ELASTIC PROPERTIES OF MONOCLINIC HAFNIUM OXIDE

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Elastic properties of monoclinic hafnium oxide

by

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ABSTRACT

The elastic properties of monoclinic hafnium oxide were studied as functions of porosity, temperature and grain size. An important finding of this study was that hafnium oxide is subject to microcracking when the grain size exceeds a critical value between 2 and 3 μm .

The behavior of the elastic moduli with porosity and temperature for crack-free hafnium oxide was typical for polycrystalline ceramics. The nature of the thermal expansion and the internal friction supported this finding. The elastic properties for the microcracked material exhibited trends similar to those observed for other microcracked materials. However, some new characteristics of the microcracking effects were observed in this study. An increase in internal friction was associated with the microcrack healing process. It was also found that there is an atmospheric effect that enhances microcrack growth. Additionally, thermal treatments of microcracked hafnium oxide were found to result in significant changes in the microcrack system.

INTRODUCTION

Although hafnium oxide (HfO_2) is one of the most stable refractory compounds known there has been very little study devoted to the engineering properties of this material. It was the purpose of this investigation to measure some of these properties in order to evaluate the usefulness of hafnium oxide in possible ceramic applications. Presently, its use is limited as a result of its scarcity and cost. However, there is a great potential for this material in high temperature ceramic applications and as such it warrants consideration and study.

LITERATURE SURVEY

Applications of Hafnium Oxide

The interest in hafnium and its compounds has lain primarily in the field of nuclear energy where hafnium is attractive as a control rod material for water-cooled reactors because of its high neutron absorption capacity (1). However, hafnium oxide also has excellent potential as a super-refractory material because of an extremely high melting point and high temperature stability. This potential can also be judged by the fact that hafnium oxide is remarkably similar in nature to zirconium oxide, a material which has found widespread use as a refractory material. The refractory characteristic of hafnium oxide makes it an excellent candidate in such areas as high-temperature oxidation resistant coatings (1) and MHD power generation (2) as well as in general refractory applications.

Properties of Hafnium Oxide

Hafnium oxide possesses a monoclinic crystal structure at room temperature. Lattice parameters were accurately determined by Adams and Rodgers (3) and are shown in Table 1. This structure is remarkably similar to that of monoclinic zirconium oxide (4) and both exhibit reversible monoclinic-tetragonal phase transformations (1).

On the basis of these and other properties, numerous

Table 1. Some physical properties of HfO_2 (1)

Property	Data
Melting point	2900°C
Vapor pressure	3×10^{-5} atm at 2667°C
Lattice parameters of the monoclinic structure	$a = 5.1156 \text{ \AA}$ $b = 5.1722 \text{ \AA}$ $c = 5.2948 \text{ \AA}$ $\beta = 99^\circ 11'$
Density (monoclinic)	10.1129 gm/cm ³
Transformation temperature:	
Monoclinic-tetragonal	1620-1650°C
(Various results reported by several investigators)	1725-1775°C
	1650-1750°C
	1500-1600°C

similarities can be drawn between hafnium and zirconium oxides. However, it is important to note some key differences. The monoclinic-tetragonal transformation for either material is diffusionless (5), that is, the atoms in the structure are displaced less than an interatomic distance and these structures are merely distorted versions of each other. But the temperature at which the transformation occurs reveals a major difference. For zirconium oxide, the transformation point is approximately 1100°C (6), while for hafnium oxide this point is much higher. Measured values for the hafnium oxide transformation temperature are given in Table 1

and there is some variation in the results. It is apparent, though, that the transformation occurs somewhere above 1600°C and perhaps not until 1700°C. The volume change associated with these transformations can lead to fracture of either material; however, in zirconium oxide the volume change is about 7.5% while in hafnium oxide the change is only about 3.4% (7). Thus the transformation in hafnium oxide should be less destructive and moreover it occurs at a much higher temperature.

Stabilization in hafnium oxide can be achieved, as with zirconium oxide, by the addition of an appropriate oxide. The additive effectively stabilizes a cubic structure which is immune to any phase transformations. Several materials have been shown to be useful as stabilizers. These include the oxides of calcium (7), yttrium (8), erbium (9), and the remainder of the lanthanides in general (1). Outside of phase equilibrium information and X-ray structure data very little is known about cubic stabilized hafnium oxide.

Thermodynamic data for hafnium oxide must be considered imprecise because of difficulties in high temperature measurements (1). Nevertheless, the melting point has been established at approximately 2900°C (7) which is about 100° higher than that for zirconium oxide. This makes hafnium oxide second only to thorium oxide in terms of melting point among the oxides (1). Stabilization of hafnium oxide lowers the

melting point, but it still remains well above 2000°C. Ackermann and Thorn (10) conducted vaporization studies and reported hafnium oxide to be the least volatile of all oxides. This information lends support to the material's excellent refractory nature.

Although there is a paucity of mechanical property data for hafnium oxide, a reasonable amount of study has been given to the thermal expansion. Curtis, et al. (7) compared the linear thermal expansions for unstabilized hafnium and zirconium oxides. The reported coefficients of linear expansion were 8.0 and 5.8×10^{-6} per degree Celcius from 200 to 1300°C for zirconium and hafnium oxide, respectively. Values very close to these were found by Fulkerson (11) for both materials. Ohnysty and Rose (12) measured the expansion of hafnium oxide up to the transformation point and reported an expansion of about $6.5 \times 10^{-6}/^{\circ}\text{C}$.

Axial thermal expansion studies revealed an interesting characteristic of monoclinic hafnium oxide. Data for the principal crystallographic axes determined by Patil and Subbarao (13) are shown in Table 2. Reasonable agreement to these data was obtained by other investigators (14,15). This information is indicative of the large extent of anisotropy in the thermal expansion. A condition such as this is conducive to microcracking (16) which will be discussed later.

Lynch, et al. (17) reported a thermal conductivity value

Table 2. Axial thermal expansion of monoclinic hafnium oxide (13)

Linear thermal expansion coefficient for each axis ($\times 10^{-6}/^{\circ}\text{C}$)		
a	b	c
9.34	2.98	13.10

of $1.5 \text{ Btu hr}^{-1} \text{ ft}^{-1} ^{\circ}\text{F}^{-1}$ between 1100 and 1900°C , a value that is nearly the same as that given by Kingery, et al. (18) for zirconium oxide. This means that hafnium oxide has a relatively low thermal conductivity and therefore should possess good insulation properties; however it also suggests that the material could be prone to thermal shock.

One data point exists in the literature for the Young's modulus of hafnium oxide (19). A value of 8.2×10^6 psi is given, but no information concerning the measurement technique or the material characterization could be found. In light of modulus data for zirconium oxide this data point appears unreliable.

