Elastic properties of partially-stabilized HfO$_2$ compositions

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The effect of metastable tetragonal HfO$_2$ on the elastic properties of partially stabilized HfO$_2$ doped with Er$_2$O$_3$, Y$_2$O$_3$ or Eu$_2$O$_3$ was studied using a sonic resonance technique. The elastic moduli were monitored at elevated temperatures to follow the effect of the tetragonal–monoclinic phase transformation.
Elastic moduli were also determined as a function of porosity and found to follow linear relations. The non-linear modulus versus temperature relations from room temperature to 500° C are explained in terms of the oxygen vacancies present in the fluorite type phase.

1. Introduction

The objective of this study was to investigate the elastic properties of partially-stabilized HfO$_2$ using Er$_2$O$_3$, Y$_2$O$_3$, and Eu$_2$O$_3$ as the stabilizing oxides. Room temperature as well as elevated temperature elasticity data were measured to determine the effects of phase growth and transformation on Young's modulus.

HfO$_2$ exhibits phase behaviour which is very similar to ZrO$_2$. Both show a low temperature structure which is monoclinic and a higher temperature structure which is tetragonal [1]. This transformation is a reversible destructive one involving a change in volume of about 3% with the tetragonal phase being more dense. The prospect of utilizing this phase change to improve material properties in ZrO$_2$ has received much attention [2–4]. The incorporation of a metastable ZrO$_2$ tetragonal phase has been accomplished, and the results indicate that the incorporation of a metastable tetragonal phase helps to arrest crack growth adding material toughness. Maintaining this metastable tetragonal phase has been shown to be dependent on a critical maximum particle size ranging from 0.3 μm to 1 μm [5] for ZrO$_2$.

Previous studies have been conducted on the elastic properties of pure monoclinic HfO$_2$ [6] and fully stabilized HfO$_2$ compositions [7]. Dole and Hunter [6] investigated microcracking in monoclinic HfO$_2$ and found that due to the anisotropy in the thermal expansion of the monoclinic phase, microcracking occurred and had a degrading effect on the elastic behaviour of HfO$_2$ when the grain size exceeded a critical size of 2 to 3 μm. Both Young's and shear modulus were found to follow Spriggs relation of exponential dependence on porosity. However, in fully stabilized HfO$_2$ compositions, no microcracking was found and Young's and shear moduli showed a linear dependence upon porosity.

2. Experimental procedure

The HfO$_2$ used in the study was obtained from Teledyne Wah Chang Albany. The HfO$_2$ was converted to HfOCl$_2$, put into solution and purified by ion exchange. The Er$_2$O$_3$, Eu$_2$O$_3$, and Y$_2$O$_3$ were all obtained from the Ames laboratory Rare Earth Separation Group and were dissolved in dilute nitric acid.

The exact compositions to be used were determined by microprobe analysis of the two phases present in the temperature region of interest. The partially-stabilized HfO$_2$ compositions, 4.4 mol% Er$_2$O$_3$ doped HfO$_2$, 4.1 mol% Eu$_2$O$_3$ doped HfO$_2$ and 7.6 mol% Y$_2$O$_3$ doped HfO$_2$ were all prepared by co-precipitation techniques. The acid solutions of Er(NO$_3$)$_3$, Eu(NO$_3$)$_3$ or Y(NO$_3$)$_3$ were mixed with Hf(NO$_3$)$_4$ to give the proper

concentration, and the hydroxide precipitated out with dilute ammonium hydroxide. The hydroxide precipitate was washed with water initially and this was followed by a series of acetone and toluene washes to give an active fast drying powder [8]. The hydroxide powder was ground to ~325 mesh and calcined at 960° C for 3 h to yield the oxide. Rectangular shaped specimens were formed by dry pressing followed by isostatic pressing. The specimens were fired in air between 1900° C and 2000° C for 1 h in a gas-fired ZrO_2 muffle tube furnace*. At these temperatures the specimens were in a single phase fluorite region of the phase diagram. They quenched to room temperature to retain as large a fraction of this high temperature fluorite phase as possible.

Following firing, the bars were machined flat with parallel surfaces, and bulk densities were determined from the mass and surface dimensions. X-ray diffraction measurements showed some variation in the phase composition within this region. The primary phase was fluorite with varying amounts of the monoclinic and/or tetragonal phases present.

The elastic moduli were measured using a sonic resonance technique. Both Young's and shear moduli were measured when the specimen geometry permitted, but where the torsional frequency could not be measured the Young's modulus was determined assuming a Poisson ratio of 0.25. Room temperature measurements were made using cotton strings. Elevated temperature measurements were made using graphite strings to suspend the specimen in a manually controlled vacuum carbon rod resistance furnance. Thermal expansion measurements were made in air using a standard dilatometer and LVDT detector system.

