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A Research Progress Report

to

THE UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
(United States Atomic Energy Commission)

CERAMIC RESEARCH ON TRANSFORMATIONAL SUPERPLASTICITY AND
STOICHIOMETRY EFFECTS ON FRACTURE

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Submitted by

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RESEARCH PROGRESS REPORT

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FOR THE PERIOD

JUNE 1, 1974 to MAY 31, 1975

submitted by

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ABSTRACT

The progress of the program is reviewed with respect to each of the study areas. In the superplasticity studies the conclusions of the two phase eutectoid work is presented and the current progress on Bi_2WO_6 discussed. The observed effects of stoichiometry on elastic properties and crack propagation are reported and briefly discussed.

RESEARCH OBJECTIVES

Objectives of this research program are best illustrated by examining each of the two strain areas separately. The objective of the superplasticity study is to obtain a fundamental understanding of the phenomenon of transformational study in otherwise "brittle" ceramics. This involves the mechanism of the deformation and related intrinsic and extrinsic effects on the transitional strain. Certain aspects of this understanding have been achieved in Bi_2O_3 and in the two phase eutectoid $\text{Bi}_2\text{O}_3\text{-Sm}_2\text{O}_3$, including both hypoeutectoid and hypereutectoid compositions. As a result of the observation of peculiar transitional thermal expansion "growth" features associated with a phase transition in Bi_2WO_6 , which also exhibits transformation superplasticity, it has become a corollary objective to understand this interesting phenomenon and investigate the relationship between these peculiar dimensional changes and superplasticity, if indeed one exists.

The objective of the fracture-stoichiometry study is to investigate the effect of stoichiometry on both subcritical and critical fracture processes in ceramics. This involves experimentally determining K-V diagrams for subcritical crack growth and measuring K_{Ic} for fracture as a function of stoichiometry in TiO_{2-x} and Fe_{1-x}O . The more plasticity prone Fe_{1-x}O did not exhibit subcritical crack growth, consequently indicating an important connection between subcritical crack growth and flaw tip plasticity. It is now also the objective of this study to clearly define this subcritical crack growth dependence on plasticity by examining the non-stoichiometric magnesium aluminate spinels.

RESEARCH PROGRESS

The following papers have been published since the last progress report:

Dennis, M. D. and Bradt, R. C. "Thickness of 90° Ferroelectric Domain Walls in (Ba,Pb) TiO_3 Single Crystals", J. App. Phys. 45, (5), 1931-33 (1974).

Johnson, C. A., Smyth, J. R., Bradt, R. C. and Hoke, J. H., "Transformational Superplasticity in Pure Bi_2O_3 and the Bi_2O_3 - Sm_2O_3 Eutectoid", 443-454 in Deformation of Ceramic Materials edited by R. C. Bradt and R. E. Tressler, Plenum (1975).

Johnson, C. A., Bradt, R. C. and Hoke, J. H., "Transformational Plasticity in Bi_2O_3 ", J. Amer. Cer. Soc. 58, (1-2), 37-40 (1975).

Additional manuscripts are in the submission, revision, or preparation stage.

Transformational Superplasticity

The Bi_2O_3 - Sm_2O_3 Eutectoid System

Transformation superplasticity has been identified in the Bi_2O_3 - Sm_2O_3 system. There are several important features of this phenomenon in the two phase system; notwithstanding the fact that it has not been previously reported for any oxide two phase system.

Both hypoeutectoid and hypereutectoid compositions exhibited the characteristic linear relationship between the transformational strain per cycle and the applied stress. This observation, along with the volumetric change during the transformation, appears to agree with the internal stress induced deformation theory of Greenwood and Johnson. A direct microstructural relationship between the superplastic strain and the amount of eutectoid structure present was also observed. It appears that a major portion of the superplasticity occurs in the eutectoid microconstituent. Any proeutectoid phase that may be present acts as some form of deformation barrier by increasing the threshold stress for transformational strain. The strain rate sensitivity index, m , one measure of superplastic behavior, is near one for the eutectoid composition. As with metallic systems, the $\text{Bi}_2\text{O}_3\text{-Sm}_2\text{O}_3$ system exhibits cumulative deformation when thermal cycled repetitively about the transformation temperature. This behavior was attributed to the thermal stability of the microstructure.