Smith and Crandall (20) investigated the elastic moduli of monoclinic zirconium oxide as functions of porosity and temperature. It was found that the moduli fit the exponential equation proposed by Spriggs (21) for moduli vs. porosity. The fit yielded extrapolated zero-porosity values of 35.4×10^6 and 13.9×10^6 psi for Young's and shear modulus, respectively. The moduli showed a surprisingly rapid decrease with increas-

ing temperature. This was readily accounted for by an investigation of the impurities in the zirconium oxide which showed that a glassy phase had formed causing the elevated temperature moduli to be lowered appreciably.

Beyond the reviewed information and the comparisons to the properties of zirconium oxide, no further mechanical property data were available for hafnium oxide.

Microcracking

The high degree of thermal expansion anisotropy in monoclinic hafnium oxide introduces the possibility of microcracking. A fair amount of recent literature has been devoted to this subject and a number of materials have been reported to exhibit microcracking.

Buessem (16) noted that a material with a high anisotropy of thermal expansion may show some unusual properties such as abnormally low elastic moduli and hysteresis in linear thermal expansion. These unusual properties were explained on the basis of "internal ruptures and recombinations".

The ruptures or cracks are produced as a material is cooled from some elevated temperature. Internal stresses are developed during cooling as a result of different contraction rates in each of the crystallographic directions of each crystallite or grain of the material. If these stresses are large enough cracks can form. It has been postulated that stresses generated through thermal expansion anisotropy can

be quite large; calculations for the α -uranium structure predict stress to develop at the rate of 360 psi per degree Celsius as the material is cooled (22).

Anisotropy is not the only mechanism for producing microcracks. Rapid phase transformations have been shown to be responsible for the development of microcracks. Unstabilized zirconium oxide was shown by Ault and Ueltz (23) to form microcracks when cycled through the monoclinic-tetragonal transformation. Multiphase ceramic bodies also can exhibit this behavior when the components have dissimilar thermal expansion coefficients (24). Greve, et al. (25) showed that this was the case for aluminum oxide containing a dispersed phase of zirconium oxide.

In hafnium oxide, the possibility exists of microcrack formation facilitated by the phase transformation. However, if this transformation is avoided, then microcracks may still be formed through the thermal expansion anisotropy. Other materials with a monoclinic structure have been studied and the presence of microcracking was inferred (26,27,28). Monoclinic samarium, gadolinium and europium oxides all exhibited symptoms of microcracking. For the last two materials it was also shown that by lowering the grain size the microcracking could be prevented.

The microcracking effects were very pronounced in a study on the elastic behavior of monoclinic niobium oxide (29,30).

Sintered specimens with large grain sizes ($\sim 20 \mu\text{m}$) showed abnormally low room temperature elastic moduli. Additionally, both elevated temperature elastic moduli and thermal expansion measurements revealed hysteresis between the heating and cooling curves. Hot-pressed material with a smaller grain size ($\sim 10 \mu\text{m}$) showed none of these effects.

Various other materials have been shown to be subject to microcracking, most notably a variety of titanates (31,32,33). In each situation, thermal expansion anisotropy was prevalent.

From the assortment of investigations on microcracking several characteristics have been established. Abnormally low elastic moduli and high internal friction (33) occur with microcracking and it is felt that modulus and internal friction measurements are the most sensitive techniques used thus far to detect microcracking (27,34). Elevated temperature measurements of elastic moduli, thermal expansion and thermal diffusivity (35) produce hysteresis between the heating and cooling data. This is attributed to healing and formation of microcracks during the thermal cycling (16).

One very important characteristic of microcracking is the dependence on grain size. When grain size was considered with respect to microcracking in the various studies it was found in general that microcracking was absent in fine grained material, but present in larger grained material (36). In some cases, the grain sizes were narrowed to a range in which lay

a critical grain size for microcracking.

Initial considerations of thermal expansion anisotropy and microcracking primarily used a stress criterion to estimate the internal stress developed in a material subjected to a temperature change (22). If the stress level exceeded some critical value, then microcracking could occur. This approach, however, made no provision for grain size and therefore could not address the important matter of grain size dependence.

Based on the results of a study on magnesium dititanate, Kuszyk and Bradt (37) proposed an energy criterion for microcracking that is analogous to Hasselman's (38) description of elastic energy as a critical quantity in causing thermal shock failure. This theory has not been conclusively proven, but the development of this idea predicts that a critical grain size for microcracking exists which should be inversely related to the degree of thermal expansion anisotropy. An expression for this was given as:

$$\ell = \frac{2(\gamma_f)}{3(SE)}$$

where ℓ is the critical grain size

γ_f is the average fracture surface energy, and

SE is the strain energy per unit volume.

Subsequently the strain energy term is a function of the degree of thermal expansion anisotropy and Cleveland (33) combined this with experimental results to develop the expression:

$$\lambda = \frac{14.4 \gamma_f}{E \Delta\alpha_m^2 \Delta T^2}$$

where E is the Young's modulus

$\Delta\alpha_m$ is the maximum difference in thermal expansion coefficients for the different crystallographic axes, and

ΔT is the temperature range over which the strain energy accumulates.

The key concept in this instance is that because the strain energy is a volume function, the amount of strain energy generated in a particular grain increases as the grain size (and grain volume) increases. Thus as the grain size increases, more strain energy can be introduced to the grain and if enough strain energy is developed, microcracking ensues.

Another approach was taken by Blendell, et al. (39) who rationalized the grain size effect as due to the greater capacity of fine-grained bodies to creep under load. Undoubtedly this very plausible conjecture was as much motivated by the supporting evidence from a variety of creep studies as by the observation that microcracking is suppressed in fine-grained bodies. The concept stems from the strong dependency of creep (stress relaxation) rates upon grain size (40). The supposition is made that, on cooling, large-grained bodies lose their capacity to creep at more elevated temperatures than do fine-grained bodies. Thus upon cooling from a sufficiently elevated temperature, the large-grained bodies develop

more unrelieved stresses due to anisotropic thermal contraction and hence are more likely to invoke microcracking as the preferred mode of stress relaxation.

This notion implies that the ΔT term in Cleveland's equation should vary with the grain size. Experimentally, this means that the incipient formation of microcracks on cooling should occur at increasingly higher temperatures for bodies of increasing grain size, other things being equal.

Clearly, the two concepts just discussed are not opposed to each other. Presumably either could be responsible for microcracking or they could contribute jointly. However, microcracking in hafnium oxide can only be discussed in terms of Cleveland's concept at this time because creep data for hafnium oxide are not available. Cleveland's work dealt with materials having $\Delta\alpha_m$ values of approximately $15 \times 10^{-6}/^{\circ}\text{C}$. According to the data from Table 2, the $\Delta\alpha_m$ for hafnium oxide is approximately $10 \times 10^{-6}/^{\circ}\text{C}$. For niobium and gadolinium oxides the values are 5×10^{-6} (29) and $6 \times 10^{-6}/^{\circ}\text{C}$ (41), respectively. It would appear from the degree of thermal expansion anisotropy standpoint that there is a potential for microcracking in hafnium oxide.