3. Results and discussion

Young's (E) and shear (G) moduli at room temperature are plotted as functions of volume fraction porosity (P) in Fig. 1. A least-squares fit of the data using a linear relation was made.

$$E = 253.3 [1-2.6P] \ (GN\,m^{-2})$$

and

$$G = 101.9 [1-2.6P] \ (GN\,m^2)$$

The extrapolated zero porosity values of the moduli are $E_0 = 36.7 \times 10^6$ p.s.i. ($253.3\,GN\,m^{-2}$) and $G_0 = 14.77 \times 10^6$ p.s.i. ($101.9\,GN\,m^{-2}$).

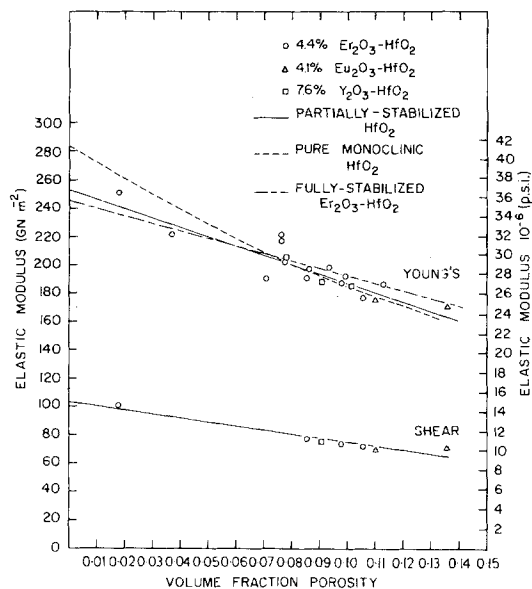* Lemont Scientific, Lemont, PA, USA.

Figure 1 Young's and shear moduli as a function of volume fraction porosity.

Using these values, Poisson's ratio was calculated to be 0.243. The scatter in the room temperature modulus values was found to be a characteristic of the two-phase partially stablized region where the amount of phases present varies from nearly pure fluorite to a mixture of fluorite and monoclinic. Fig. 1 shows that all three stabilizers (Er_2O_3, Eu_2O_3, Y_2O_3) show the same linear dependence on porosity.

A comparison of the room temperature modulus values can be made with that found in pure HfO_2 [6], and in fully stabilized HfO_2 [7]. These lines are also shown in Fig. 1.

For pure monoclinic HfO_2

$$E = 283.6 \exp [-4.17P] \ (GN\,m^{-2})$$

For 80% HfO_2–20% Er_2O_3

$$E = 245.9 [1-2.17P] \ (GN\,m^{-2})$$

The value found for HfO_2 was measured on monoclinic HfO_2 and was found to obey Sprigg's exponential relation, whereas, HfO_2 stabilized in the fluorite phase obeys a linear relation. The value at zero porosity fell between the pure monoclinic HfO_2 and the fully stabilized HfO_2 values, but the porosity dependence was linear as in the fully stabilized HfO_2.

Thermal expansion was measured on a 4.4% Er_2O_3–HfO_2 specimen from room temperature to

1200° C. The average linear thermal expansion coefficient over this temperature range was $8.5 \times 10^{-6} \, °C^{-1}$, which falls between that found in pure HfO_2 $(6.3 \times 10^{-6} \, °C^{-1})$ and that found in 20 mol % Er_2O_3–HfO_2 $(9.8 \times 10^{-6} \, °C^{-1})$.

Fig. 2 shows representative profiles of the temperature dependence of Young's modulus for Y_2O_3–, Eu_2O_3–, and Er_2O_3–HfO_2 compositions. The temperature dependence of the heating curve of the partially-stabilized HfO_2 was found to follow the general shape of that found in fully-stabilized HfO_2. They all exhibit an initial sharp decrease followed by a relatively temperature insensitive region, and at high temperatures the modulus decreases again, which corresponds to the onset of grain boundary sliding. For Y_2O_3–HfO_2, the initial change in slope occurs around 500° C, in Eu_2O_3–HfO_2 the change occurs around 800° C, and in Er_2O_3–HfO_2 the change occurs around 1000° C.

