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on

CERAMIC RESEARCH ON TRANSFORMATIONAL SUPERPLASTICITY AND
STOICHIOMETRY EFFECTS ON FRACTURE

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RESEARCH PROGRESS REPORT

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submitted by

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ABSTRACT

The progress of the program is reviewed by treating each of the areas separately. In the superplasticity investigation, the results of the Bi_2WO_6 and Bi_2MoO_3 systems are discussed both in terms of the transformational deformation and also the thermal cycling growth phenomenon. The "growth" phenomenon on thermal cycling through the phase transition shows some interesting bulk and microstructural features in terms of specimen strain and highly anisotropic grain growth. The stoichiometry effects on the fracture (K_{Ic} and K-V behavior) of TiO_{2-x} and Fe_{1-x} are reviewed as that study has been completed. Progress on the $\text{MgO} \cdot x \text{Al}_2\text{O}_3$ system is discussed.

RESEARCH OBJECTIVES

The research objectives of this program are to obtain a better fundamental understanding of the phenomenon of transformational superplasticity in otherwise "brittle" ceramics in the one portion of the study and to ascertain the effects of stoichiometry on the fracture process, both critical, K_{Ic} , and subcritical, $K-V$, in the other portion.

The transformation superplasticity studies originally began by searching for the phenomenon in a ceramic system. It was identified in Bi_2O_3 and studied there. Subsequently it was studied in the two phase $Bi_2O_3 - Sm_2O_3$ eutectoid system. Currently it is being studied in the Bi_2WO_6 and Bi_2MoO_6 compound. The preponderance of Bi_2O_3 based systems is because the monoclinic-cubic transition in pure Bi_2O_3 at $\approx 90\% T_{mp}$ extends to many binary eutectoids as well, and perhaps also is related to the general propensity of related compounds to exhibit phase transitions at high temperatures. Directly associated with the phase transitions is the "peculiar" transitional growth phenomenon where a ceramic material exhibits a non-recoverable dimensional change upon thermal cycling through a phase transition. It is also the objective of this research to understand this dimensional change or growth phenomenon and its relationship, if any, to transformational superplasticity.

Study of the effects of stoichiometry on the fracture process in TiO_{2-x} and $Fe_{1-x}O$ have been completed and are summarized in this report. Parallel effects on elastic moduli, thermal expansion, and thermal diffusivities were also observed. The effects appear to be directly related to the nature of the defects that occur when non-stoichiometry is present in a structure. Lack of subcritical crack growth in $Fe_{1-x}O$, coupled with calculations on the diffusional contribution to slow crack growth in TiO_{2-x} suggest potentially fruitful area of research is in a high temperature non-stoichiometric system where both crack tip plasticity and diffusion as affected by stoichiometry may be important. Just such a system is non-stoichiometric spinel, where studies are now in progress.

PUBLICATIONS SINCE LAST PROGRESS REPORT

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

Minnear, W. P. and Bradt, R. C., "(K-V) Diagrams for Ceramic Materials", J. Amer. Cer. Soc. 58, 7-8, 345-346 (1975).

Smyth, J. R., Bradt, R. C., and Hoke, J. H., "Transformational Superplasticity in the Bi_2O_3 - Sm_2O_3 Eutectoid System", J. Amer. Cer. Soc. 58, 9-10, 381-384 (1975).

Siebeneck, H. J., Minnear, W. P. Bradt, R. C., and Hasselman, D. P. H., "Stoichiometry Effects on the Thermal Diffusivity of Rutile", J. Amer. Cer. Soc. 59, 1-2, 84 (1976).

Reprints of these three articles as well as the article on pure Bi_2O_3 are attached to the end of this progress report. Additional manuscripts are in progress.

TRANSFORMATION SUPERPLASTICITY AND TRANSITIONAL GROWTH

In the previous progress report, COO-3420-4, the original difficulties associated with obtaining good specimens of Bi_2WO_6 and Bi_2MoO_6 were discussed along with the solutions. Measurements in these two systems are currently underway. Figures 1 and 2 illustrate the linear dependence of transformational strain on the applied stress for these two materials in the as-hot pressed condition. Both of these materials exhibit transformational superplasticity! A obvious difference between the two is that this Bi_2WO_6 exhibits a much greater transitional strain per cycle/100 psi, an often applied parameter of comparison. The reasons for this are not fully understood at the present. Additional measurements are in progress on annealed specimens to enable a comparison of the effects of grain size in these two materials.