EXPERIMENTAL PROCEDURE

Specimen Preparation and Characterization

The hafnium oxide used in this project was originally of commercial grade (Wah Chang Corporation). Purification and dissolution of the material was performed by the Ames Laboratory Rare Earth Separation Group. The commercial material was reacted with chlorine gas to form the chloride and subsequently dissolved in water. Purification was facilitated by an ion exchange process after which the hafnium was precipitated with ammonium hydroxide. The material was again dissolved into aqueous solution using nitric acid as the solvent and was received from the separation group in this form.

Hafnium oxide powder for specimen preparation was prepared by the Toluene-Acetone Process (42). This technique was instrumental in producing highly sinterable material. The process involves several steps as follows:

- (1) The aqueous hafnium solution is diluted to a concentration of 25 grams oxide yield per liter and then precipitated into an aqueous ammonium hydroxide solution to form a hafnium hydroxide precipitate.

- (2) Distilled water was pulled down through the precipitate to remove any ammonia salts present. This is carried out by placing the precipitate on sintered glass filters and utilizing a vacuum suctioning system to pull the wash fluid through the precipitate.

(3) After the excess water has been suctioned through, the precipitate is similarly washed with acetone to replace the aqueous medium with an organic medium.

(4) The acetone wash is then followed with toluene which is immiscible with water. Thus the toluene effectively displaces any remaining free water from the precipitate.

(5) A final acetone wash is used to remove the toluene. When filtration is complete, the precipitate can be dried rapidly in air in a period of approximately one hour.

A time-saving alternative to the last step was developed in which the "acetone-wet" precipitate is "hot-ground" with a porcelain mortar and pestle pre-heated to 100°C. This produces dried material in a matter of minutes and effectively incorporates any necessary crushing operations into the drying step. After initial processing studies this technique was used exclusively for producing powders.

The dried hafnium hydroxide powder was passed through a 325 mesh sieve to remove any coarse particles and then calcined to form the oxide. A spectrographic analysis was obtained on the calcined oxide powder (Ames Laboratory Spectrographic Analysis Group). Results of this analysis are shown in Table 3.

Two techniques were employed to prepare experimental samples: sintering and hot-pressing. The procedure for the sintered specimens involved the formation of compacts in a

Table 3. Spectrographic analysis of impurities in the hafnium oxide

Element	Concentration (ppm)
Al	50
Ca	100
Cu	200
Fe	100
Mg	500
Nb	200
Ni	20
Si	1000
Ta	300
Ti	100
Zr	1000

double-action steel die having a rectangular cavity of 7.6 x 0.6 cm. A pressure of 2500 psi was used in this operation. Rectangular prisms thus formed were further densified with the use of an isostatic press. The specimens were sealed in rubber containers and pressed isostatically to 30,000 psi. Sintering of the specimens was carried out in air utilizing a gas fired muffle furnace. The specimens were fired at 1500°C for up to 4 hours. The oxidizing atmosphere eliminated the possibility of partial reduction effects, thus avoiding volume changes, stoichiometry shifts, cracking, etc. which can attend subsequent anneals in oxidizing atmospheres.

The hot-pressing procedure involved loading hafnium oxide powder into a graphite die with a 6 cm x 1 cm rectangular

cavity. The die was heated under a 50-100 μ m vacuum in a graphite-susceptor induction furnace. Densification was carried out at temperatures varying from 1400 to 1600°C and at pressures ranging from 4000 to 7000 psi. Heating rates were 50°C per minute to 1000°C at which point the initial pressure was applied and then 12.5°C per minute to the peak temperature. Peak temperature was maintained for times ranging from 2 to 60 minutes and then the pressure was released and the die allowed to cool. Only a small amount of reaction between the graphite and the specimen surface occurred during the process, but this reaction layer was removed by subsequent machining and re-oxidation operations.

Following densification, both the sintered and hot-pressed specimens were shaped into rectangular prisms with a dimensional tolerance of ± 0.001 cm using a surface grinder employing a diamond grinding wheel. Typical dimensions for the shaped specimens were 5.7 cm x 0.8 cm x 0.3 cm. All specimens were annealed in air at 1000°C for 24 hours to establish a well-defined stoichiometry. The bulk density of each specimen was determined from its mass and dimensions. X-ray diffraction techniques were used to determine the crystallographic form and average grain sizes were determined from scanning electron microscopy of fracture sections.

Elasticity and Internal Friction Measurements

The sonic resonance technique was used for the determination of elastic moduli in this study. This procedure is outlined by Spinner and Tefft (43) and since detailed descriptions of the actual equipment are given by several authors (29,44) they will not be repeated here. A diagram of the equipment for room temperature determinations is shown in Fig. 1.

Briefly, the specimen was suspended by cotton thread between a magnetic record cutting head and a phonograph cartridge, designated as the driver and pickup, respectively. A variable frequency oscillator was used to generate an electronic signal which, after amplification, was converted to a mechanical signal by the driver and fed to the specimen. The resultant excitation of the specimen was re-converted to an electronic signal by the pickup and monitored with a vacuum tube voltmeter. Both the input and output signals were monitored with an oscilloscope and the frequency of the input signal was measured with a frequency counter.

The frequency of the input signal was varied and the resonant frequencies identified as those frequencies at which the signals were easily transmitted through the test specimen. The mode of resonance was determined by probing the specimen during excitation to locate the nodal planes. Diagrams of the resonance vibrational modes are shown in Fig. 2.

Figure 1. Block diagram of resonant frequency apparatus

Elevated temperature measurements were made using the same technique, but with some modification of the system. The specimen was suspended with carbon yarn in a manually controlled carbon rod resistance furnace. The specimen, furnace, driver and pickup were covered with a bell jar and a vacuum drawn to a pressure of less than 10^{-1} μ m. Specimen temperature was measured using a Pt-Pt 10% Rh thermocouple and a digital voltmeter.

Resonance data were converted into moduli using the equations of Pickett (45) in a form given by Hasselman (46). Shear modulus for the specimen shape used in this study was obtained directly from the equation:

$$G = \frac{4LRmf_t^2}{S}$$

where G is the shear modulus,

L is the length of the specimen

m is the mass of the specimen

f_t is the resonant frequency of the fundamental mode of torsional vibration

S is the area of the cross section, and

R is a shape factor given by:

$$R = \frac{A/B + B/A}{4(A/B) - 2.52(A/B)^2 + 0.21(A/B)^6}$$

where A is the length of the shorter side and

B is the length of the longer side of the cross section.