The effect of the applied stress on the transformational strain was studied in compression. The results from the study of the $96\text{Bi}_2\text{O}_3\cdot 4\text{Sm}_2\text{O}_3$ composition are shown in Figure 1 as the transformational strain per cycle versus the average true stress during the cycle. The linear relationship between these variables agrees well with similar observations in metals and pure Bi_2O_3 . The linear relationship also agrees with Greenwood and Johnson's proposed theory for transformational superplasticity. The deviation from linearity at high stresses is due to the frictional forces between the specimen and rams of the testing apparatus. The stress applied must overcome the frictional force as it imparts a permanent strain in the specimen. This effect results in an overestimate of the stress

FIGURE #1 Transformational Strain per Cycle Versus Stress for $96\text{Bi}_2\text{O}_3 \cdot 4\text{Sm}_2\text{O}_3$ Compared with Pure Bi_2O_3 .

TABLE I

Comparison of Eutectoid Which Exhibit Transformational Superplasticity

<u>Material</u>	<u>Transition</u>	<u>$\Delta V/V$</u>	<u>T/T_{mp}</u>	<u>$\epsilon_{trans}/\text{cycle}$ at 500 PSI</u>
Pure Bi_2O_3	Mon $\rightarrow$ Cubic	0.069	0.91	7.0×10^{-1}
$\text{Bi}_2\text{O}_3\text{-Sm}_2\text{O}_3$	"Eutectoid"	0.030	≈ 0.80	4.2×10^{-1}
AISI 4340 Steel	Hypoeutectoid	-----	≈ 0.50	1.0×10^{-3}
AISI 1080 Steel	Eutectoid	-----	≈ 0.50	2.0×10^{-3}
Fe + 0.2C	Hypoeutectoid	0.011	≈ 0.50	6.0×10^{-3}
AISI 1095	Hypereutectoid	-----	≈ 0.50	1.7×10^{-3}

required to produce a given strain when very large deformation occurs.

An interesting result is revealed by comparing the slope of this linear relationship with that of pure Bi_2O_3 and several metallic eutectoids. An equivalent comparison is made in Table I which lists the reported transformation strains per cycle at 500 psi. This data reveals that the transformation effect in the $\text{Bi}_2\text{O}_3\text{-Sm}_2\text{O}_3$ system is more than an order of magnitude greater than that reported for any metal eutectoid, but only approximately one-half that of pure Bi_2O_3 . The difference between the ceramic and metal eutectoids can be explained qualitatively on the basis of Greenwood and Johnson's derivation.

It can also be applied to rationalize the difference in transformational strain per cycle between pure Bi_2O_3 and the "eutectoid" composition. From the isothermal creep data in this study and that of Johnson for pure Bi_2O_3 , it was determined that Bi_2O_3 exhibited a creep strength about 1.3 times greater than the $96\text{Bi}_2\text{O}_3\cdot4\text{Sm}_2\text{O}_3$ composition at 690°C . This data along with the known $\Delta V/V$ values of each material can be used to estimate the ϵ_{trans} for the $96\text{Bi}_2\text{O}_3\cdot4\text{Sm}_2\text{O}_3$ composition from the ϵ_{trans} known for Bi_2O_3 at a given stress. This may be done from the relationship:

$$\frac{\epsilon_{\text{trans, eut}}}{\epsilon_{\text{trans, pure}}} = \frac{(\Delta V/V)_{\text{eut}} / (\Delta V/V)_{\text{pure}}}{S_{\text{eut}}/S_{\text{pure}}}$$

where the subscript eut indicates the values of the variables pertaining $96\text{Bi}_2\text{O}_3\cdot4\text{Sm}_2\text{O}_3$ and pure indicates the values for Bi_2O_3 . The estimated value for $\epsilon_{\text{trans, eut}}$ is 0.4 at 500 psi which is quite satisfactory agreement with the experimentally determined value of 0.42.

Figures 2 and 3 present the results for the other compositions in-

investigated in this study. These compositions exhibit the same linear relationship between strain per cycle and applied stress up to a stress of approximately 800 PSI as observed for 96% Bi_2O_3 ·4% Sm_2O_3 composition. Slopes of the curves are approximately the same for the five compositions studied, as has been reported for metallic eutecoids. Figures 2 and 3 also show that the curves intersect the stress axis, which indicates a threshold stress must be reached before the transformation deformation process can be initiated.

