In situ transmission electron microscopy observations of electric-field-induced domain switching and microcracking in ferroelectric ceramics

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Abstract

In situ transmission electron microscopy (TEM) technique was developed to examine micromechanisms of the electric fatigue in ferroelectric ceramics. The technique was based on a specially designed specimen connected to a modified TEM heating stage. With this technique, domain switching and nanodomain alignment near crack-like flaws were observed under cyclic electric fields. Following repeated electric cycles, microcracks were found to develop along domain and grain boundaries. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ferroelectric ceramics, such as lead zirconate titanate (PZT), are widely used in transducers, actuators, filters and storage devices due to their unique dielectric, electromechanical, and ferroelectric properties. Though intended to take on primarily electrical loads, these materials were found to suffer from mechanical damage in forms of stable macroscopic crack growth and microcracking after driven for extended periods under repeated electric fields [1–7]. Since the domain switching is the fundamental process underlying the electric behavior of the ferroelectric ceramics, it has been widely postulated that the mechanical damage process, i.e. crack initiation and propagation, may be intimately related to domain switching.

To understand the mechanism of domain-switching induced cracking in ferroelectric ceramics, it is essential that observation of the domain activities be made (a) within the fracture process zone of the ceramic and (b) in situ while the electric field is being applied because of the ferroelectric nature of the domain change. Since the domain size of ferroelectric ceramics ranges from nanometers in the relaxor ferroelectrics [8] to micrometers in the normal ferroelectric ceramics [8,9], and the fracture process zone is limited to a few micrometers for most ceramics, TEM would be the ideal technique for the observation. Accordingly, an in situ TEM technique was developed to observe domain activities near a crack or a crack-like flaw. The technique was based on a specially designed specimen connected to a modified TEM heating stage. Domain activities and subsequent crack development were directly observed in ceramics with nanodomain and micron-sized domain structures.

2. Materials and procedure

Three ferroelectric materials were selected for this study: a fine-grained PZT doped with 1 at.% Mn, Pb(Zr0.52Ti0.48)0.99Mn0.01O3, a coarse-grained PZT-EC65, and ferroelectric 0.66Pb(Mg1/3Nb2/3)O3-0.34PbTiO3 (PMN-PT) single crystal. Pb(Zr0.52Ti0.48)0.99Mn0.01O3 was prepared by hot-pressing followed by a conventional atmosphere sintering [10]. It had an average grain size of about 0.1 μm and a well-defined ferroelectric domain structure. PZT-EC65 was a commercial soft piezoelectric ceramic (EDO Corporation, Salt Lake City, UT), with an average grain size of 8 μm and a mixed nanodomain and
micron-sized domain structure. It contained 4% porosity with most pores less than 30 μm in size. At room temperature, the EC65 has a tetragonal crystal structure and a coercive field about 0.8 MV m⁻¹. The PMN-PT crystal was grown with a vertical Bridgman method, using a sealed platinum crucible by (110) seeding. The as-grown crystal was twinned when examined under an optical microscope. The crystal exhibited high piezoelectric and electromechanical coupling coefficients of $d_{33} = 2500$ pC/N and $K_{33} = 91\%$.

In situ TEM studies of domain switching under applied electric fields have been previously reported. In most of these experiments, electric fields were applied through specimen thickness, i.e. the applied field was parallel to the electron beam [11–15]. To study microcrack initiation and propagation under applied electric fields in TEM, the electric field has to be applied across the specimen surface, perpendicular to the electron beam. For this purpose, TEM specimens with the electrode configuration shown in Fig. 1a were prepared. The specimens were obtained from the plates by ultrasonically cutting 3-mm diameter disks and then polishing the disks to a thickness of ~120 μm. The central area of the bottom side of the disk was further thinned to about 15 μm by mechanical dimpling. Half-circle shaped Au electrodes were coated on the top side of the disk as shown in Fig. 1a. A special mask was utilized to form the 150 μm wide central gap. The final perforation was achieved by argon ion milling through the dimpled side at 5 kV and 12° incident angle. The morphology of central hole of the ion-milled sample and its geographic relation to the electrodes were examined by an optical microscope in order to locate the electrodes (and the direction of electric field) in the successive TEM study.

