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CERAMIC RESEARCH ON TRANSFORMATIONAL SUPERPLASTICITY AND
STOICHIOMETRIC EFFECTS ON FRACTURE

A

RESEARCH PROGRESS REPORT

(COO-3420-2)

to the

UNITED STATES ATOMIC ENERGY COMMISSION

FOR THE PERIOD

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submitted by

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THE PENNSYLVANIA STATE UNIVERSITY
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A Research Progress Report

to

The United States Atomic Energy Commission

CERAMIC RESEARCH ON TRANSFORMATIONAL SUPERPLASTICITY AND
STOICHIOMETRY EFFECTS ON FRACTURE

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ABSTRACT

The progress of the program is reviewed with respect to each of the individual study areas. The ferroelectric study has been completed, the student has graduated, and papers are being written and presented. The investigation of stoichiometry effects on fracture has progressed to the point where all of the initial experimental difficulties appear to be solved, so that initial results are about to be obtained. The transformational superplasticity research has progressed most satisfactorily, as the phenomenon in pure Bi_2O_3 has been extensively investigated and characterized with respect to intrinsic and extrinsic variables. In addition, pure Bi_2O_3 has been found to also exhibit superplastic behavior in the stable phases above and below the transformation; consequently, offering the unique opportunity to directly compare the two forms of superplasticity in the same material. It is expected that the pure Bi_2O_3 study will be completed within the next year.

Transformational superplasticity has now also been observed and identified in the binary Bi_2O_3 - Sm_2O_3 eutectoid. Unlike pure Bi_2O_3 , this material does not exhibit superplastic behavior above and below the transformation. The eutectoid composition has been moderately well characterized, and one hypoeutectoid composition has been prepared and is being studied. Extensive study of other hypo and hypereutectoid compositions is planned, as well as study of other eutectoids and phase transitions.

RESEARCH OBJECTIVES

The objectives of this research are related to the two study areas. The effects of stoichiometry on fracture has as its primary objective, the understanding of how variations in stoichiometry affect fracture initiation and propagation in brittle ceramics, and how this is further affected and interdependent with non-stoichiometric structural variables such as grain size and porosity.

The objective of the superplasticity study is to gain a fundamental understanding of the phenomenon of transformational deformation in otherwise brittle ceramics. In the case of pure Bi_2O_3 this also involves understanding the superplasticity of the stable phases above and below the phase transformation and if the two forms of extensive deformation are related. Perhaps the most important result of this investigation will be the comparison of the two types of superplasticity in the same pure material.

Superplasticity of the transformational variety also occurs in the Bi_2O_3 - Sm_2O_3 eutectoid; however, the isothermal variety of superplasticity was not found. The objective of this study is to determine the role and characteristics of the second phase, its volume fraction, size, and crystallography as they affect the transformational deformation. It is also an objective of this study to discover what aspects of eutectoid transformations contribute to superplasticity, especially in Bi_2O_3 based systems, where only one of three eutectoids studied to date exhibit transformational deformation.

RESEARCH PROGRESS

Transmission Electron Microscopy of Ferroelectric Domain Boundaries - (Completed during 1972-1973 period)

This study has been completed with Dr. Mahlon D. Dennis writing his thesis. At the present three papers resulting from this investigation are in manuscript form, reprints will be included in the next progress report after their publication. These papers are:

- (i) "Domain Boundary Interactions at Phase Transitions in BaTiO_3 " - a complete description and characterization of domain boundary processes during the phase transitions in BaTiO_3 .
- (ii) "Ninety Degree Domain Wall Thickness in $(\text{Ba,Pb})\text{TiO}_3$ " - the variation of the boundary thickness with temperature and composition is directly observed over the extensive stable range of the tetragonal structure in these solid solutions.
- (iii) "Domains in Fine Grain Size BaTiO_3 " - describes the peculiarities of the very fine grain size ferroelectrics and in terms of the domain structure lends support to the domain nucleation theory of aging and internal stress theory of ferroelectric phenomenology.