Figure 3 is a plot for the Bi_2MoO_6 of the maximum strain rate during the phase transition vs. the applied stress. From the equation:

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

plotted log log paper, the slope is the strain rate exponent. Values of m greater than $1/2$ are indicative of superplasticity, and a value of 1 is analogous to viscous flow. The Bi_2MoO_6 data in Figure 3 has a slope of 0.90, clearly in the superplastic range.

In addition to the transformational superplasticity, the transitional growth phenomenon has been studied in Bi_2WO_6 . Observations on both Bi_2O_3 and also on Bi_2MoO_6 have lead to specimen degradation via cracking on multiple thermal cycling. The Bi_2WO_6 does not appear to deteriorate, but rather continues to grow perpendicular to the transition front with increased transformation cycling. Figure 4 illustrates the dilatometer traces

Figure 1. Transformational strain vs. stress for Bi_2WO_6 in the condition as - hot pressed.

TRANSFORMATIONAL STRAIN PER CYCLE

0.70

0.60

0.50

0.40

0.30

0.20

0.10

0

200

400

600

800

1000

STRAIN, PSI

Figure 2. Transformational strain vs. stress for Bi_2MoO_6 in the as-hot pressed condition.

Figure 3. Stress vs. maximum strain rate during transformational deformation of Bi_2MoO_6 .

for a Bi_2WO_6 specimen cycled through the phase transition ten times. It is apparent that after the first cycle, which is a mixture of deformation, expansion, and volume change, the Bi_2WO_6 does not appear to recover the volume change of the phase transition. It does not appear that the material retransforms to the low temperature phase, at least not from the dilatometer traces; however, x-ray diffraction confirms the retransformation. Figure 5 shows the cumulative strain to be linear. Micrometer measurements afterwards, confirm the dilatometer dimensional changes. Microstructurally, these specimens, bars approximately 2 inches long, consist of large elongated grains that extend over the complete length of the specimen. It appears that a preferred crystallographic texture develops. X-ray and microscopic studies are in progress.

STOICHIOMETRY EFFECTS ON FRACTURE

Results of the study of the stoichiometry effects on fracture during the previous year can be divided into those on TiO_{2-x} and Fe_{1-x}O , which have been completed in the Ph.D. thesis of W. P. Minnear, currently at G. E. Research Lab., Schenectady, N.Y., and, the material preparation of the non-stoichiometric spinel, $\text{MgO} \cdot x \text{Al}_2\text{O}_3$. The spinel work just began during this past year, so it is still in the specimen preparation stage.

In the course of the measurement of fracture related parameters of TiO_{2-x} and Fe_{1-x}O , it was necessary to measure the elastic moduli of the specimens. In the Wustite, the defects are three dimensional clusters the structure of which resemble the magnetite structure. In the Fe_{1-x}O , the elastic modulus change with defect concentration was relatively mild, and could be approximated by a Voight-Reuss type of average between the end members, Wustite and magnetite. The effect of stoichiometry on the elastic moduli of rutile, TiO_{2-x} , was drastic. It resulted from the

Figure 4. Transitional growth of Bi_2WO_6 through ten cycles.

Figure 5. Transitional Growth of Bi_2WO_6
cumulative strain vs. cycles.

particular structure of the defects, planar defects on {132} planes. A model treating these planar defects in rutile as internal microcracks was applied to explain the decrease. Figure 6 illustrates the agreement between the model prediction and the regression line of the data.

In addition to the elastic modulus of the rutile, there were also measurements made of thermal expansion anisotropy and thermal diffusivity as a function of stoichiometry. The thermal diffusivity measurements were made in conjunction with Hasselman at Lehigh and are described in the attached note on that topic. The thermal expansion measurements, done by high temperature x-ray diffraction will be published and illustrate that the thermal expansion anisotropy decreases as the material becomes less stoichiometric. Both α_a and α_c decrease, as does β_r . In addition, there is a large decrease in α perpendicular to the {132}, suggesting that some of the expansion is taken up as the closing of the planar defects.

