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ONR FY94 End of Fiscal Year Letter

(01 October 1993 - 30 September 1994)

Contract Title:

Investigation of Microscopic Mechanisms of Failure of Electronic Smart Materials/Systems

Performing Organization: University of Nebraska-Lincoln

Principal Investigator: Qing Jiang

Contract Number: N00014-94-1-5300

R & T Project Number: 3324903-01

ONR Scientific Officer: Dr. Roshdy S. Barsoum

A. The project goals

Being capable of exhibiting memory behavior through electrically-induced microstructural transformations, ferroelectric ceramics have been the commonly-used materials for manufacturing smart actuators. These actuators, especially those used for position control which involves repetitive positioning, are operated under cyclic loading conditions. It has been observed that macroscopic fracture takes place in these materials under cyclic loading conditions with strengths substantially lower than their monotonic-loading strengths. Recent experimental investigations indicate that a large number of microcracks are formed in these materials under cyclic loading before fracturing takes place and the fracturing process is dominated by the growth of microcracks. Another commonly encountered operation failure of ferroelectric actuators is the so-called *electric fatigue*, which refers to deterioration of material properties after a large number of cycles of applied electric field, such as changes in the shape of the hysteresis loop in the electric field-polarization response which lead to degradation of ferroelectric actuators. Further experimental observations have revealed that electrically-fatigued specimens contain a large number of microcracks. This indicates that microcracking is likely the cause of the electric fatigue and the deterioration of the strength of ferroelectric ceramics. The objectives of this investigation are the following:

(i) Understand the microscopic mechanism of formation of microcracks in these ferroelectric ceramics;

(ii) Quantify the dependence of the strength of these ceramics upon their microstructural parameters, that can be controlled through the manufacturing processes;

(iii) Tailor these ceramics for maximum strength by optimizing the microstructural parameters.

B. The Results in the Past Year

Since this project started on October 1, 1993, the PI and his associates have studied the lattice structures of ferroelectric crystals and the lattice distortions occurring during the phase transformation and domain switching. They have concluded that stress and electric field concentrations occur at the intersections of domain walls with grain boundaries because of the incompatibility of grain boundary constraints with the lattice distortions associated with the domain switching and that microcracks can be formed at these locations under cyclic loading programs which enhance these concentrations. Their analysis is summarized in this section.

(B1) The Microstructures

Ferroelectric actuators commonly used in position control are made of ceramics of barium titanate, lead zirconate titanate and lead lanthanum zirconate titanate. The latter two are also known as PZT and PLZT. These oxide ceramics have the general chemical formula ABO_3, where O is oxygen, A represents a cation with a larger ionic radius, and B a cation with a smaller ionic radius, and the corresponding structure is named the ***perovskite structure***.

In the absence of externally applied electric fields and mechanical loads, barium titanate ($BaTiO_3$) has a cubic structure at temperatures above the Curie point, which is about $120°C$. In the temperature range from $0°C$ to $120°C$, barium titanate has a tetragonal structure, for which the centers of positive and negative charges of each lattice unit do not coincide and hence the crystal is polarized even in the absence of applied electric fields. This phenomenon is referred to as ***spontaneous polarization***, and the corresponding state is called the ferroelectric phase.

PZT is a generic term for a family of solid solutions of lead titanate and lead zirconate, being a binary system. The chemical formula of PZT is $Pb[Zr_xTi_{1-x}]O_3$ with x being the molar ratio. Below the Curie point, PZT has either a tetragonal structure (on the Ti-rich side) or a rhombohedral structure (on the Zr-rich side), depending on the molar ratio x, except on the extreme Zr-rich side. PZT is widely used for manufacturing ferroelectric actuators because its chemical compositions can be adjusted to achieve certain properties required for specific applications.

