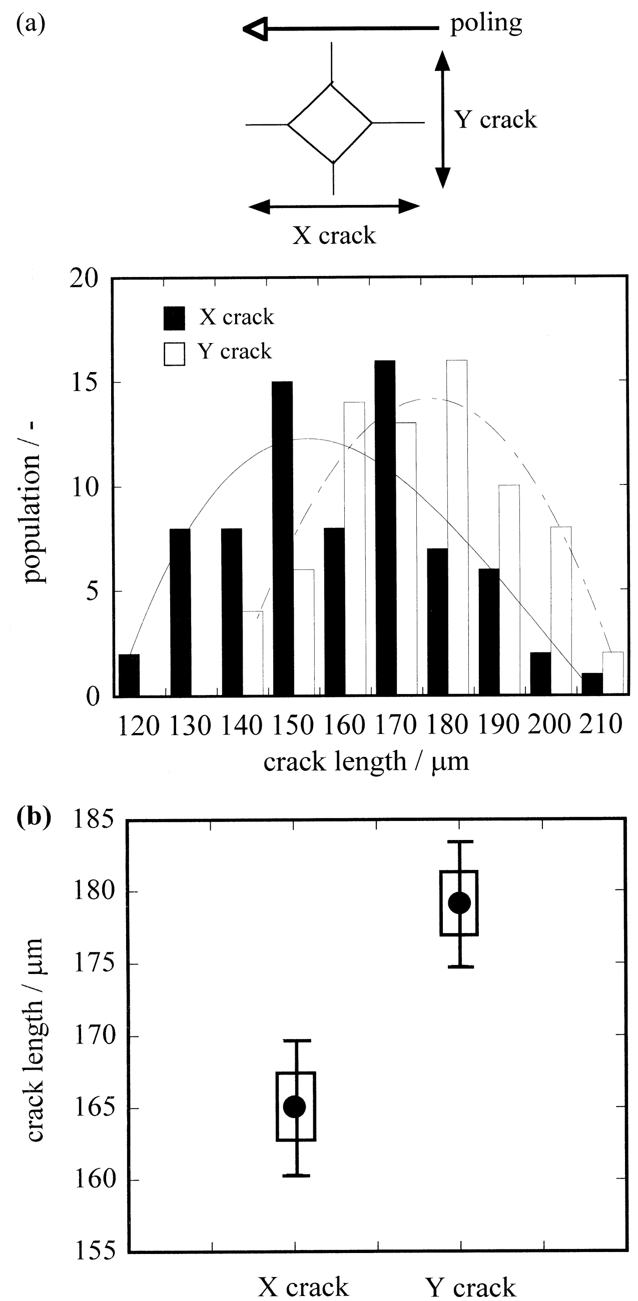

Fig. 5. (a) Distribution of crack length in the parallel and perpendicular direction to poling; (b) the statistical difference of crack length.

Kroupa et al.[10] has proposed a theoretical model to describe the anisotropic distribution of internal stresses on poled PZT ceramics, based on the Eshelby's solution of the "elliptical inclusion" problem.[11] They assume the situation that one spherical ferroelectirc grain surrounded by material with different relative orientation of spontaneous polarization. Their result can be roughly applied to our results, while the surrounding matrix is a paraelectric ceramic in our study.

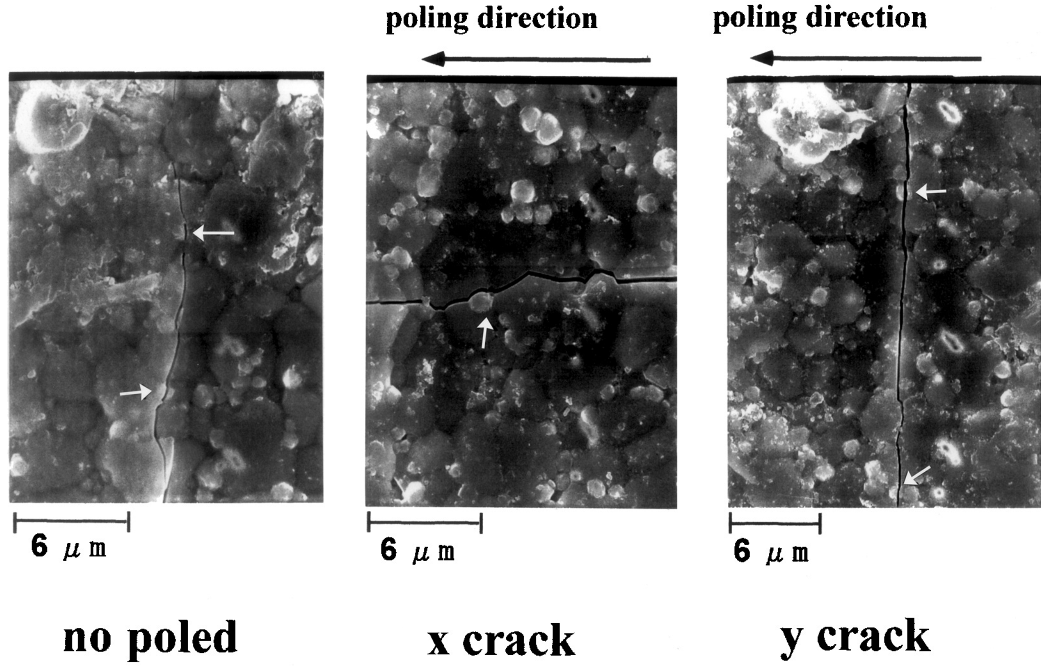

Fig. 6. SEM micrographs of crack propagation in 10 mol% $BaTiO_3$/8YSZ: (a) no poled; (b) the parallel direciton to poling; (c) the perpendicular direction to poling.

Their result indicates that the stress in the surrounding matrix is very complicated and decays inversely proportional to third power of distance from the particle. Then the strengthening should be based on the short range interaction which would exist between the particle-matrix interface and the cracks.

The detour of crack indicates the generated internal tensile stress in the matrix at the vicinity of dispersoid in the poling direction, and this phenomenon is thought to cause the increase in strength shown in Fig. 2 or 3.

4. Conclusions

In the system of zirconia ceramics dispersed with barium titanate particles, the increase in bending strength is observed when electric field is applied to the longitudinal direction, and then the strengthened specimen by polarization treatment returns to the almost original state by heating above T_c of barium titanate. These results indicate that the internal stress generates in the zirconia matrix at the vicinity of barium titanate in the poling direction because barium titanate deforms on polarization treatment.

Furthermore, the crack propagation depending on the direction of the applied electric field was observed, and several detours of cracks around barium titanate grains were observed in the poling direction. Considering the increase in strength in the poling direction, it is thought that the crack in the poling direction detours around barium titanate grains influenced by the generated internal stress and this phenomenon should cause the increase in strength.

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