MASTER

000-3420-1

THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA

A Research Progress Report
to
The United States Atomic Energy Commission
on
CERAMIC RESEARCH ON TRANSFORMATIONAL SUPERPLASTICITY AND THE
ELECTRON MICROSCOPY OF FERROELECTRIC DOMAIN BOUNDARIES
formerly
Contract No. AT(30-1)-4085
presently
Contract No. AT(11-1)-3420
Report No. C00-3420-1
for the period
June 1, 1971 through May 31, 1972

Submitted by
Richard C. Bradt and John H. Hoke
Department of Material Sciences
College of Earth and Mineral Sciences

March 1, 1972

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Adl

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

A Progress Report On

Ceramic Research on Transformational Superplasticity
and the Electron Microscopy of Ferroelectric Domain Boundaries

for the period June 1, 1971 through May 31, 1972

Submitted by:

Richard C. Bradt
Associate Professor
Ceramic Science

John H. Hoke
Associate Professor
Metallurgy

Approved by:

P. L. Walker, Jr., Head
Dept. Material Sciences

During the term of this agreement, Professor R. C. Bradt
has devoted 15% of his time to the research and Professor John
H. Hoke has devoted 5% of his time.

Abstract

The overall progress of the research program with regard to the ferroelectric and the superplasticity areas are reviewed in relation to the original objectives. The transmission electron microscopy of ferroelectric domains has yielded extensive information concerning the structure and interactions of domain boundaries in several single crystal and polycrystalline forms of barium titanate, and the characterization of domain processes at the phase transformations. Initial experimental difficulties of the superplasticity observations have been overcome, and both isothermal and transformational superplasticity have been observed and studied in bismuth oxide. Some characterization of the superplasticity has been completed, indicating some of the effects of stress, microstructure, and transformational heating rate. The ferroelectric study is in its final stages, while the superplasticity research has made the initial breakthrough and has outlined many of the pertinent variables, such that it has proceeded to the physical mechanism study and theory stage.

Research Objectives

The objectives of this research are multi-fold as related to the two areas of study. In the ferroelectric research it is to directly observe ferroelectric domain boundaries via transmission electron microscopy and characterize their structure and interactions in barium titanate. The superplasticity study is oriented toward searching for, identifying, and studying the superplastic behavior of crystalline ceramics in potential systems based on bismuth sesquioxide and zirconia.

Transmission Electron Microscopy of Ferroelectric Domain Boundaries

Ferroelectric domain boundaries have been studied in several different single crystal and polycrystalline forms of barium titanate via transmission electron microscopy. Samples have been prepared by combined mechanical polishing and ion-gun thinning techniques. The single crystals studied are the KF flux grown Remeika crystals, borate flux grown $(\text{Ba}, \text{Pb}) \text{TiO}_3$ solid solutions, and a melt grown Mithras crystal. Polycrystalline samples of high purity sintered material from Dr. K. S. Masdiyasni of Wright-Patterson AFML, and a hot pressed dense sample from Erie Technological Products have also been investigated. Extensive study of all of the materials except the Mithras crystal and the hot pressed polycrystalline sample has been completed, and these two are in their final observational stages. It is expected that this work will be completed by the end of this report period, May, 1972.

In addition to observing and characterizing the domain boundaries and their interactions, it has also been possible with the use of the cold stage to directly observe the domain reactions and subsequent twinning during the tetragonal to orthorhombic and the orthorhombic to rhombohedral phase transitions. The study of the Ba-Pb solid solutions single crystals, grown from a borate flux by Dr. F. W. Perry of The Sprague Electric Co., North Adams, Mass., has been particularly rewarding. The introduction of Pb into solid solution suppresses the low temperature phase transitions to such an extent that observations of the same crystallography may be made over a very wide temperature range. This has permitted direct observation of the wall thickness of 90° domains as a function of temperature. In all three Ba-Pb compositions studied, the 90° wall thickness decreased with decreasing temperature. These results are presently being coupled with electrical property data for these solid solutions to examine the nature of the polarization transition through the internal structure of the 90° domain boundary.

The ferroelectric transitions, tetragonal $\rightarrow$ orthorhombic $\rightarrow$ rhombohedral, were characterized in the Remeika crystals by cold stage electron microscopy. The tetragonal to orthorhombic transition is somewhat sluggish as the specimen was substantially supercooled before transforming completely. As the transition occurred, twin lamellae of the new phase nucleated in different areas of the crystal and propagated very slowly along the twin planes. Many non-equilibrium twin structures with the domain

walls bowed out of their low energy positions were observed. In general, the orthorhombic phase exhibited the most complex twin structures of the three ferroelectric phases. The orthorhombic to rhombohedral transition occurred quite rapidly resulting in very distorted twin structures initially. However, after the crystal was held in this phase long enough for "annealing" to occur, the domain walls came to rest at their low energy positions and very symmetric arrays resulted. The majority of the domain boundaries in this region were 180° 's which were extremely mobile and often twisted and furled through the crystal.