To illustrate the effect of composition on the superplastic strain more clearly, an equivalent comparison is made in Figure 4. This graph is a plot of the transformation strain per cycle, at an average stress of 500 psi as a function of the amount of eutectoid microconstituent present. From the graph, it can be readily seen that the transformational strain per cycle at a given stress increases to a maximum as the composition approaches the eutectoid composition. Figure 4 also shows that the hypoeutectoids with a lower percentage of the eutectoid microconstituent exhibit smaller strains than the hypereutectoids. Extrapolation of the curves to 100 percent eutectoid predicts a maximum transformational strain per cycle at 500 psi for the Bi_2O_3 - Sm_2O_3 system to be about 0.53. Figure 5 is a plot of the transformational strain per cycle at 500 PSI as a function of the grain size of the proeutectoid phase. If the curve is extrapolated to zero grain size, no proeutectoid present, approximately the same value of strain, 0.53, is obtained as is found in Figure 4. This result further suggests that the maximum strain is to be expected when the material contains only the eutectoid structure.

The threshold stresses required before the materials in this study exhibit deformation can also be explained in terms of the proeutectoid

FIGURE #2 Transformational Strain per Cycle Versus Stress for $98\text{Bi}_2\text{O}_3 \cdot 2\text{Sm}_2\text{O}_3$, $97\text{Bi}_2\text{O}_3 \cdot 3\text{Sm}_2\text{O}_3$, and $96\text{Bi}_2\text{O}_3 \cdot 4\text{Sm}_2\text{O}_3$.

FIGURE #3 Transformational Strain per Cycle Versus Stress for $96\text{Bi}_2\text{O}_3 \cdot 4\text{Sm}_2\text{O}_3$, $94\text{Bi}_2\text{O}_3 \cdot 6\text{Sm}_2\text{O}_3$, and $92\text{Bi}_2\text{O}_3 \cdot 8\text{Sm}_2\text{O}_3$.

FIGURE #4 Transformational Strain per Cycle Versus Percent Eutectoid at $\sigma = 500 \text{ psi}$.

FIGURE #5. Transformational Strain Versus Grain Size of Proeutectoid Microconstituent.

microconstituent. There appears to be a direct relationship between the volume fraction of the proeutectoid microconstituent and the threshold stress. There may also be a direct relationship between the grain size of the proeutectoid microconstituent and the threshold value as shown in Figure 6. This relationship is not conclusive in this study since the volume fraction and grain size of the proeutectoid were not varied independently. The proeutectoid appears to act as a barrier to deformation by increasing the threshold stress.

The strain rate sensitivity index, m , has been applied to transformational superplasticity by a number of investigators. It is observed that m approaches one, characteristic of a viscous flow type of behavior. The results of this study are presented in Figure 7 and 8 as plots of log transformational strain rate vs. log average true stress. There exists a linear relationship between log stress and log strain rate. The data presented in Figure 7 for the $96\text{Bi}_2\text{O}_3 \cdot 4\text{Sm}_2\text{O}_3$ composition are typical of all the compositions investigated. The m values from the slope is found to be 0.92, in agreement with the metallic eutectoid investigations. Figure 8 presents the data obtained from the reported eutectoid composition and the $98\text{Bi}_2\text{O}_3 \cdot 2\text{Sm}_2\text{O}_3$ composition. These compositions represent the extremes in m values for the compositions measured in this study. The data and curves for all of the other compositions lie between these two. The m values which may be considered a measure of the tendency toward superplasticity, indicate that the amount of eutectoid structure present is the dominating factor. Figure 9 illustrates the correlation between the strain rate sensitivity and the amount of the eutectoid present. The two curves extrapolate to approximately the same m value at 100 percent eutectoid phase. A strain rate sensitivity index near one is

FIGURE #6 Threshold Stress Versus Grain Size of Proeutectoid Microconstituent.

FIGURE #7 Stress Versus Strain Rate for
 $96\text{Bi}_2\text{O}_3 \cdot 4\text{Sm}_2\text{O}_3$.

FIGURE #8 Stress Versus Strain Rate for $98\text{Bi}_2\text{O}_3 \cdot 2\text{Sm}_2\text{O}_3$ and $96\text{Bi}_2\text{O}_3 \cdot 4\text{Sm}_2\text{O}_3$.

estimated for the eutectoid composition. Therefore the m value for each composition maybe interpreted as consisting of some combination of a unity value for the eutectoid portion of the structure, that is diluted by the proeutectoid phase present.