Paper (i) has been presented, and (ii) will be presented at this year's American Ceramic Society meeting. The (iii) paper will probably be presented at the American Ceramic Society Fall Meeting.

Superplasticity (Transformational and Isothermal)

Superplasticity of both the isothermal and transformational varieties has been observed in pure bismuth sesquioxide. It has been clearly identified and characterized. Results suggest that perhaps the phenomenon results from internal stresses enhancing deformation by

the physical mechanism of grain boundary sliding. This superplastic behavior is probably not only significant in understanding transformational superplasticity per se, but appears to offer, at least in the isothermal behavior, an excellent case for the intensive study and understanding of grain boundary sliding.

The principle material of this study has been pure 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 does exhibit transformational superplasticity, and in addition, while characterizing the isothermal creep, evidence of isothermal superplasticity was observed.

As indicated in last year's progress report (C00-3420-1), the isothermal effect is evidenced by the high strain rate sensitivity of approximately 0.8 and by the sigmoidal behavior of the log stress vs. log strain rate plot during tests in compression at 700°C . The transformational effect is evidenced by very large anomalous deformations while heating through the 730°C monoclinic to cubic phase transition under small applied stresses. This superplastic or transformational strain is substantially over and above that expected from the normal creep behavior of the material. Also included in last year's report were the effects of stress, initial grain size, and heating rate on the transformational strain. These results are

included as Figures 1-3 for later reference when discussing possible deformation mechanisms.

Since the last progress report, the transformational effect has been characterized with respect to the very important material parameter, of porosity. A range of densities from 82-97 percent of theoretical were prepared by numerous hot pressings at pressures ranging from 700-3000 psi, all at 650°C for 45 minutes at temperature and pressure. Pressure, rather than temperature or time, was chosen as the hot pressing variable. This choice was made on the basis that variations in hot pressing pressure would result in a range of porosity with the least effect on other variables such as grain size and interparticle bonding. Polished sections of the hot pressed material indicate that the variation of the hot pressing pressure does indeed have very little effect on the resulting grain size.

Cylindrical compressive creep samples were core drilled from the hot pressed billets. Densities were measured by bulk measurement of dimensions and by a water immersion technique. The transformational behavior of these samples was then tested using the previously described procedure. Figure 4 shows the results of the study of porosity as transformational strain per cycle vs. percent theoretical density for three levels of applied stress. The three curves all have minima at approximately 90 percent theoretical density.

The elastic modulus of bismuth oxide was also measured as a function of density. The modulus was measured by the flexural resonance technique on an acoustic spectrometer using samples measuring approximately 1.9 X 0.2 X 0.2 inches. These results are presented on Figure 5 showing the expected trend of decreasing modulus with increasing porosity. Interestingly the trend appears linear as opposed

to the more frequently observed exponential decrease.

Greenwood and Johnson⁽¹⁾ have proposed a hypothesis for the cause of transformational superplasticity. In bismuth oxide, it appears to satisfactorily explain the effects of all of the variables which have been studied. The basis of this model holds that transformational superplasticity is an internal stress induced deformation, where the large internal stresses caused by the volume change while going through the transformation, when combined with a relatively small externally applied stress, and an effective microscopic deformation mechanism, result in a large transformational strain. Analysis shows that this transformational strain should be proportional to the volume change through the transition and the applied stress, and inversely related to the yield strength or creep strength. The proportionality between the applied stress and the transformational strain per cycle was especially meaningful since this behavior has been observed experimentally in nearly all materials of this type, including pure Bi_2O_3 , as seen in Figure 1.

We feel that this model can be successfully extended to explain additional experimental observations on Bi_2O_3 . Figure 2 shows that increasing grain size reduces the amount of transformational strain per cycle. An internal stress induced strain model predicts this trend if the isothermal creep rate also decreases with increasing grain size. Although the controlled study of the isothermal creep rate as a function of grain size has not been completed to date, partial results yield evidence that increasing grain size does indeed decrease the isothermal creep rate, as one would expect if grain

(1) G. W. Greenwood and R. H. Johnson, Proc. Roy. Soc. A 283, 403 (1965).