A commercial TEM heating stage was modified to permit in situ application of cyclic electric fields on the TEM sample surface, as illustrated in Fig. 1b. TEM specimen was fixed on the bottom of the sample cup using insulating varnish and the power delivering wires of the original heating stage were soldered onto the two Au electrodes through platinum thin wires. A high-voltage source comprised of a Tektronix CFG 253 Function Generator and a Trek 610D HV Amplifier was connected to the outside terminals of the sample holder. Static and cyclic (1–60 Hz) electric field was applied to the specimen. A peak voltage of up to 800 V, corresponding to a peak field of 6.0 MV m⁻¹, was used during in situ TEM studies; under these conditions our device remained safe. Upon application of the external field, an electric field concentration develops around the perforation in the TEM specimen. Previous studies on field-induced crack growth in the bulk piezoelectric samples have established that the field concentration was necessary to crack development at external fields far below the dielectric strength of the solid [1–7]. Since the applied field was perpendicular to the optic axis of the TEM, it caused electron beam deflection, which was compensated for by adjusting beam deflection and tilting on the microscope. Images were recorded under a constant electric field or a zero electric field after cycling by a charge-coupled device (CCD) camera.

3. Results and discussion

3.1. Domain switching at crack tip

Responses of the domains at the crack tip to a cyclic electric field are shown in Fig. 2, where a roughly equiaxed grain of ~100 nm in diameter, pointed by a dark triangle in Fig. 2a, was located at the tip of a preexisting crack in Pb(Zr₀.₅₂Ti₀.₄₈)₀.₉₉Mn₀.₀₁O₃ specimen. Before the field was applied, several well-defined 90° domains were found within this grain, distinguished as bright and dark strips by the differences in the TEM contrast in Fig. 2a. In the initial quarter of the electric cycle, both the contrast and the width of these domains began to change (Fig. 2b) as the electric field increased from zero to its peak value. These changes are direct indications that the polarizations in the individual domains were rotating or switching to align themselves with the direction of the local electric field. The polarization change continued in the second and third quarters of the electric cycle until the grain became almost a single domain (domain contrast disappeared in the

Fig. 1. In situ TEM experimental set-up for electric-field-induced domain switching and crack growth in ferroelectric ceramics: (a) schematic diagram for the specimen; (b) testing system.
Fig. 2. Domain switching at the crack tip in Mn-doped PZT specimen: (a) original domain structure; (b) electric field $+4.0 \text{ MV m}^{-1}$; (c) electric field $-4.0 \text{ MV m}^{-1}$; (d) electric field released.

Fig. 3. Electric-field-induced nanodomain alignment within a single grain in PZT-EC65: (a) domain structure at original annealed state; (b) electric field $+4.0 \text{ MV m}^{-1}$; (c) electric field $-4.0 \text{ MV m}^{-1}$.

Another common domain morphology is the nanodomain structure found in relaxor ferroelectric and some soft piezoelectric ceramics. The response of such a domain structure near a crack-like flaw to a cyclic electric field is shown in Fig. 3, which was obtained from the interior of a single grain in the PZT-EC65. The pore in the specimen was produced by the TEM sample preparation. The grain was oriented with its $\langle111\rangle$ direction parallel to the electron beam and a cyclic field was applied along the direction indicated by the arrow.

In the annealed (depoled) state, the grain contained randomly oriented nanodomains with short-range tweed features (Fig. 3a). Diffraction analysis indicated these tweed features were along the $\{110\}$ plane, as marked by the $\{110\}$ trace line. When the electric field increased from zero to $+4.0 \text{ MV m}^{-1}$, these nanodomains were forced to align along another $\{110\}$ plane that a long-range tweed structure was formed, as shown in Fig. 3b. The long-range tweed structure remained during the second quarter of the electric cycle when the field was decreased to zero. Upon reversing the electric field to $-4.0 \text{ MV m}^{-1}$, these long-range tweed structures were disrupted near the pore (Fig. 3c). No significant change was further observed in the long-range tweed structure when the electric field returned to zero.

The electric field induced alignment of nanodomains along the $\{110\}$ plane in ferroelectric materials has not been observed before. Attempts have been made to image the nanodomain pattern of a relaxor crystal in its virgin state with an optical microscopy, but there was no contrast due to the limited resolution [18]. For the tetragonal PZT-EC65 ceramic, the nanodomain alignment involves both $180^\circ$ reversal and $90^\circ$ reorientation of the polarization. Because of the associated large lattice mismatch, the $90^\circ$ domain switching requires very high electric field strength. Here the alignment was
observed in the vicinity of the crack-like flaw where the applied field was intensified. The difference in the domain patterns under the positive (Fig. 3b) and negative electric field (Fig. 3c) indicates that the negative electric field was more efficient to induce domain switching. The difference was caused by the initial orientation of the polarization in the area of the observation. The lack of contrast in the vicinity of the pore suggests that micron-sized domains formed in that area as the applied field forced the randomly oriented individual nanodomains to switch their polarization toward the field direction and these switched nanodomains coalesced.