The K_{Ic} results for Wustite, $Fe_{1-x}O$, did not reveal any significant change over the O/Fe ratios investigated, approximately 1.066 to 1.096. As for (K,V) results, it was not possible to obtain slow crack growth in the Wustite, perhaps as a result of crack tip plasticity. Microhardness results showed the non-stoichiometric material to be harder as the degree of non-stoichiometry increased.

The effects of stoichiometry on the fracture of TiO_{2-x} are illustrated in Figure 7 for both K_{Ic} and the subcritical crack growth, (K,V) behavior. Several features are evident; first the reduction causes a decrease in K_{Ic} , one that appears to increase with increased reduction. It is believed that this is directly related to the crack-like planar nature of the defects. The (K,V) behavior is definitely one of shifting the lines to lower stress intensities with increased reduction. There also appears

Figure 6. Variation of Elastic Moduli with Stoichiometry for rutile.

to be a "slight" slope decrease, although there is some scatter of data particularly between $\text{TiO}_{1.987}$ and $\text{TiO}_{1.995}$.

Estimates of the contributions of various diffusional processes to slow crack growth in the non-stoichiometric rutile were made based on the model of Dutton, et.al. (Fract. Mech. Cer., Vol. II. p. 647), Plenum, 1974). Liberal estimates of diffusivities were utilized, yet the largest contribution, that of surface diffusion, could account for crack velocities of only 10^{-9} m/sec, whereas values of 10^{-5} m/sec and larger are observed. It is concluded that in rutile at room temperature, the diffusion contribution to slow crack growth is relatively insignificant.

The synthesis of non-stoichiometric spinel has several interesting features as these processing aspects are prone to exhibit. Initial reaction tests between high purity alpha Al_2O_3 (Meller) and a high purity MgO (DOW) yielded little evidence of completion of the reaction, as multiple firings as high as 1600°C failed to complete the reaction. It was apparent that a different approach was in order. A brief note in an older text (Rhyskewitch, Oxide Ceramics) stated that spinel could be readily formed at 1000°C by utilizing fine MgO and a gamma Al_2O_3 . The explanation was vague, only stating that at 1000°C the gamma Al_2O_3 transformed to the alpha form was highly reactive. Sure enough, a sample batch fired for only 1 hour at 1000°C yielded nearly complete conversion to spinel.

Seven stoichiometrics between 1:1 and 1:3, MgO: Al_2O_3 were prepared by first ball milling the MgO (DOW) and a gamma Al_2O_3 (Meller) using a distilled water vehicle and "pure" alumina balls for 1 hour. The slurry was then dried in an oven for two days and the resultant cake fired in air for 2 hours at 1000°C . This ball mill mixing technique and particular firing schedule were adequate up through the 1MgO:1.5 Al_2O_3 compositions, but the 1:1.75 batch had a significant amount of residual MgO with the

Figure 7. The fracture toughness and K-V variation of rutile with stoichiometry.

same treatment. This material was therefore re-mixed and fired for an additional hour at 1000°C with satisfactory conversion to the spinel solid solution + corundum. The reaction schedule for the remainder of the compositions, (1:2, 1:2.5, 1:3) were altered to $2\frac{1}{2}$ to 3 hours at 1000°C . Thus far, through the 1:2.5 batches good reactions have been obtained. The final batch of $1\text{MgO}:3\text{Al}_2\text{O}_3$ is currently being reacted.

The powders consolidated by this reaction procedure are currently being hot pressed into $6'' \times 6'' \times \frac{1}{2}''$ plates by the Carborundum Company, Niagara Falls, N.Y. These will then be diamond sawed to appropriate sizes and heat treated to yield a variety of grain sizes. It is expected that actual fracture measurements will commence with the next month.

PERSONNEL

The graduate students doing the research reported in this progress report are Mr. Larry Winger, who is in his second year of graduate study on the superplasticity and transitional growth phenomena, and Mr. Ronald Stewart who just returned to graduate school in September, after 4 years in industry. Mr. Stewart is working on the spinel. W. P. Minnear, who completed his doctoral program in August on the rutile and Wustite is currently employed by the General Electric Laboratory in Schenectady, New York.