Figure 2. Fundamental modes of resonant vibration in rectangular prisms (from Hasselman (4))

Similarly, Young's modulus was calculated from the following equation:

$$E = 0.94645 \frac{C \cdot m \cdot f_f^2}{B}$$

where E is the Young's modulus

f_f is the resonant frequency of the fundamental mode of flexural vibration, and

C is a shape factor given by:

$$C = [1 + 6.5850(1 + 0.0752\mu + 0.8109\mu^2)(A/L)^2 - \frac{8.340(1 + 0.2023\mu + 2.173\mu^2)(A/L)^4}{1 + 6.338(1 + 0.14081\mu + 1.536\mu^2)(A/L)^2} - 0.86806(A/L)^4] (A/L)^{-3}$$

where L is the length of the specimen, and

μ is Poisson's ratio.

Since Poisson's ratio is introduced by this shape factor, the equation:

$$\mu = \frac{E}{2G} - 1$$

is necessary for solution. The moduli were computed by first solving for the shear modulus, then assuming an initial value for μ , and finally solving the equations for E and μ in an iterative manner until the desired degree of precision was attained. In the event that the torsional frequency and thus shear modulus could not be determined for a particular specimen, the Poisson's ratio from a similar specimen could be assumed in computing Young's modulus since a small error in μ

has only a minor effect on the computation (47).

The experimental error involved in measuring the elastic moduli by the sonic resonance technique was studied by Marlowe and Wilder (48). For room temperature measurements, the overall error should be less than 1.3% with dimensional inaccuracy contributing the largest error. Spinner et al. (47) reported that Young's modulus should be exact to four significant figures with this technique.

Determination of the bulk modulus (B) was made from the independently measured values of Young's and shear modulus using the equation:

$$B = \frac{EG}{3(3G-E)} .$$

To correct moduli for the effects of thermal expansion in elevated temperature measurements an equation from Hasselman (46) was employed:

$$M_t = M_o \frac{f_t^2}{f_o^2} \frac{1}{(1+\alpha\Delta T)}$$

where M_t is either Young's or shear modulus at temperature t

M_o is the modulus at room temperature

f_t is the resonance frequency at temperature t

f_o is the resonance frequency at room temperature

α is the coefficient of linear thermal expansion, and

ΔT is the difference between temperature t and room temperature.

A second correction was made for the effect of the carbon

strings and the evacuated environment used in the elevated temperature measurements. The equation used for this correction was:

$$M_t' = \frac{M_A}{M_V} M_t$$

where M_A is either modulus at room temperature in air with the specimen suspended by cotton strings

M_V is the same modulus at room temperature under vacuum with the specimen suspended by carbon yarn

M_t is the measured elevated temperature modulus at temperature t , and

M_t' is the corrected modulus at temperature t .

Internal friction measurements were made with the sonic resonance apparatus using a technique described by Wachtman and Tefft (49). The specimen was vibrated at the fundamental flexural frequency and the internal friction was determined by stopping the input signal and measuring the time for the amplitude of the vibrations to fall to some fraction of an initial amplitude value by free decay. The relation for the internal friction is then given by:

$$Q^{-1} = \frac{\ln A_0/A_t}{ft}$$

where Q^{-1} is the internal friction

A_0 is the amplitude of the first vibration considered

A_t is the amplitude of a vibration occurring after the elapsed time t , and

f is the frequency of the vibrations.

The product (ft) was measured directly by employing a device to count the number of cycles occurring as the amplitude decreased from A_0 to A_t . The amplitude levels were regulated by the use of external voltage gate controls which switched the cycle counter on and off as the designated amplitude levels were encountered. The variable gate controls were used to set the high amplitude level corresponding to A_0 and the low amplitude level corresponding to A_t . By utilizing the proper settings the ratio of A_0 to A_t could be adjusted such that:

$$A_0/A_t = e$$

and

$$\ln A_0/A_t = \ln e = 1 .$$

The equation for the internal friction becomes:

$$Q^{-1} = \frac{1}{\pi N}$$

where N is the number of cycles occurring as the amplitude decays from A_0 to A_0/e .

Basically, the procedure involved locating the flexural resonant frequency, adjusting the amplitude of the specimen vibrations to a level above A_0 and then switching the input signal off. The decay of the specimen vibrations was monitored through the pickup. As the amplitude passed through the A_0 level, the counter began counting. When the amplitude passed through the A_0/e level, counting ceased. The number of cycles counted in the free decay was used to compute Q^{-1} .

Measurements were made at several amplitude levels, but with the $A_o:A_t$ ratio held constant.

It was found that the internal friction of the specimens varied with the position of the support strings on the specimen. This indicated that the inherent damping capacity of the measuring apparatus was affecting the measurements. Thus it was necessary to use the corrections suggested by Wachtman and Tefft (49).

This was accomplished by measuring three values of internal friction for each specimen with the support strings located at different positions along the specimen length for each measurement. These values were used to solve three simultaneous equations of the form:

$$Q_m^{-1} = \frac{Q_s^{-1} + KQ_a^{-1} (y/y_o)^2}{1 + K(y/y_o)^2}$$

where Q_m^{-1} is the measured internal friction

Q_a^{-1} is the damping contributed by the apparatus

K is a constant

Q_s^{-1} is the true internal friction of the specimen, and

y/y_o is a vibrational displacement correction factor given by:

$$y/y_o = \frac{1.018[\cosh 4.730(x/l) + \cos 4.730(x/l)]}{2.036} - \frac{[\sinh 4.730(x/l) + \sin 4.730(x/l)]}{2.036}$$

where l is the length of the specimen, and

x is the distance of the symmetrically positioned support strings from the respective specimen ends.

All room temperature measurements were performed using this method. Elevated temperature measurements were made coincidentally with the elevated temperature modulus measurements with the support strings at a single position so that relative values of Q^{-1} were measured rather than the true values. These relative values were corrected to the room temperature values by a similar scheme to that used with the elevated temperature elastic moduli.

Thermal Expansion Measurements

Linear thermal expansion measurements were made with a commercial dilatometer (Brinkman model TD IX). A linear variable differential transformer in contact with the specimen by means of an alumina push rod measured length changes as the specimen was heated in an alumina tube. An electric resistance furnace was used to heat the specimen in an air atmosphere. Temperature was monitored with a Pt-Pt 10% Rh thermocouple positioned near the specimen.

RESULTS AND DISCUSSION

The original intent of this study was to measure the elastic properties of hafnium oxide with respect to porosity and temperature. In many instances, such an investigation would be straightforward and the results generally predictable. The implication of additional factors affecting the properties of the material, however, necessitated further experimentation to fully realize the characteristics of hafnium oxide.