In this partially-stabilized HfO_2 system where two and three phases, cubic fluorite, monoclinic, and/or tetragonal, exist simultaneously, the change in slope of the modulus temperature plot might be attributed to a variety of phase changes. This was apparently not the case in the heating portion of the curve which showed the same initial rapid decrease in modulus under a variety of conditions. The break in the slope did occur at different temperatures and varied with the amount and type of stabilizer present in HfO_2. Wachtman and Lam [10] have found this same non-linear modulus response to temperature in partially-stabilized ZrO_2. In a further investigation of this system, Wachtman and Corwin [11] measured the internal friction and found a peak in damping around 300° C. Based on these measurements, they concluded that this behaviour was due to the effects of the oxygen vacancies introduced into the structure with the addition of a stabilizer. In
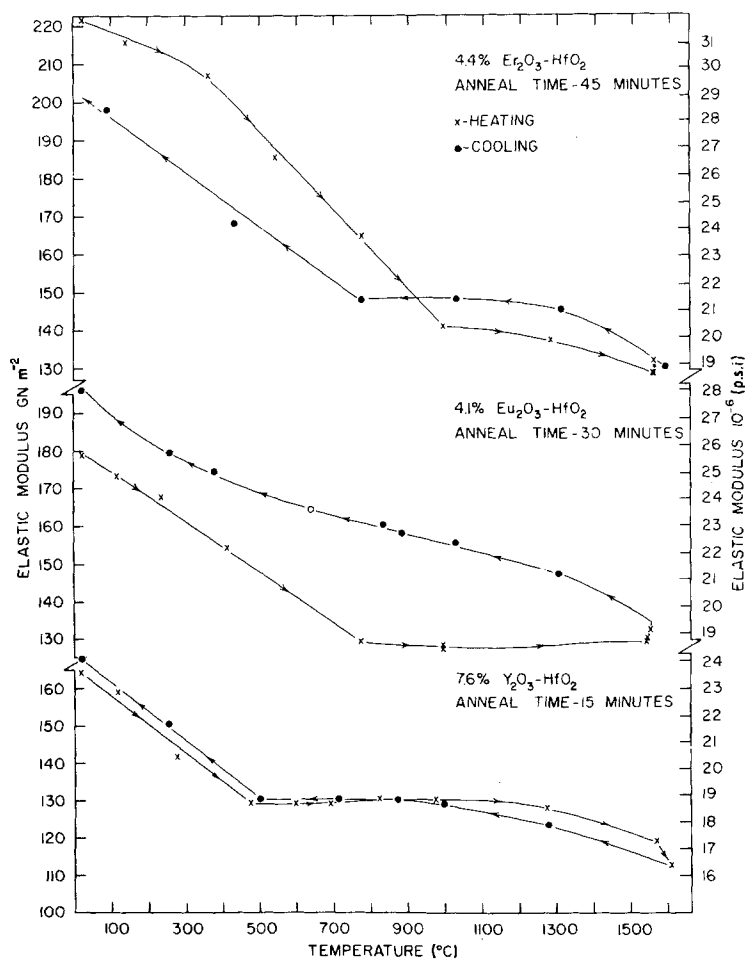

Figure 2 Young's modulus as a function of temperature.

particular, the peak in internal friction values was the result of a relaxation process of the oxygen vacancies in the fluorite lattice. This same behaviour was also found in the ThO_2—CaO system [12], where the movement of the anion vacancies present is affected by temperature and applied stress yielding the non-linear response of modulus to temperature.

Dole *et al.* [7] observed the same temperature phenomenon in fully stabilized HfO_2 and have proposed a similar relaxation concept and association—dissociation relation of the anion vacancies as the mechanism affecting the normal linear modulus behaviour. This study of partially-stabilized HfO_2 compositions shows the same interactions taking place by the non-linear response of the modulus upon heating. This would be expected although not to the degree found in fully-stabilized HfO_2 where the defect concentration would be considerably higher.

The anneal temperature was chosen to fall within the two phase region — fluorite and tetragonal. The growth and amount of the more dense tetragonal phase could be controlled by the anneal time and could be monitored by an increase in modulus during this time. The growth of the tetragonal phase and the resultant increase in modulus is noted in both the 30 min and 45 min anneal times. The amount and size of tetragonal particles at this point influences both the modulus behaviour on cooling and the final room temperature modulus value.

The cooling curve varies considerably depending on the heat treatment given between 1500 and 1600° C. Each of the three curves shown represents a different annealing time and quite striking differences occur on cooling. In Fig. 2, where there was a 15 min anneal at 1600° C, the cooling curve follows the heating curve fairly closely back to room temperature with only a small improvement in the room temperature value. A 30 min anneal as shown in Fig. 2 results in the cooling curve being significantly above the heating curve with a higher room temperature modulus and Fig. 2 also shows the curve that results from a 45 min anneal at 1550° C to 1600° C. With the longer anneal time of 45 min, a cross-over occurs in the modulus values upon cooling in the temperature region between 900 and 1000° C.

The phase diagrams of the Er_2O_3—HfO_2 [9] and Y_2O_3—HfO_2 [9] systems show that the composition used will produce a tetragonal phase

around 1600° C. The monoclinic—tetragonal phase changes could be monitored by measuring the Young's modulus while annealing around 1600° C for various time intervals. Fig. 2 reflects this phase growth associated with the monoclinic $\rightleftarrows$ tetragonal transformation. The growth of the more dense tetragonal phase at 1550 to 1600° C is reflected by an increase in the overall modulus during the anneal, and in addition structural changes and the transformation back to mono-clinic are also shown.

Both the 15 min anneal and the 30 min anneal gave successively greater improvement in Young's modulus at room temperature. However, this was not the case after a 45 min anneal where the room temperature value on cooling was lower than the starting value. As shown in partially-stabilized ZrO_2, a critical particle size exists which is necessary for metastable tetragonal phase to be present at room temperature. As the anneal time was increased from 30 to 45 min, the tetragonal phase transformed to the stable monoclinic phase on cooling and X-ray analysis confirmed the loss of the tetragonal phase. The volume change associated with this transformation would cause localized cracking from microcracking. This is shown in the cross-over occurring in 45 min anneal with the resulting decrease in modulus with cooling, instead of the normal increase.

Acknowledgement

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