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boundary sliding is responsible. Thus the Greenwood-Johnson model explains the observed trend in the transformational behavior.

This same line of reasoning can then be used to explain why Bi_2O_3 exhibits the large transformational strain only upon the first cycling about the transformation. Further cycling is found to cause extensive cracking of the sample with very little additional strain. There are two important related observations. After a single cycle about the transformation, the average grain size has grown from about 10 to greater than 50 microns, and the isothermal creep rate of both the monoclinic and the cubic phases decreases by at least two orders of magnitude. This could be a cause and effect relationship, if the microscopic deformation mechanism is grain boundary sliding. After the first cycle there is not an effective deformation mechanism present, therefore as the sample is cycled the second time, it fractures due to the large internal stresses caused by the 7% change in volume which cannot be effectively relieved via grain boundary sliding.

Figure 3 shows that the heating rate through the transformation has a strong inverse logarithmic influence on the transformational strain per cycle. This trend can be explained in terms of the proposed model since the internal stresses are relieved by a time dependent creep mechanism in Bi_2O_3 . The heating rate through the transformation is probably directly related to the velocity of the advancing transition front of the new phase. Therefore slower heating rates should allow more time for internal stresses to be relieved and in turn, should result in a larger observed transformational strains per cycle.

The effect of porosity on the transformational strain is unique, as can be seen on Figure 4. It can be explained qualitatively in

terms of the proposed model, but it must be described in terms of the sum of two opposing effects in order to produce the observed minima. One would expect that increasing the porosity of the structure would increase the isothermal creep rate. According to the proposed model, a higher isothermal creep rate, i.e. higher porosity, should increase the transformational strain per cycle and thus explain the trend of the curves below 90% theoretical density. Lower density ceramics exhibit higher creep rates and thus a greater ability to relieve the transitional strains by creep processes. On the other hand, increasing density should increase the modulus as confirmed by Figure 5. Since the internal strain caused by the volume change through the transformation is independent of density, then qualitatively according to a simple Hooke's law relation, an increase in modulus should cause an increase in the internal stress. The internally stress induced deformation model then predicts that this increase in internal stress will cause an increase in the transformational strain per cycle and thus explain the trend of the curves above 90% of theoretical density.

Several Bi_2O_3 based eutectoid systems are being studied to determine if they exhibit transformational superplasticity when heated through their eutectoid transformations as has been observed in many metallic systems. Four systems have been studied to date: (i) $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5$, (ii) $\text{Bi}_2\text{O}_3\text{-CaO}$, (iii) $\text{Bi}_2\text{O}_3\text{-Sm}_2\text{O}_3$, and (iv) $\text{Bi}_2\text{O}_3\text{-La}_2\text{O}_3$. The first two systems have not been observed to exhibit superplastic behavior. Transitional superplasticity has been clearly identified in the $\text{Bi}_2\text{O}_3\text{-Sm}_2\text{O}_3$ system and characterized with regard to applied stress and composition. The fourth system is presently being prepared for testing.

The principle system studied to date has been Bi_2O_3 - Sm_2O_3 which exhibits a (mon + Rh_{ss}) to cubic eutectoid transformation at approximately 690°C . The compositions studied were prepared by mixing reagent grade Bi_2O_3 and Sm_2O_3 in the proper proportion and solid state reacting at a maximum temperature of 750°C . The compositions were continually monitored by x-ray diffraction to determine when the reactions were completed. Suitable samples of each composition were then consolidated by hot pressing at 3000 psi and at 675°C in a graphite die. Cylindrical samples 1/2 inch long by 1/2 inch in diameter were diamond core drilled from the billets. The following samples were tested in compression and have been extensively investigated (see Figure 6).

- (a) The reported eutectoid composition of 96 mole % Bi_2O_3 4 mole % Sm_2O_3 (BS 9604), and
- (b) The hypoeutectoid composition, 98 mole % Bi_2O_3 -2 mole % Sm_2O_3 (BS 9802).

