COO-3420-6

THE PENNSYLVANIA STATE UNIVERSITY
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A Research Progress Report to
The United States

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ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
ON
CERAMIC RESEARCH ON TRANSFORMATIONAL SUPERPLASTICITY AND
STOICHIOMETRY EFFECTS ON FRACTURE

presently

CONTRACT NUMBER EY-76-S-02-3420

REPORT NUMBER COO-3420-6

June 1, 1976 through May 31, 1977

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March 1, 1977

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RESEARCH PROGRESS REPORT

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to the

United States

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

for the period

June 1, 1976 through May 31, 1977

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ABSTRACT

Progress is reviewed by treating the phase transformational superplasticity and transitional growth study and the stoichiometry effects on fracture study separately. Differences and similarities of Bi_2WO_6 and Bi_2MoO_3 are pointed out, and analogies with previous studies emphasized. Problems with specimen preparation of non-stoichiometric spinels $\text{MgO} \cdot x \text{Al}_2\text{O}_3$ are discussed.

TRANSFORMATIONAL SUPERPLASTICITY AND TRANSITIONAL GROWTH

It was previously noted that the compounds Bi_2WO_6 and Bi_2MoO_3 both exhibited transformational superplasticity, the Bi_2WO_6 at a phase transition near 900°C and the Bi_2MoO_3 at transition near 685°C . Both of these materials have been found to deform in the manner prescribed by the Greenwood and Johnson derivation:

$$\epsilon_{\text{trans.}} = \frac{A \sigma_{\text{app}} (\Delta v/v)}{S} \quad (1)$$

The observed transformational strain (ϵ_t) is linearly related to the applied stress (σ_{app}), one of the criteria for transformational superplastic behavior. Similarly, when examining the strain rate exponent (m) from:

$$\sigma = K \dot{\epsilon}^m \quad (2)$$

both materials were found to yield m values near unity, about 0.85 for the Bi_2WO_6 and nearly 0.90 for the Bi_2MoO_3 . Thus both of these compounds and their transitions are prime candidates for study of ceramic superplasticity associated with phase transitions.

Several things, however, have become evident from study of these compounds. First, the Bi_2WO_6 is considerably more superplastic than the Bi_2MoO_3 . For example, to achieve a true strain of approximately 0.4 in compression at comparable grain sizes only requires a stress of 30 psi for the Bi_2WO_6 , but nearly 1000 psi for the Bi_2MoO_6 . Several points could account for this, but the lower fraction of T_{mp} for the Bi_2MoO_3 transition is the most logical. In that manner, the strength

parameter, (S), of the Greenwood and Johnson equation (1) is much higher for the Bi_2MoO_3 , yielding a lower ϵ_{trans} . However, there is at least one other difference which is probably equally important, namely the transitions are different, the Bi_2WO_6 changing from an orthorhombic to what appears to be a non-indexable (yet) non-cubic structure at high temperatures, and the Bi_2MoO_6 from one orthorhombic structure to another. Thus the transitions in the two compounds are not equivalent. The consequence of this is that these two compounds do not provide the form of systematic variation in crystal chemistry that was hoped for. Fortunately, there have been other recent studies on the rare earth WO_3 's and MoO_3 's that indicate a number of those systems do possess phase transitions analogous to the Bi_2WO_6 and Bi_2MoO_3 systems. In the renewal proposal it is suggested to study some of those transitions.

Specifically, with regard to the superplasticity, the effect of grain size has been extensively investigated in Bi_2WO_6 . This was accomplished by annealing hot pressed specimens below the transition temperature, then subjecting them to transformation while under stress. Figure 1 illustrates the 3 μm and the 14 μm average grain size data, while Figure 2 illustrates the effect of grain size on transformational strain. Several points are obvious. Large grain sizes yield less transformational strain and grain sizes above about 30 μm yield no superplastic strain! Also apparent is that the strain axis intercept appears to decrease with increasing grain size. That is the zero stress, transitional strain decreases when the grain size is larger. This is in agreement with the general effect of grain size on superplastic strain. These grain size effects exactly parallel those of Johnson for Bi_2O_3 in that the strain per cycle or transformational superplasticity disappears at larger grain sizes, greater than about 25 μm . Obviously the

Figure 1. Effect of stress and grain size on transformational strain.

Figure 2. Effect of average grain size on transformational strain.

mechanism responsible for the extensive flow is inoperative at large grain sizes! Since dislocation creep processes are grain size independent and diffusional processes are far too slow, this again strongly supports a grain boundary sliding mechanism!

The transitional growth phenomenon, discussed in COO-3420-5, last year's progress report, for Bi_2WO_6 has been investigated in Bi_2MoO_6 and also searched for in Bi_2O_3 . Both of these latter two exhibit similar growth to Bi_2WO_6 on the initial cycle, but fail to continue the phenomenon on subsequent cycles. Figures 3 and 4 illustrate the Bi_2MoO_6 and Bi_2O_3 for the first several cycles. The Bi_2MoO_6 which stays in a metastable crystalline form really doesn't do much of anything, except expanding and contracting after the initial transition. The Bi_2O_3 just exhibits the expected transformation hysteresis of the monoclinic to cubic transition, return to nearly its original dimensions. It should be recalled that the Bi_2WO_6 continued to grow parallel to the thermal gradient causing the transition. Obviously, all three of these exhibit different behavior, dependent on the phase transitions and the crystallography thereof!