Although there is some question as to the applicability of the term isothermal superplasticity to ceramic materials, the isothermal strain rate as a function of temperature was measured for the reported eutectoid composition in order to better characterize the superplastic effect as related to the eutectoid transformation. The term isothermal superplasticity has been used in metals to describe the condition where the strain rate sensitivity index is in the range of one-half to one, much higher than that commonly observed for conventional metals. In the case of crystalline ceramics a large percentage of reported strain rate sensitivity indices are greater than 0.5. The major difference between the two materials appears to be that the ceramics exhibit much less deformation when compared to metals.

In the absence of a clearly defined steady-state creep rate, which is difficult to identify in compression, the transient creep rate at a strain of 0.1 was chosen for the determination of the strain rate sensitivity index. The strain rate sensitivity index, m , can be derived by plotting log stress versus log strain rate and measuring the slope of the resulting curve. The m 's were determined for nine temperatures in the range between 630°C and 750°C, including the reported transition temperature of 690°C. Figure 10 illustrates m as a function of temperature, for the $96\text{Bi}_2\text{O}_3 \cdot 4\text{Sm}_2\text{O}_3$ composition. It can be seen that the strain rate sensitivity index is approximately 0.3 at both the low and high temperature but increases as the temperature approaches the eutectoid temperature. The observed maximum of approximately 0.6 at the transition temperature is below the

FIGURE #9 The Strain Rate Sensitivity Index Versus Percent Eutectoid Microconstituent.

0.92 estimated for the same material when cycled through the transition, suggesting that the actual phase transition is the primary contributor to the superplastic behavior of this material.

An important characteristic of transformational superplasticity in metals is that the specimens will exhibit the transitional strain repeatedly upon thermal cycling about the transformation, finally yielding an extensive cumulative strain. We reported earlier that Bi_2O_3 did not exhibit this behavior, and attributed the lack of repetitive deformation to extensive grain growth and microcracking after or during the initial thermal cycle.

Microstructural analysis of the Bi_2O_3 - Sm_2O_3 eutectoid materials revealed that these compositions experienced considerably less grain growth and microcracking than observed in pure Bi_2O_3 . Based on these observations, several samples of the $92\text{Bi}_2\text{O}_3 \cdot 8\text{Sm}_2\text{O}_3$ composition were thermally cycled under the initially applied stresses of 100, 200, and 400 psi. This composition was selected for the multiple thermal cycling study because it exhibited the greatest temperature difference between phase boundaries which would be expected to insure the greatest microstructural stability during the repetitive thermal cycling. The results of this study are illustrated in Figure 11, where the accumulated strain is plotted as a function of the number of cycles for each of the stresses. The linear relationship is similar to the multiple cycling behavior reported in metal systems; however, as previously noted, the major difference persists in that the oxide eutectoid exhibits much larger strains per cycle. The ability of the $\text{Bi}_2\text{O}_3 \cdot \text{Sm}_2\text{O}_3$ compositions to be multiply cycled as compared to pure Bi_2O_3 is attributable directly to the presence of the two phases lending stability to the microstructure. This stability considerably reduces grain growth and microcracking. This result indicates that oxides

FIGURE #10 Strain Rate Sensitivity Versus Temperature for $96\text{Bi}_2\text{O}_3 \cdot 4\text{Sm}_2\text{O}_3$.

FIGURE #11. Accumulated Strain Versus Number of Cycles - 92% Bi_2O_3 Composition.

exhibiting transformational superplasticity can be repetitively thermal cycled if their microstructure is sufficiently fine and thermally stable.

The Bi_2WO_6 Structures (Bi_2O_3 - WO_3 & Bi_2O_3 - MoO_3 Systems)

The majority of effort in these systems has been the synthesis of the compounds and their hot pressing to dense billets to obtain satisfactory samples for transformational superplasticity testing and for transitional growth studies. The crucial aspect of this processing is to react the separate powders, for example Bi_2O_3 and WO_3 , at a sufficiently low temperature to yield a very fine particle size powder that will readily hot press to near theoretical density. For example, if the separate powders are reacted at too high a temperature, grain growth occurs and the resulting hot pressed body only achieves about 85% density. For $\text{Bi}_2\text{O}_3 + \text{WO}_3 \rightarrow \text{Bi}_2\text{WO}_6$ the satisfactory schedule is three separate 24 hr. firings at 600°C reaction temperature and a final 400 mesh screening of the powder. The Bi_2WO_6 prepared in this manner, readily hot presses to density at 675°C for 30 minutes at 3000 psi. Billets of this material are currently being tested and also annealed to cause grain growth so that the effect of grain size on the superplastic transformational strain can be measured.