The effect of microcracking was a prominent factor in the determination of these properties. Thus this section is divided into four parts; one each covering porosity, grain size and temperature effects and a fourth dealing with special effects that are characteristics of the microcracked material.

All of the data referred to in this section are tabulated in the appendices. Appendix A contains dimensional and microstructural properties of each specimen. Appendix B lists room temperature properties while elevated temperature data are given in Appendices C and D.

Porosity Effects at Room Temperature

The results of the elastic modulus measurements with respect to porosity are shown in Fig. 3 through 5 for Young's (E), shear (G) and bulk (B) modulus, respectively. In each case, the data yield a definitive pattern.

Several equations have been proposed to relate modulus to

Figure 3. Young's modulus as a function of volume fraction porosity

Figure 4. Shear modulus as a function of volume fraction porosity

Figure 5. Bulk modulus as a function of volume fraction porosity

porosity, but the most commonly accepted are the exponential equation proposed by Spriggs (21) and a linear equation (50) given in general form as:

$$M = M_0 \exp(-bP)$$

and

$$M = M_0 - cP$$

where M is the modulus, M_0 is the zero-porosity modulus, P is the volume fraction porosity, and b and c are constants.

Thirteen data points for each modulus over the porosity range from 3.83 to 24.69% were fit to both types of equations and it was found that the exponential relation gave the best fit based upon the lowest standard error of estimate. The resulting equations are (in GN/m^2):¹

for Young's modulus:

$$E = 283.6 \exp(-4.17P),$$

for shear modulus:

$$G = 109.2 \exp(-3.93P),$$

and for bulk modulus:

$$B = 233.1 \exp(-5.48P).$$

The coefficients of variation were 0.47, 0.47 and 1.2%, respectively. For the linear equation fits, the coefficient of variation exceeded 3% in each case.

The zero porosity values for E and G given in more common

¹ GN/m^2 = geganewton per meter squared = 10 Kilobars = 1.45×10^{-4} psi.

units are $E_0 = 41.1 \times 10^6$ psi and $G_0 = 15.8 \times 10^6$ psi. These values are in close agreement with those found for zirconium oxide (20), being only slightly higher. The empirical b constants also show a close similarity to those of zirconium dioxide and are in close agreement with values reported for aluminum oxide (51) and magnesium oxide (52).

Several specimens showed anomalously low elastic modulus values. These values are plotted in Fig. 3 and 4 for illustration although they were not used in the previously mentioned data fits. This was a clear indication that hafnium oxide was subject to microcracking.

The possibility existed that the phase transformation was involved in the anomalous elastic behavior. Great care had been taken in the fabrication steps to assure that the transformation would be avoided. All specimens were sintered below the transformation temperature and subsequent X-ray diffraction measurements revealed that only the monoclinic crystal structure was present. A test specimen was sintered at 2000°C , well above the transformation range, and then characterized. It was found that not only was the specimen too cracked to determine modulus values, but that some of the tetragonal phase was actually frozen into the structure. This was verified by X-ray diffraction and visual microscopic analysis. The obvious difference between the test specimen and the rest of the specimens served to rule out any further consideration of the trans-

formation as a factor.

As mentioned in the Experimental Procedure section, all specimens were annealed at 1000°C after fabrication and machining. Modulus measurements were made before and after the anneal. The crack free specimens showed very little or no change in the modulus values. Any change was attributable to mass changes due to carbon burn-off and reoxidation. The microcracked specimens, however, showed gains of as much as 20% in the moduli. It was possible that the anneal permanently healed some of the cracks because after the anneal, the moduli for these specimens remained stable with time. Another possibility was that the machining induced some microcrack growth which was subsequently removed by the anneal. As a result, only data for the annealed specimens were used in this study.

The possibility of permanent crack healing warrants consideration. Several factors could have been involved in the formation of microcracks, one of which was the cooling rate from the elevated temperatures. Increasing cooling rates may be expected to cause more stress in the material and therefore provide more driving force for crack formation and propagation. Simply, thermal stresses (38) can be developed in addition to the microstresses effected by the inherent thermal expansion anisotropy in the hafnium oxide. As the cooling rate after the anneal was slower than any cooling rate used during the elevated temperature measurements, it was expected that any

significant permanent crack healing would be achieved at this point. Experimental evidence related to this concept will be discussed in the Additional Effects section.

As can be seen by the plotted data for the microcracked specimens, there was no obvious relation with porosity. It appeared that the effects of microcracking outweighed the porosity effects. The highest density microcracked specimen had only 3.29% porosity, yet its modulus values corresponded to values for a crack-free specimen with over 35% porosity. Thus the open volume created by a crack in the material has a much more pronounced effect than the open volume associated with a pore.

The reduction of the elastic modulus with the introduction of microcracks into a material has been discussed by Berry (53) and Hasselman (54) following the approach of Griffith (55,56). Basically, the decrease in modulus is a function of the increase in surface area created by a crack. Consequently, increasing crack population and size result in a lowered effective elastic modulus. A similar approach has been used to describe the decrease in modulus associated with increasing porosity (21). Hasselman (57) further points out that by lowering the effective modulus, microcracks improve the thermal shock resistance of a material. Thus microcracks, and similarly porosity, would increase the thermal shock resistance. Microcracks, though, have the advantage over porosity of facilitating modulus reduction without the introduction

of substantial open volume which may be undesirable for many applications.

Poisson's ratio is plotted as a function of porosity in Fig. 6. There was considerable scatter so no attempt was made to fit an equation to these data. Regardless of the scatter, there was a general trend for Poisson's ratio to decrease with increasing porosity. Using the empirically determined zero-porosity E and G values, a zero-porosity Poisson's ratio of 0.2984 was determined. The values for the microcracked specimens are not shown in the plot because, as with the modulus data, there is no obvious relation with porosity. The only conclusion that can be drawn with respect to the microcracked material is that the Poisson's ratio generally was lower with increasing severity of microcracking. This forms a consistent pattern; both increasing porosity and microcracking caused modulus and Poisson's ratio to decrease.

As a further step in characterizing the microcracking effect, the internal friction was measured. Zener (58) discusses several energy absorption mechanisms that result in increased damping or internal friction. Such things as defects, pores, grain boundaries and cracks in a material result in increased internal friction. Furthermore, a previous report (34) suggests that this type of measurement may be extremely sensitive to cracking.