Dilatometric studies have been done on these compositions for a direct comparison with the transformation temperature as predicted by the phase diagram and to determine the volume change associated with the transformation. Figure 7 shows the dilatometric trace for heating at $3^\circ\text{C}/\text{minute}$, for the eutectoid composition (BS 9604), for which the transformation was found to be over the temperature range of 655 - 715°C . For the composition (BS 9802) the transformation was over the temperature range 680 - 730°C . Both compositions exhibited a large increase in volume associated with the transformation from the two phase to the single phase region.

The transformational deformation tests were cycled between 660 - 720°C for BS 9604 and 660 - 750°C for BS 9802. A single cycle run

consists of the following steps: heat to the low temperature, load to a specified applied stress and allow isothermal creep to stabilize, then heat through the transformation at a specified heating rate to the higher temperature and allow isothermal creep to stabilize at the high temperature, then cool through the transformation and allow to stabilize at the low temperature and unload. Figure 8 is a schematic of the 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 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 thermal creep rate is undoubtedly a low estimate of the creep behavior from the low temperature to the transformational temperature, but the error is counteracted by the fact that the isothermal creep rate at the high temperature to high temperature. 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 have been faced with the same problem in other materials. Experimental justification of this approximation is very difficult to obtain; however, the self consistency of the results indicates that the approximation is probably a reasonable one.

Figure 9 is a plot of the "superplastic strain" as a function of applied stress for the eutectoid composition (BS 9604). The slope in the low stress region is approximately 8×10^{-4} per psi as compared to that of pure Bi_2O_3 of 1.4×10^{-3} per psi. At the higher

stresses there is an increase and then decrease in the slope. The eutectoid composition exhibits this large superplastic strain only upon the heating stage of the first cycle. Further cycling about the transformation resulted in negligible additional strain, which agrees with results on pure Bi_2O_3 .

Figure 10 is a plot of true strain rate vs. stress, the slope of this curve is the strain rate sensitivity (m).

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

True strain rate $(\dot{\epsilon})_t$ was estimated from the maximum slope on the curve in Figure 8. This was done by determining the slope of the curve which is the deformation rate and converting to $(\dot{\epsilon}_t)$, taking into account the thermal expansion rate through transformation and also the $(\dot{\epsilon}_t)$ which could be attributed to the isothermal behavior of the material above and below the transformation. The "m" value for (BS 9604) was found to be ≈ 0.9 . This value of "m" is considerably above the minimum 0.5 used in arbitrarily defining superplasticity and almost approaches the unity value ($m = 1$) for viscous flow.

A study of the strip chart curves, such as in Figure 8, revealed that the isothermal strain and strain rate for both the low temperature (below T_E) and high temperature (above T_E) was quite low relative to that observed during transformation. Based on this observation the isothermal creep rate as a function of temperature was studied. This study was two fold - (i) to determine if (BS 9604) exhibited isothermal superplasticity as found with pure Bi_2O_3 and (ii) to determine if (m) the strain rate exponent changes with temperature.

Experimentally, each of a series of samples was heated to a specified temperature and a stress was applied. Figure 11 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 12 shows the results of the isothermal creep tests for one temperature. The slope of the curve is the strain rate sensitivity, (m) . Figure 13, shows how (m) varies with temperature. It can be seen that (m) is approximately 0.3 at both low and high temperatures but increases as the temperature approaches that of the transformation. The maximum appears near the transformation temperature, but more work is required to exactly define the relationship of (m) vs. (T) . Based on the tentative definition of superplasticity ($m > 0.5$), it appears that the eutectoid composition in the Bi_2O_3 - Sm_2O_3 systems does not exhibit isothermal superplastic behavior except very near the transformation temperature. ✓

Acoustic emission monitoring of the phase transition during superplastic behavior has not been successful to date. However, additional testing and scanning of frequencies is in progress.