PLZT stands for a family of solid solutions of stoichiometric lead zirconate titanate with lanthanum as additional chemical modifier, and its chemical formula is generally written as $Pb_{1-x}La_x[Zr_yTi_{1-y}]_{1-0.25x}V^{B}_{0.25x}O_3$, with lanthanum ions replacing lead ions on the A sites of the perovskite structure and V^{B} representing lattice site vacancies on B sites. The phase diagram of PLZT with a small amount of lanthanum is similar to that of PZT. PLZT has a great potential for design of optical devices because of the memory behavior in the optical response.

(B2) The lattice distortions

Most PZT and PLZT actuators in applications of position control are made with chemical compositions such that they have a tetragonal ferroelectric phase, which are very similar to that of barium titanate from the viewpoint of lattice structure. This permits a unified theoretical treatment.

The lattice distortion associated with the cubic-to-tetragonal transformation can be decomposed into two deformations as follows: (i) one of the three major axes of the cubic is stretched to become the longer axis of the tetragonal, named the c axis; (ii) the other two are compressed to become the shorter axes of the tetragonal, named the a axes. In the case that all the lattice units are polarized along the same direction, polarized charges accumulate on the surfaces of the crystal, generating electric fields which increase the total energy of the system and hence cause the instability of this configuration. Therefore, it is often observed that such a crystal is divided into a number of macroscopic regions in which the directions of polarization differ from one to another so that the induced electric fields cancel each other at least partially, resulting in a stable configuration. These regions are referred to as *ferroelectric domains*, and a surface separating two domains is called a *domain wall*. In the case that the normal component of the polarization intensity suffers jump discontinuities across a domain wall, polarized charges accumulate on this domain wall and induce an additional electric field, which also leads to instability. Minimization of polarized charges requires that the crystal polar direction rotates either 180° or 90°, approximately, across a domain wall. They are commonly referred to, respectively, as 180° and 90° domain walls. The x-ray investigations have revealed that formation of 90° domain walls, unlike 180° domain walls, is always accompanied by both switching of the polar direction and macroscopic deformations.

(B3) The effects of grain boundaries

The macroscopic deformations caused by the formation of 90° domain walls are referred to as spontaneous deformations. In ferroelectric ceramics, deformations of each grain are constrained by its neighboring grains. This causes the incompatibility of grain boundaries with the lattice distortions occurring during the formation of 90° domains and hence results in internal stresses. Stress concentrations occur at intersections of domain walls with grain boundaries because of the severer incompatibility. Domain switching, which takes place repeatedly under cyclic loading conditions, enhances stress concentrations and eventually leads to formation of microcracks.

(B4) The stress and electric field concentrations

Stress concentrations in ferroelectric ceramics are often accompanied by concentrations of electric fields because of the strong electromechanical coupling. Electric field concentrations lead to dielectric breakdown which may cause catastrophic damages to a polarization-control system. To carry out a quantitative analysis, the PI developed a mathematical model within the framework of electrostatics in deformable media. Due to the fact that the electromechanical state in each of the ferroelectric domains is only slightly distorted from one of the natural states of the crystal, this model results in a piecewise linearized formulation for which concentrations of stress and electric fields correspond to singularities of these fields. The causes of the concentrations of stress and electric fields are the material anisotropy and the discontinuity of spontaneous polarization across domain walls and grain boundaries. This investigation has concluded that the concentration of stress and electric fields due to the material anisotropy corresponds to the so-called power-law singularity, i.e., the magnitudes of the stress and electric fields are proportional to r^λ, with r being the distance to the intersection of domain walls with a grain boundary and λ being such a constant that $-1 < \lambda < 0$. The order parameter λ, which measures the intensity of the concentration, depends upon the crystal orientation and the orientations of the domain walls with respect to the grain boundary which they intersect. The investigation on the concentration of stress and electric fields resulting from the discontinuity of spontaneous polarization is currently being undertaken. A simplified analysis, which neglects the effect of macroscopic deformations, shows that the electric field concentration caused by the discontinuity of spontaneous polarization corresponds to the so-called logarithmic singularity, i.e., the magnitude of the electric field is proportional to $log(r)$ with r again being the distance to the intersection of domain walls with a grain boundary. This suggests that the major cause of the concentrations of stress and electric fields in ferroelectric crystals is likely the material anisotropy because the concentration corresponding to the power-law singularity is much severer than that corresponding to the logarithmic singularity. However, this issue will not be completely resolved until the effects of macroscopic deformations are fully understood.