3.3. Grain boundary cracking

Bulk studies have shown that electric-field-induced crack growth in ferroelectric ceramics tends to be intergranular [2–7,19]. There are at least three factors that could render the grain boundaries vulnerable in ferroelectric ceramics under an electric loading: pores, glassy phase, and termination of domains. The effect of sintering pores on electric performance of PZT ceramics has been studied where a ferroelectric ceramic with a higher porosity was found to suffer from more severe and more rapid fatigue degradation under cyclic field [20]. The role of the sintering pore in initiating cracks under electric loading is shown in Fig. 4, where cracks developed from a triple-junction pore under cyclic electric fields in the PZT-EC65 ceramic. The pore was located far away from the perforation at the center of the specimen and was a by-product of the sintering process rather than from the TEM sample preparation. The initial shape of the pore is shown in Fig. 4a, which was subjected to a cyclic electric field along the direction indicated by the arrow. After cycling for 50,000 cycles at a field-amplitude of $\pm 2.7$ MV m$^{-1}$, the pore was expanded and cracks developed along all three grain boundaries (Fig. 4b).

The glassy phase was found along the grain boundary in the PZT-EC65. While serving as sintering aid, the grain boundary glass weakened the resistance of PZT-EC65 to field-induced cracking in two ways. Electrically, the glass phase has a much lower dielectric constant than that of the ferroelectric grain and thus experiences a much higher electric field than the grain. Mechanically, the glass is also rather weak in resisting potential cracking.

The termination of the ferroelectric domains at the grain boundaries creates intersections between the domain boundary and the grain boundary. During cycling of the external field, the domains around the intersection tend to deform unequally, as they assume different crystallographic orientations. The incompatibility of the deformation among those domains can result in severe stress concentrations at the intersection, leading to grain boundary cracking.

3.4. Domain boundary cracking

Crack development along the domain boundary under cyclic electric field is shown in Fig. 5, where a fine
pore of about $0.22 \times 0.15 \, \mu m^2$ in size in the PMN-PT crystal was subject to an applied alternating field along the marked direction. The crystal was a relaxor-based ferroelectric and had a nanodomain structure [21]. No microcracks were detected around this pore after a static electric field up to $2.0 \, MV \, m^{-1}$ (the coercive field of the crystal is $0.25 \, MV \, m^{-1}$) was applied to the specimen for 10 min (see Fig. 5a and 5b). However, after an alternating electric field of $2.5 \, MV \, m^{-1}$ was applied to the specimen for 20 cycles, microcracks were developed, as illustrated in Fig. 5c and 5d. There was a substantial shift, indicated by arrows in Fig. 5d, of the upper crack surface relative to the lower crack surface, suggesting that there might be a strong Mode-II component in the crack driving force. According to the electron diffraction analysis, the microcrack lay on the $\{110\}$ planes, the domain boundaries of the crystal. Since the domain structure of the crystal is similar to that found in the PZT-EC65, alignment of the nanodomains seen in Fig. 3 is likely to have been the immediate response of the crystal to the applied electric field. Following the domain alignment along the $\{110\}$ plane, the crack was then induced by the electric field concentration around the central pore and by the repeated ferroelectric domain switching under a high cyclic electric field.

4. Conclusions

A new in situ TEM technique has been developed to study the domain switching and the associated microcracking in ferroelectric ceramics. The technique has been applied to fine-grained, and coarse-grained ceramics and single crystals, in which several micromechanisms of electric fatigue, i.e. domain switching, nanodomain alignment, grain boundary cracking and domain boundary cracking, have been observed. The domain switching at the crack tip resulted in formation of single domain structure within individual grains, thereby introducing large incompatible strains across the grain boundary. Alignment of the nanodomains was found in soft piezoelectric ceramics. The alignment could result in the same effect as the long-range tweed domain structure grew to become a large domain. The incompatible strains induced across the grain boundaries and the domain boundaries resulted in grain boundary cracking from pores at the triple junction of the grain boundaries and domain boundary cracking in the interior of the grain.

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