Results of these studies of superplasticity have been presented as the following:

- (i) "Transformational Deformation in Pure Bi_2O_3 " - presented at the annual meeting of the American Ceramic Society Washington, D.C. (1972). (Paper in preparation)
- (ii) Similar talk to (i) but with some isothermal data at 1972 Gordon Conference on Solid State Ceramics.
- (iii) "Transformational Deformation of the Bi_2O_3 - Sm_2O_3 Eutectoid" - to be presented at the 1973 annual meeting of the American Ceramic Society, Cincinnati, Ohio.
- (iv) "Transformational Deformation in Bismuth Oxide Systems" - general paper to be presented at symposium on "Phase

Transitions and Their Applications in Material Science"

to be held at Penn State University, May 23-25, 1973.

Stoichiometry Effects on Fracture

Progress on the effects of stoichiometry on the fracture initiation and propagation in wustite has progressed very satisfactorily for the initial year. A controlled atmosphere furnace has been adapted to gas flow meters to allow mixing of CO and CO₂ in the proper ratios to yield the partial pressures of O₂ necessary to equilibrate the wustite over the entire range of stoichiometry. It appears that there is no difficulty attaining proper atmosphere control for any composition within the wustite field. Manufacture of test samples has taken two complimentary routes, (i) conventional pressing and sintering and (ii) hot pressing. Both are based on the processing of Fe and FeO₃ powders in the proper proportion to yield wustite, which can then be equilibrated at the proper temperature and partial pressure of O₂ to yield the desired stoichiometry. The conventionally processed samples appear to yield slightly warped, but acceptable, samples, while the hot pressed samples are excellent. Mechanical testing is expected to commence soon.

PROGRESS SUMMARY

The ferroelectric study has been completed, papers have been presented and are now being written. The superplasticity, both transformational and isothermal has progressed very well, with the pure Bi_2O_3 study expected to be completed during the next year. The eutectoid transformational superplasticity is also showing interesting results and is expected to yield important fundamental data during the coming year. The fracture studies of nonstoichiometric wustite have really just overcome the initial experimental difficulties.

FIGURE 1., The effect of applied stress on the transformational strain of pure Bi_2O_3 during the 730°C monoclinic to cubic transformation.

FIGURE 2. The effect of grain size on the transformational strain of pure Bi_2O_3 during the 730°C monoclinic to cubic transformation.

FIGURE 3. The effect of heating rate through the transformation on transformational strain in pure Bi_2O_3 during the 730°C monoclinic to cubic transformation.

FIGURE 4. The effect of porosity on the transformational strain of pure Bi_2O_3 during the 730°C monoclinic to cubic phase transition.

FIGURE 5. The effect of density on the Young's Modulus of pure Bi_2O_3 .

FIGURE 6. The reported Bi_2O_3 - Sm_2O_3 phase diagram (E. M. Levin and R. S. Roth, J. Res. Nat. Bur. Stand. 68A, 2, 200 (1964)).

FIGURE 7.. Dilatometric trace of the $\text{Bi}_2\text{O}_3\text{-Sm}_2\text{O}_3$ eutectoid,

FIGURE 8. A schematic of the strip chart recording showing the transformational strain.

FIGURE 9. Transformational strain of the $\text{Bi}_2\text{O}_3\text{-Sm}_2\text{O}_3$ eutectoid as a function of stress. Compare with Figure 1.

FIGURE 10. Estimated strain rate exponent during transformational strain of the $\text{Bi}_2\text{O}_3\text{-Sm}_2\text{O}_3$ eutectoid composition.

FIGURE 11. Schematic of an isothermal creep curve of a $\text{Bi}_2\text{O}_3\text{-Sm}_2\text{O}_3$ composition.

FIGURE 12, The strain rate exponent of the Bi₂O₃-Sm₂O₃ eutectoid at 660°C.

FIGURE 13. Variation of the strain rate exponent with temperature in eutectoid $\text{Bi}_2\text{O}_3\text{-Sm}_2\text{O}_3$.