Under a cyclic loading program, microcracks are initiated at these intersections when the stress exceeds the material strength locally. The stress and electric field distributions predicted by this analysis indicate that microcracks should appear as clusters within surrounding areas of these intersections and they can subsequently grow either along grain boundaries or through the interior of a grain. The former leads to intergranular cracks and the latter results in transgranular cracking. A fracture process in these ceramics can be dominated by either intergranular cracking or transgranular cracking, depending upon the microstructural parameters, such as grain size. This issue is currently under investigation.

C. Plans for Next Year's Research

The further investigation will be carried out along the following directions:

(1) Studying the concentrations of stress and electric fields due to discontinuity of spontaneous polarization across domain walls and grain boundaries, taking into account of the effects of macroscopic deformations;

(2) Quantifying the dependence of these concentrations upon the microstructural parameters, such as grain size;

(3) Simulating the macroscopic behaviors of ferroelectric ceramics, such as electric fatigue.

D. List of Publications/Reports/Presentations

1. Papers Published in Refereed Journals

[1] On modeling of phase transformations in ferroelectric materials, *Acta Mechanica*, Vol. 102, pp.149-165, 1994.

[2] On the driving traction acting on a surface of discontinuity within a continuum in the presence of electromagnetic fields, *Journal of Elasticity*, Vol. 34, pp. 1-21, 1994.

[3] On coupled heat-moisture transfer in deformable porous media, *Quarterly Journal of Mechanics and Applied Mathematics*, (with N. Rajapakse), Vol. 47, pp. 53-68, 1994

[4] Macroscopic behavior of a bar undergoing the paraelectric-ferroelectric phase transformation, *Journal of the Mechanics and Physics in Solids*, Vol. 41, pp.1599-1635, 1993

[5] On modeling of thermo-mechanical phase transformations in solids, *Journal of Elasticity*, Vol. 32, pp.61-91, 1993

[6] Deformations with discontinuous gradients in plane elastostatics of compressible solids, *Journal of Elasticity*, (with P. Rosakis), Vol. 33, pp. 233-257, 1993.

2. Non-Refereed Publications and Published Technical Reports:

[1] On the mechanisms of microcracking in ferroelectric ceramics, **Proceedings of the Second International Conference on Intelligent Materials**, pp. 677-685, Technomic Publishing Co., Lancaster, 1994.

[2] On the driving traction acting on a surface of discontinuity within a continuum in the presence of electromagnetic fields, *Technical Report*, No. 1, ONR Grant No. N00014-94-1-0053, 1994.

[3] On the electro-mechanical response of electrically active materials, *Technical Report*, No. 2, ONR Grant No. N00014-94-1-0053, 1994.

[4] On the morphology of ferroelectric domains, *Technical Report*, No. 3, ONR Grant No. N00014-94-1-0053, 1994 (with P. Rosakis).

[5] Investigation on microscopic mechanisms of failure of electronic smart materials/systems, *Technical Report*, No. 4, ONR Grant No. N00014-94-1-0053, 1994.

[6] Microcracking in ferroelectric ceramics. Part 1: Ferroelectric Twining, *Technical Report*, No. 5, ONR Grant No. N00014-94-1-0053, 1994 (with Y. Zhang).

3. Presentations:

a. Invited:

[1] On axisymmetric anti-plane shear deformations of compressible elastic materials, *the 12th U.S. National Congress of Applied Mechanics*, Seattle, Washington, June 27-July 1, 1994 (with J.K. Knowles).