Internal friction values are plotted in Fig. 7. As expected there was an increase with increasing porosity for

Figure 6. Poisson's ratio as a function of volume fraction porosity

Figure 7. Internal friction as a function of volume fraction porosity

the crack-free specimens. The microcracked specimens again yielded data that were apparently independent of porosity. The internal friction values for these specimens are substantially higher than for the crack-free specimens. This correlated very nicely with the modulus results. It should be noted that for the two highest density specimens, designated as HP-1 (microcracked) and HP-11 (crack-free), the modulus values differed by a factor of about 4 whereas the internal friction values vary by a factor of nearly 100. This is evidence that internal friction is probably more sensitive to the microcracking than the elastic moduli.

Surprisingly, two specimens that were considered crack free because of reasonable modulus values possessed abnormally high internal friction values. This anomaly will be discussed in the next section.

Grain Size Effects at Room Temperature

As mentioned in the literature survey, there is considerable evidence that microcracking is highly dependent on grain size. The presence of microcracks in hafnium oxide necessitated the determination of the specimen grain sizes.

Internal friction was considered the most sensitive measurement of microcracking, so those values are plotted as a function of grain size in Fig. 8. A definite pattern developed for the microcracked specimen data in this instance. Most striking was the rapid jump in internal friction for

Figure 8. Internal friction as a function of grain size

specimens with average grain size between 2 and 3 μm . This clearly indicates the critical grain size for microcracking in hafnium oxide is between 2 and 3 μm .

The two apparently crack-free specimens with abnormally high internal friction had grain sizes that fell into the critical region. Clearly, these specimens must have had some microcracking, but not enough to affect the modulus values. This was further evidence that the internal friction measurements were extremely sensitive to microcracking.

The modulus values followed a similar pattern to that of the internal friction. Specimens with grain size exceeding the critical size showed moduli lower than expected while those with grain size of ~ 2 μm or less showed no apparent deviation from the expected values.

To test the critical grain size supposition, a crack-free specimen with a grain size of 1.8 μm was annealed for 6 hours at 1400°C. Grain growth occurred so that the new grain size was 3 μm and exceeded the critical size. There was a corresponding 60% decrease in the moduli and an increase in internal friction by a factor of ~ 40 , indicating the formation of microcracks.

Comparison of the critical grain size for hafnium oxide to those for other materials reveals a pattern when the degree of thermal expansion anisotropy is considered. The $\Delta\alpha_m$ discussed in the Literature Survey is compared to the critical

grain sizes for various materials in Table 4. It can be seen that Cleveland's (33) equation relating $\Delta\alpha_m$ to critical grain size holds some merit. The highly anisotropic materials; i.e. the titanates and hafnium oxide, have small critical grain sizes while less anisotropic materials, like aluminum oxide, have larger critical grain sizes.

Table 4. Critical grain size for microcracking compared to $\Delta\alpha_m$

Material	Critical grain size (μm)	$\Delta\alpha_m$ (per $^{\circ}\text{C}$)	Reference
HfO_2	2-3	10×10^{-6}	(13, this study)
MgTi_2O_5	3-5	13.6×10^{-6}	(33)
Al_2TiO_5	1-2	23.0×10^{-6}	(33)
Fe_2TiO_5	3	15.7×10^{-6}	(33)
Al_2O_3	100	0.66×10^{-6}	(36, 59)
Nb_2O_5	10-20	5×10^{-6}	(29)
Gd_2O_3	10	6×10^{-6}	(27, 41)
Eu_2O_3	8	2.5×10^{-6}	(28, 60)
TiO_2	20-50	2.4×10^{-6}	(36)

Visual analysis of the microstructures of some of the specimens by electron microscopy showed indications of microcracking in the larger grain size material. Fig. 9 through 11 show microstructures of representative hafnium oxide specimens. Fig. 9 shows the microstructure of a crack-free specimen while the last two figures show microstructures for

Figure 9. Scanning electron micrograph of a fracture section of specimen HP-11 with average grain size = $2.2\ \mu\text{m}$ (2500X)

Figure 10. Scanning electron micrograph of a fracture section of specimen HP-1 with average grain size = 16 μm (2000X)

Figure 11. Scanning electron micrograph of a fracture section of specimen S-1 (after grain growth anneal) with average grain size = 14 μm (4000X)

microcracked specimens. Microcracking is apparent at the grain boundaries in the microstructures of the two microcracked specimens.

Temperature Effects

Elevated temperature measurements yielded interesting comparisons between the crack-free and the microcracked hafnium oxide. Fig. 12 and 13 show comparative data for Young's and shear moduli of specimens HP-1 (microcracked) and HP-11 (crack-free). Both specimens were approximately 96.5% of theoretical density, but the grain sizes were 16 and 2.2 μm for HP-1 and HP-11, respectively.

Turning attention first to the crack-free material, the Young's and shear moduli each showed linear decreases with temperature up to about 1100°C. Above this point, the moduli decreased more rapidly in a non-linear fashion. The linear nature of the data is typical for polycrystalline ceramics (61). The non-linear portion of the data above 1100°C was attributed to grain boundary sliding (62). This also is typical of polycrystalline ceramics and results from the anelastic nature of the grain boundaries at elevated temperatures.

To account for the non-linearity, the modulus values were fit to an exponential equation proposed by Wachtman et al. (61) and the resulting relations were (in GN/m^2):

$$E = 237.8 - 0.05T \exp\left(\frac{-1078}{T}\right)$$

and

Figure 12. Young's modulus as a function of temperature for specimens HP-1 (microcracked) and HP-11 (crack-free)

Figure 13. Shear modulus as a function of temperature for specimens HP-1 (microcracked) and HP-11 (crack-free)

$$G = 91.6 - 0.02T \exp\left(\frac{-805}{T}\right)$$

where T is the absolute temperature. The bulk modulus, shown in Fig. 14, was similarly fit and the relation was (in GN/m^2):

$$B = 201.8 - 0.30T \exp\left(\frac{-4051}{T}\right).$$

Many of the modulus vs. temperature studies presented in the literature consider only the linear portion of the data and subsequently linear data fits are given. If the moduli for specimen HP-11 are given the same treatment, the results are (in GN/m^2):

$$E = 241.31 - 0.0313T$$

and

$$G = 92.45 - 0.0126T$$

where T is the temperature in degrees Celcius. Data in the temperature range from 25 to 1100°C were used in these fits. These relations indicate percent changes in the moduli of about 1.3% per 100°C . Changes of this magnitude agree favorably with those reported for other polycrystalline oxide ceramics (63,64,65).

Modulus data are shown in Fig. 15 for crack-free specimen HP-19. Linear fits of the data obtained between 25 and 1200°C are (in GN/m^2):

$$E = 213.87 - 0.0227T$$

and

$$G = 83.79 - 0.0094T.$$

These relations indicate percent changes in the moduli of

Figure 14. Bulk modulus as a function of temperature for specimen HP-11

Figure 15. Young's and shear moduli as functions of temperature for specimen HP-19 (crack-free)

about 1.1%. Again this is in agreement with data for other ceramics.