The isostructural compound Bi_2MoO_6 has also been synthesized and hot pressed. It only required a 500°C reaction temperature and can be hot pressed at 625°C . Preliminary runs indicate that it has two transitions, one at $\sim 675^\circ\text{C}$ and one at $\sim 900^\circ\text{C}$. Both appear to be superplastic.

The study of the peculiar transitional growth characteristics, first reported in C00-3420-3 last year have been observed; however, the exact details of the phenomenon have not as yet been disentangled.

Although it is clear that Bi_2WO_6 exhibits expansion on both heating and cooling through its transformation, the deformation caused by the quartz rod transducer coupling on the dilatometer causes problems. In order

to isolate all of the individual contributions to the measurements, it is necessary to get some optical and also x-ray thermal expansion data on Bi_2WO_6 . We are proceeding with the optical, while local crystallographers are independently measuring the x-ray thermal expansions. It is anticipated that this mystery can be solved and the phenomenon understood with the additional data.

Stoichiometry Effects on Fracture

The effects of stoichiometry on the elastic moduli and the fracture mechanics parameters of TiO_{2-x} and Fe_{1-x}O have been studied. Specimens were prepared by hot pressing powders and equilibration of encapsulated samples. For the TiO_{2-x} , hot pressed TiO_2 was treated in a CO/CO_2 mixture at literature ratios at 1150°C for 24 hours, then further heat treated in capsules for 4 days at 1200°C . Final densities exceeded 95% with grain size between $30\mu\text{m}$ and $50\mu\text{m}$. Test specimens were diamond ground. Final TiO_{2-x} stoichiometries were checked by back oxidation of specimens after testing. Oxygen values to 1.965 were obtained.

The wustite was consolidated from Fe powder and Fe_2O_3 at the appropriate stoichiometry, dry blended and hot pressed to 90-94% density. Rough cut specimens were encapsulated and homogenized for 24 hours. Since no back oxidation end member existed in a manner similar to that for rutile, the stoichiometry was checked by precision lattice parameter methods. Oxygen to iron ratios from 1.065 to 1.095 were readily obtainable. For both materials, other characterization methods, including density, x-ray, microstructure, and scanning electron microscopy of fracture surfaces are being employed.

Elastic constants of both materials at room temperature have been measured by the resonance bar method. The results are shown in Figure 12 and 13. Both materials exhibit near linear changes in elastic moduli.

Figure #12

ENGINEERING MODULI OF 90% DENSE
WUSTITE VS. STOICHIOMETRY

Figure #13

ENGINEERING MODULI VS.
STOICHIOMETRY OF RUTILE

Figure #14
SUBCRITICAL CRACK GROWTH IN $TiO_2 \cdot 0.00$ IN
DIFFERENT ENVIRONMENTS

Figure #15

SUBCRITICAL CRACK GROWTH IN RUTILE vs STOICHIOMETRY

G and E, with changing stoichiometry. Additional data are being taken on both of these systems as other specimens are being generated for fracture mechanics measurements.

Subcritical crack growth in TiO_{2-x} was observed experimentally by the double torsion technique. Figure 14 illustrates the effect of different environments, as plotted in terms of the K-V curves for TiO_2 . At room temperature, subcritical crack growth was fastest in water, then toluene, and slowest in dry argon. The data of the toluene tests are from four separate runs. Clearly, environment affects subcritical crack growth in rutile. Figure 15 illustrates the effect of stoichiometry on subcritical crack growth of TiO_{2-x} in dry argon. Clearly, the deviation from stoichiometry in these samples leads to increased subcritical crack growth velocities. All attempts to achieve subcritical crack growth in FeO_{1-x} failed. It is believed to be the result of plastic flow at the crack tip in this rock salt structure oxide.

The fracture toughness K_{Ic} of TiO_{2-x} was reported to decrease with non-stoichiometry in the last progress report COO-3420-3. This parameter is currently being measured in the Fe_{1-x}O .