[2] On the mechanisms of microcracking in ferroelectric ceramics, *the 2nd International Conference on Intelligent Materials*, Williamsburg, Virginia, June 5-8, 1994.

[3] On the mechanisms of microcracking in ferroelectric ceramics, Massachusetts Institute of Technology, Cambridge, Massachusetts, April 14, 1994.

[4] On the mechanisms of microcracking in ferroelectric ceramics, University of Florida, Gainsville, Florida, March 29, 1994.

[5] Microcracking in ferroelectric ceramics, Huazhong University of Science and Technology, Wuhan, P.R. China, January 4, 1994.

[6] Microcracking in ferroelectric ceramics, Chinses Academy of Sciences, Beijing, P.R. China, December 25, 1993.

[7] Microcracking in ferroelectric ceramics, Beijing University, Beijing, P.R. China, December 24, 1993.

[8] Microcracking in ferroelectric ceramics, Tsinghua University, Beijing, P.R. China, December 23, 1993.

[9] Microcracking in ferroelectric ceramics, Hong Kong University of Science of Technology, Hong Kong, December 14, 1993.

[10] The shape and growth of ferroelectric domains, *the 23rd Midwestern Mechanics Conference*, Lincoln, Nebraska, October 10-13, 1993 (with P. Rosakis).

[11] On the effects of electric fields and stresses upon phase transformation in ferroelectric crystals, *the 23rd Midwestern Mechanics Conference*, Lincoln, Nebraska, October 10-13, 1993.

b. Contributed: NONE

4. Articles in Books:

[1] On stress relaxation associated with an electrically-induced phase transformation, **Adaptive Structures and Material Systems**, Ed., G. Carman and E. Garcia, Vol. 35, pp. 43-52, ASME Applied Mechanics Division, 1993.

E. Honors and Awards:

Recipient	Recipient's Institution	Name and Sponsor
Qing Jiang	University of Nebraska	Research Initiation Award National Science Foundation

F. Participants and their Status:

1. Senior Personal:

Ying Zhang — Visiting Assistant Professor

2. Graduate Assistants:

Yongqiang Wang — Ph. D. candidate

3. Degrees Granted:

Mine Tasci — M.S. degree granted in December, 1993.

G. Other Sponsored Research:

Investigation of Macroscopic Models and Microstructures of Ferroelectric Crystals, the National Science Foundation, approximately $30,000 per year for the period: September 1, 1993 - August 31, 1996.

One summer month was charged to this grant during the past year.

SUMMARY OF FY94
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/PARTICIPANTS
(Number Only)

			ONR	non ONR
a.	Number of Papers Submitted to Referred Journal but not yet published:		4	3
b.	Number of Papers Published in Refereed Journals:		1	5
c.	Number of Books or Chapters Submitted but not yet Published:		1	0
d.	Number of Books or Chapters Published:		1	0
e.	Number of Printed Technical Reports & Non-Referred Papers:		6	0
f.	Number of Patents Filed:		0	0
g.	Number of Patents Granted:		0	0
h.	Number of Invited Presentations at Workshops or Prof. Society Meetings		10	1
i.	Number of Contributed Presentations at Workshops or Prof. Society Meetings:		0	0
j.	Honors/Awards/Prizes for Contract/Grant Employees: (selected list attached)		0	1
k.	Number of Graduate Students and Post-Docs Supported at least 25% this year on contract grant:		2	1
	Grad Students:	TOTAL	1	1
		Female	0	1
		Minority	0	0
	Post Doc:	TOTAL	1	0
		Female	0	0
		Minority	0	0
l.	Number of Female or Minority PIs or CO-PIs			
		New Female	0	0
		Continuing Female	0	0
		New Minority	0	0
		Continuing Minority	0	0

Enclosure (4)