The completion of the observation of the Mithras crystal and the hot pressed polycrystalline material are in the final stages and will be combined with the previous observations on the three materials to fully characterize the domain boundaries.

Superplasticity

Superplasticity of both the isothermal and the transformational varieties has been observed in pure bismuth sesquioxide. It has been clearly identified and characterized microscopically with regard to the variables of stress, grain size, and transformational heating rate where applicable. Preliminary results suggest that perhaps the physical mechanism is one of grain boundary sliding; consequently, the discovery of this superplastic behavior is not only significant for transformational superplasticity per se, but appears to offer in the isothermal behavior an excellent case for the intensive

study of and the understanding of grain boundary sliding as a deformation mechanism.

It is generally accepted in the field that there are two major types of superplasticity:

1) Isothermal or structural superplasticity requires a very fine grain size at temperatures greater than one-half the absolute melting temperature. The applied stress needed for deformation in this class of materials is very sensitive to the strain rate and is described well by the equation:

$$\sigma = K\dot{\epsilon}^m$$

where m is the strain rate exponent or strain rate sensitivity, $\dot{\epsilon}$ is the strain rate and σ is the applied stress. Most materials under normal conditions have a relatively low strain rate sensitivity with an m value in the range of 0.1 to 0.3. Those materials which are considered superplastic have much higher strain rate sensitivities varying from 0.5 to 1.0, where a value of 1.0 corresponds to a Newtonian-viscous solid.

2) Transformational superplasticity is found in some systems possessing allotropic transformations. This type of superplasticity is characterized by anomalous deformation under small applied stresses while cycling the temperature about the transformation temperature.

The principle material studied in this work has been bismuth sesquioxide, Bi_2O_3 , which exhibits a monoclinic to cubic, allotropic transformation at approximately 730°C. It

melts at 825°C. This particular system was chosen for two reasons. First, it possesses a transformation at an experimentally convenient temperature, and secondly, there are a wide range of solutes which form eutectoid systems when combined with Bi_2O_3 . The latter point appeared to be an important consideration in choosing a material since many analogous metallic systems exhibit transformational superplasticity in the eutectoid form, but not in the pure state. As the work progressed, it was found that pure Bi_2O_3 could exhibit transformational superplasticity, and in addition, while characterizing the isothermal creep, evidence of isothermal superplasticity was observed.

Suitable samples of bismuth oxide were consolidated by hot pressing Baker Reagent Bi_2O_3 at 2000 psi at 650°C in an induction hot press using a graphite die. Cylindrical samples 1/2 inch long by 1/2 inch in diameter were cut from the billets. These samples were tested in compression in a high temperature creep rig under varying conditions. Deformation was detected with an LVDT arrangement and was recorded along with the temperature by a dual channel strip chart recorder.

A knowledge of the isothermal creep behavior of Bi_2O_3 at temperatures both above and below the transformation was needed before progressing to the transformation behavior. The results of these studies done below the transformation temperature unexpectedly revealed a very high strain rate sensitivity. Experimentally, each of a series of identical samples was heated to 700°C and loaded to a specified applied stress.

Figure 1 is a schematic of a deformation curve as recorded by the strip chart recorder for one of these runs. The slope of this curve at any point is the deformation rate and is easily converted to the true strain rate. Figure 2 shows the results of a series of isothermal creep tests as log stress vs. log strain rate, where the strain rate was measured at 0.1 strain. This sigmoidal relationship is characteristic of nearly all metallic systems which exhibit isothermal superplasticity. The slope of Figure 2 at any point is the strain rate sensitivity, m , over a narrow range of strain rates and is plotted as a function of strain rate on Figure 3. The maximum value of m is approximately 0.8, well above the accepted minimum of 0.5 to qualify for isothermal superplasticity. Work is continuing in this area to characterize the effect of grain size and porosity and to determine the maximum strain rate sensitivity as a function of temperature.

Dilatometric studies were done on Bi_2O_3 to verify the reported transformation temperature of 730°C and the large increase in volume of approximately 6.9 volume % through the transformation. Figure 4 shows a schematic of the dilatometer trace. The heating curve (solid line) corresponds to a 3°C per minute heating rate and shows a large increase in length at a temperature of $730 \pm 5^\circ\text{C}$. The cooling curve (dashed line) corresponds to a very fast cooling rate of approximately 30°C per minute which appears to lower the transformation temperature more than 50°C , but does not quench in the high temperature cubic form. Slower cooling rates allowed the cubic to

monoclinic transformation to take place much closer to 730°C.