The microcracked material exhibited behavior quite different from that of the crack-free material. The Young's and shear moduli for microcracked specimen HP-1 shown in Fig. 12 and 13 exhibited hysteresis between heating and cooling. The room temperature moduli for HP-1 were only ~26% of those for HP-11. Upon heating, the moduli for the microcracked specimen showed an obvious increase as low as 200°C and this increase continued up to 1100°C. At this point, the moduli for the two specimens were nearly equal. At higher temperatures, the moduli decreased similarly for both specimens.

The increase in the moduli for the microcracked specimen can be explained on the basis of a crack healing mechanism. The microcracks healed during heating and the moduli rose accordingly until about 1100°C where the specimen was essentially crack-free. The specimen maintained the crack-free state through further heating and during subsequent cooling to 400°C. This was evident from the crack-free behavior of the moduli during this temperature excursion. In the vicinity of 400°C the microcracks began to form and continued to do so as cooling continued to room temperature as indicated by the decreasing moduli in this temperature range. At room temperature the moduli did not immediately return to the original values, but took several hours to do so. This indicated that crack forma-

tion was a much slower process than the healing under the experimental conditions. The time delay in crack formation was a special characteristic of all the microcracked specimens tested and this subject is treated in the next section.

Fig. 16 and 17 show additional plots of moduli data for microcracked specimens HP-19 (after annealing to produce microcracks) and S-1, respectively. The behavior of the moduli exhibited in these plots is very similar to that of specimen HP-1. The fact that crack healing occurred at temperatures as low as 200°C rules out the possibility of a mass transport mechanism contributing to crack healing because significant diffusion would not be expected at such low temperatures in hafnium oxide. Probably the healing is facilitated by the same thermal expansion processes that caused the cracks to initially form. In other words, thermal expansion during heating merely pushes the crack surfaces together allowing bonding to occur between the two opposite surfaces.

The internal friction was monitored during the thermal cycling and the measured values accompanying the data in Fig. 12 and 13 are shown in Fig. 18. As expected, the internal friction for the crack free specimen showed no particularly large changes with temperature until the grain boundary sliding effect was encountered above 1100°C. The data did not show a smooth relation with temperature, but scatter of this type was typical for elevated temperature internal friction as

Figure 16. Young's and shear moduli as functions of temperature for specimen HP-19 (after annealing to produce microcracking)

Figure 17. Young's modulus as a function of temperature for specimen S-1 (microcracked)

Figure 18. Internal friction as a function of temperature for specimens HP-1 (microcracked) and HP-11 (crack free)

this measurement was quite sensitive to many processes.

For the microcracked specimen the room temperature internal friction was ~100 times greater than that for the crack-free specimen. During heating a pronounced peak was observed in the internal friction at ~825°C which coincided with the maximum rate of modulus increase for this specimen. Thus an increase in internal friction accompanies the crack healing process. When crack healing and moduli increases began to cease, the internal friction decreased. During cooling, the internal friction peak was not encountered and the values were substantially lower.

The internal friction was consistent with the moduli in that crack healing brought about crack-free behavior (higher moduli and lower internal friction) after the healing process was completed and then during cooling until the cracks began to form again. Obviously, the elimination of microcracks through the healing process should result in lowered internal friction, but the peak presents an anomaly. The fact that this peak occurred at a particular intermediate point in the crack healing process suggests that some mechanism in the process contributes to high damping.

A reasonable explanation is that as the cracks close, the opposing surfaces of the cracks "rub" against each other as the material is sonically vibrated resulting in a frictional impedance. In other words, as the crack surfaces close upon

each other and begin to adhere by virtue of the molecular bonding forces, there is a resistance to vibration (and thus increased damping) from this incomplete bonding structure. When crack healing approaches completion and the crack surfaces are well-bonded, this damping effect decreases.

The internal friction peak was found to occur for other microcracked specimens, but it was not as well-pronounced in all cases. In general there was an increase in internal friction associated with the crack healing process for each microcracked specimen tested while the sharp peak was essentially a special situation.

Thermal expansion measurements were conducted on specimens HP-1 and HP-11 to further the comparison and the results are shown in Fig. 19. The temperature range from room temperature to 1250°C covered by these measurements amply encompassed the microcrack healing/formation cycle.

Results for the microcracked specimen agreed favorably with the behavior found for microcracked MgTi_2O_5 (31) and Nb_2O_5 (66). The expansion was much lower than that for the crack-free specimen on heating and this can be attributed to a volume contraction associated with the closure of the cracks. When cooled, the expansion curve exhibited hysteresis with the cooling curve becoming steeper than the heating curve. The portion of the cooling curve down to 400°C had a slope (and thus a coefficient of thermal expansion) very nearly the same

Figure 19. Linear thermal expansion of specimens HP-1 (microcracked) and HP-11 (crack-free)

as that of the crack free specimen. This was consistent with the modulus data in that during cooling the material showed crack-free behavior. The fact that the cooling expansion curve fell below the heating curve indicated that crack closure had occurred resulting in a volume contraction of the specimen.

Below 400°C a flat expansion curve was observed indicating that cracks were opening and causing an expansion counteracting the normal elastic contraction of the specimen as it cooled. The 400°C break off point coincided with the point where the moduli began decreasing during cooling. Overall, there was very close correlation between the moduli and the linear thermal expansion for the microcracked specimen.

The crack-free specimen showed a higher expansion that was essentially linear with temperature. The calculated coefficient of linear thermal expansion is $6.3 \times 10^{-6}/^{\circ}\text{C}$ which agrees closely with data reported in the Literature Survey section. However, upon cooling, a small increase ($\sim 0.06\%$) in dimensions was noted. Repeated cycling yielded similar results. It was felt that because of repeated cycling and exposure to elevated temperatures a small amount of microcracking had taken place in the specimen and caused the small dimensional change. This is a reasonable assumption as the grain size for this specimen (HP-11) was in the range of the critical grain size.

The crack healing process in microcracked materials is a process that has been inferred from the behavior of various properties (such as the elastic moduli) during thermal excursions. To promote a better understanding of this process and perhaps support the concept of crack healing itself, a mechanical model is presented with accompanying mathematical analysis. The model incorporates two properties of interest in this study; the Young's modulus and the internal friction.

The model, diagrammed in Fig. 20, consists of two springs, one of which is in series with a dash pot. The springs represent the elastic characteristics of the material and the dash pot represents the damping effect of the microcrack healing process. The spring constant, k_1 , is the effective Young's modulus of the material with microcracks present while k_2 gives the modulus change brought about through crack healing.