Since Bi_2WO_6 exhibited the very interesting transitional growth phenomenon, whereas the others really don't, the aspects of that transformation must play a major role. One of the factors is that the Bi_2WO_6 transforms to large grains the entire length of the specimen. Several of the large grains have been extracted and mounted for Buerger precession X-ray analysis. It appears that the orthorhombic growth direction is the $[110]$. The long grains are so oriented in the low temperature phase. It appears probable that the nature of the transitional growth phenomenon is related to the thermal expansion anisotropies in the two phases and the crystallographic correspondence of the two phases during the transformation. Since neither the axial thermal ex-

44×10^4 inches

Figure 3. Transitional behavior of Bi_2MoO_6
through 3 cycles

Figure 4. Transitional behavior of Bi_2O_3 through 2 cycles.

pansion coefficients, nor the transformation crystallography is known, they will have to be determined.

STOICHIOMETRY EFFECTS ON FRACTURE IN $\text{MgO} \cdot X \text{Al}_2\text{O}_3$

In the initial portion of this study, stoichiometries of 1:1, 1:1.25, 1:1.5, 1:1.75, 1:2.00, 1:2.50, and 1:3.0 were prepared by reacting high purity MgO (DOW) and gamma - Al_2O_3 at 1000°C . The 1000°C and gamma - Al_2O_3 being chosen because of the higher reactivity of alpha freshly converted from the gamma. As pointed out by Bratton (J. Amer. Cer. Soc. 57, (7), 1974) for the 1:1 spinel, 1% of CaO was added as a sintering aid prior to hot pressing. Large 6" x 6" x 1/2" billets of these stoichiometries were hot pressed at Carborundum, Niagara Falls, N.Y. Hot pressing was at 1550°C on the graphite die wall at a pressure of 3000 psi. Times at temperature varied for the stoichiometries, but generally were about 1/2 - 1 hour until ram motion ceased. All stoichiometries have achieved theoretical density.

These billets have been diamond sawed to yield 30 double torsion specimens at each stoichiometry. The scrap material is being utilized to establish the appropriate annealing heat treatments to achieve the spectrum of grain sizes for a matrix of grain size vs. stoichiometry. Several unanticipated problems have arisen during the annealing and examination of these different stoichiometries. These difficulties are currently being worked out prior to annealing the actual specimens. The problems are, not necessarily in order of importance: (i) a bloating and cracking of specimens if heat up is too rapid, (ii) a variation of grain size increasing with increased deviation from stoichiometry, and (iii) the appearance of several $\text{CaO} \cdot 6 \text{Al}_2\text{O}_3$ X-ray

diffraction peaks in the high Al_2O_3 compositions. Each of these will be discussed in detail with the current solutions(?).

The phenomenon of bloating and cracking of hot pressed specimens, if heated too rapidly has been previously observed for MgO and BaTiO_3 . The solution applied here is exactly analogous. The specimens are heated up very slowly at 25°C per hour to 1000°C and annealed at 1000°C for 48 hours to oxidize and allow diffusion to the surface of any entrapped gas species. This process quite satisfactorily converts the light gray as-hot-pressed specimens to an off-white translucent body, particularly the near 1:1 compositions. Higher Al_2O_3 contents did not clear up, prompting closer examination.

Two factors became evident when examining the higher Al_2O_3 , less stoichiometric samples. First, there is a discontinuous grain growth problem. As the Al_2O_3 content increases, there is a general tendency for grain growth, and a generally greater tendency for discontinuous grain growth. Thus with increasing non-stoichiometry, the microstructures are "less-desirable". Daw and Nicholson (J. Amer. Cer. Soc. 58, 3-4, 1975) attribute this to a primary recrystallization phenomenon, although there is some controversy as to that point. The other point is that the Al_2O_3 - rich samples revealed a small amount of second phase, believed to be $\text{CaO} \cdot 6 \text{Al}_2\text{O}_3$. Kevex energy dispersive examination by SEM suggests that the CaO is located primarily at the grain boundaries, although no obvious second phase is visible. Specimens are being polished and etched to reveal the location and amount of $\text{CaO} \cdot 6 \text{Al}_2\text{O}_3$. At the present, no successful etch has been located; however, attempts are continuing. In addition, another set of non-stoichiometric compositions, free of CaO , has been prepared and are currently being hot-pressed.

With regard to the formation of $\text{CaO} \cdot 6 \text{Al}_2\text{O}_3$, it appears that near

or at the 1:1 composition, the CaO readily substitutes for the MgO in the spinel structure. However, at increasingly non-stoichiometric compositions the $\text{CaO} \cdot 6 \text{Al}_2\text{O}_3$ phase readily forms. This problem could not be anticipated as previous results did not even hint at its existence and phase equilibria data were of no help.

As for actual fracture measurements, the 1:1 spinel, with CaO addition is currently being annealed to yield a spectrum of grain sizes. Both (K_I, V) and K_{Ic} measurements will commence on this material in the very near future.

PERSONNEL

The two graduate students on the project are Mr. Larry Winger and Mr. Ronald Stewart. Mr. Winger is just finishing his M.S. thesis on the superplasticity/growth portion, so a new student will be obtained on that portion. Mr. Stewart has just passed his candidacy exams and is working on the spinel fracture work for his thesis.

PAPERS SINCE LAST PROGRESS REPORT

No additional papers have been published since the last progress report. Manuscripts are in progress on "Transformation Superplasticity in Bi_2WO_6 and Bi_2MoO_3 " (also being presented at this year's 1977, American Ceramic Society Meeting in Chicago), "Stoichiometry Effects on Elastic Properties of TiO_{2-x} ", "Anisotropic Thermal Expansion of TiO_{2-x} ", and "Stoichiometry Effect on Fracture of TiO_{2-x} and Fe_{1-x}O ".