The transformational deformation tests were cycled between 700°-760°C. A single cycle run then consists of the following steps: heat to 700°C, load to a specified applied stress, allow isothermal creep to stabilize, heat through the transformation at a specified heating rate to 760°C, allow isothermal creep to stabilize at high temperature, cool through the transformation, allow to stabilize at 700°C and unload. Figure 5 is a schematic of a strip chart recording of the deformation and the temperature. The extensions of the isothermal creep rates (dashed lines) show rather dramatically that something besides normal creep occurs during the monoclinic to cubic transformation. The separation of the extrapolated dashed lines at the transformation temperature was used to calculate the strain which cannot be explained by normal creep through the first one-half cycle. The utilization of the 700°C isothermal creep rate is undoubtedly a low estimate of the creep behavior from 700 to 730°C, but the error is counteracted by the fact that the isothermal creep rate at 760°C is an over estimate of the creep behavior from 730° to 760°C. The assumption that these errors are equal in magnitude and opposite in direction is an intuitively reasonable approximation which has been used by other investigators who were faced with the same problem in other materials. Experimental justification of this approximation is very difficult to obtain, but the self consistency of the results indicates that the approximation is probably a reasonable one.

Figure 6 is a plot of the "superplastic strain" as a function of the applied stress. The linear relationship is not surprising as it has been reported in several metallic systems; however, the slope of the line is very surprising. This might best be illustrated by comparing the strains which result by a single cycle about the transformation of several different superplastic materials under an applied load of 1000 psi. Bi_2O_3 cycled about the 730°C monoclinic to cubic transformation results in a strain of approximately 1.4. Similar strains in metallic systems under comparable stresses are reported as: 7×10^{-2} for the α - β titanium transformation at 882°C , 2×10^{-2} for the iron α - γ transformation at 910°C , and 2×10^{-4} for the 417°C ϵ - α transformation in cobalt. Unlike all of the metallic transformations, Bi_2O_3 was found to exhibit a large superplastic strain only upon the heating stage of the first cycle. Further cycling about the transformation resulted in negligible additional strain and extensive cracking. Scanning electron microscopy suggests that this is probably the result of grain growth in the high temperature phase. Figure 7 also illustrates the magnitude of the strain through the first transformation as a photograph comparing a sample of Bi_2O_3 prior to testing, to one cycled about the transformation once under an applied stress of only 200 psi.

The strain through the transformation in Bi_2O_3 was found to be sensitive to the heating rate through the transformation as shown by Figure 8. This plot of (log strain) vs. (log heating rate) shows that slower heating rates enhance

larger strains. Figure 9 shows the effect of grain size on the strain through the transformation indicating that materials with grain sizes larger than approximately 20 microns may exhibit no superplastic strain through the transformation. This strongly suggests that the physical mechanism of this deformation is one of grain boundary sliding; however, additional study of the system is necessary for a definite conclusion.

Studies of several of the eutectoids with bismuth oxide have also been initiated. Samples at the reported eutectoid composition of $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5$ and $\text{Bi}_2\text{O}_3\text{-CaO}$ have been consolidated and tested; however, initial observations are inconclusive. The $\text{Bi}_2\text{O}_3\text{-Sm}_2\text{O}_3$ eutectoid has been prepared and is presently under study. Other materials and compositions are being considered.

Progress Summary

The investigation of transmission electron microscopy of ferroelectric domain boundaries has reached its terminal stages with extensive observation and characterization of domain interactions and structures and phase transitions in barium titanate. In the superplasticity phase of the research, superplasticity has been observed and characterized in bismuth sesquioxide. Study of the physical mechanism is presently underway.

Figure 1

Schematic of strip chart record showing deformation
vs. time for an isothermal compressive creep test

Figure 2

Applied stress vs. strain rate due to isothermal
creep at 700°C

Figure 3

Strain rate sensitivity ($\frac{\partial \log \sigma}{\partial \log \dot{\epsilon}}$) vs. strain rate for the data given in Figure 2

Figure 4

Schematic dilatometer trace for Bi_2O_3
showing the large expansion through the
monoclinic $\rightarrow$ cubic allotropic phase transformation

Figure 5

Schematic of strip chart record showing deformation and temperature vs. time for a single cycle transformational creep test

Figure 6

The effect of applied stress on transformational strain in Bi_2O_3

Figure 7

Photograph comparing sample of Bi_2O_3
prior to testing (left) to one cycled about
the transformation once under an applied
stress of only 200 psi (right)

Figure 8

The effect of the heating rate from
700° to 760°C on the
transformational strain in Bi_2O_3

Figure 9

The effect of prior grain size
on transformational strain in Bi_2O_3