It is assumed for simplification that k_1 remains constant and that the contribution from k_2 increases as the cracks heal. Thus the modulus with all cracks healed is the quantity (k_1+k_2) . Additionally, the assumption is made that the internal friction (damping) from the dash pot also changes as the cracks heal. This follows from the earlier explanation of increasing internal friction during crack healing. Basically, as the crack surfaces close the friction between these vibrating surfaces increases continuously until the crack is healed. At this point the friction is high enough that the crack sur-

Figure 20. Mechanical model for microcrack healing process

faces adhere and no longer "rub" against each other. Thus, the friction, or viscosity of the dash pot, increases as the crack healing progresses.

For the determination of the modulus change in the model, the equations describing the forces are written as (67):

$$m\ddot{x}_1 = F_0 e^{i\omega t} - k_1 x_1 - c(\dot{x}_1 - \dot{x}_2) \quad (1)$$

and

$$k_2 x_2 = c(\dot{x}_1 - \dot{x}_2) \quad (2)$$

where m is the mass

x_1 is the displacement of the mass during vibration

x_2 is the displacement of spring k_2

$F_0 e^{i\omega t}$ is the sinusoidal driving force for vibration

c is the dash pot damping constant (viscosity), and

$\dot{x}, \ddot{x}$ are the first and second derivatives of x .

Solving (1) and (2) simultaneously yields:

$$m\ddot{x}_1 + \frac{m}{c} k_2 \ddot{x}_1 + (k_1 + k_2) \dot{x}_1 + k_1 k_2 x_1 = F_0 e^{i\omega t} \left[i\omega + \frac{k_2}{c} \right] \quad (3)$$

The assumption is made that the displacement, x_1 , is given by:

$$x_1 = x_0 e^{-i\delta} e^{i\omega t} \quad (4)$$

where δ represents the phase angle between the force and the motion. The phase angle arises from the condition of damped vibrations. Equation 4 is substituted into Equation 3 and this result is evaluated at resonance conditions where:

$$\frac{\partial x}{\partial \omega} = 0 \quad (5)$$

where ω is the vibrational frequency. This yields a cubic polynomial type equation which, when solved, gives a solution, r , which is:

$$r = \omega/\omega_n \quad (6)$$

where ω_n is the natural (resonant) frequency and:

$$\omega = (k/m)^{1/2} \quad (7)$$

Thus the solution in Equation 6 and the relation in Equation 7 yield the Young's modulus.

The internal friction is obtained from Equations 1 and 2 with the exception that a free decay situation prevails so that:

$$F_0 e^{i\omega t} = 0 \quad (8)$$

Further, it is assumed that the displacements are:

$$x_1 = Ae^{-pt+iqt} \quad (9)$$

and

$$x_2 = Be^{-pt+iqt} \quad (10)$$

where A and B have different fixed phase angles because the displacements x_1 and x_2 are out of phase with each other. The exponential term describes the displacement (amplitude) decay with time.

Simultaneous solution of the force equations and substitution of Equation 9 and Equation 10 again yields a cubic polynomial which has the values of p and q as its roots.

The internal friction was defined in the Experimental Procedure as:

$$Q^{-1} = \frac{\ln(A_o/A_t)}{\pi N} \quad (11)$$

The logarithmic term can be evaluated using Equation 9 and determining the displacement after n cycles and after $n+1$ cycles (68). This gives the internal friction as:

$$Q^{-1} = \frac{2p}{q} \quad (12)$$

where $N=1$ cycle (the difference between n and $n+1$ cycles).

To obtain results from the mathematical derivations, values for k_1 , k_2 and c are necessary. As an example, it is assumed $k_1=k_2=100 \text{ GN/m}^2$ and c varies from 0 to 1. Fig. 21 shows the behavior of the modulus and the internal friction as the crack healing proceeds under these conditions. The horizontal axis merely represents the progress of the crack healing process which is proportional to the viscosity. Of course it is known that crack healing occurs with increasing temperature so that comparison of derived values and experimental data allows the application of temperature values to this axis. Comparison of the derived curves to the experimental curves for specimen HP-1 show good agreement as far as the general curve shapes are concerned. It must be realized that the model is only a simple approximation of what the physical situation could be so that close agreement to experimental data may not be obtainable. The important point, however, is that the behavior of the modulus and the internal friction derived from

Figure 21. Behavior of Young's modulus and internal friction as derived from the model

the model are in accordance with experimentally observed results.

Additional Effects

As this study progressed, a number of characteristics pertaining to the microcracked material were noted. These effects are not necessarily interrelated and so are categorized as "Additional Effects."

In the previous section, it was reported that after thermal cycling the moduli of the microcracked specimens did not immediately return to the original starting values. Rather the moduli maintained a higher value after the specimens were cooled suggesting some permanent microcrack healing. Only after several hours exposure to air did the moduli return to approximately the original values. This phenomenon was also experienced in studies on microcracked europium (28), gadolinium (27) and niobium oxides (29), but no definite evaluations were given.

In order to study this behavior, crack-free specimen HP-19 was held at 1400°C for 3 hours and 1500°C for 1 hour in the modulus measurement apparatus furnace. This in situ annealing was used to facilitate grain growth sufficient to exceed the critical value for microcracking. The grain size was initially 1.6 μm and increased to 3.3 μm during the treatment. The moduli vs. temperature plots for this specimen were shown in Fig. 15 and 16, respectively, in the previous section. These

data verified that microcracks had formed as hysteresis was observed for the elevated temperature moduli after the anneal.

When the specimen was cooled from the anneal temperature, the moduli returned linearly to the original crack-free room temperature values. This indicated no microcrack formation. The experiment had been conducted under vacuum ($<10^{-1}$ μm) and the specimen was kept under this vacuum at room temperature for 24 hours, but no modulus change occurred. Upon exposing the specimen to air, though, the moduli began decreasing rapidly.

The Young's modulus was measured in air as a function of time at room temperature and the relative Young's modulus vs. time values are plotted in Fig. 22. The modulus decreased by ~8% in the first hour, over 20% in the first 10 hours and finally stabilized at a net decrease of 25.8% after more than 50 hours. Additionally, the internal friction was monitored during this test and was found to increase monotonically as the modulus decreased.

The specimen was then subjected to a heating-cooling cycle and the expected hysteresis loops for the moduli were generated. Again, on cooling, the moduli returned to crack-free values at room temperature. This time the vacuum was released to 5 μm pressure. The Young's modulus decreased as before, but at a slower rate (~4.5% in 10 hours) than when exposed to air at 1 atmosphere pressure.

Figure 22. Relative Young's modulus as a function of time in air at room temperature for specimen HP-19 (micro-cracked)

All microcracked specimens tested showed this aging effect after thermal cycling. The exact mechanism for this was not conclusively determined in this study, but it is apparent that there is an atmospheric effect upon the microcracking. This subject was discussed in a recent study on aluminum niobate and it was felt that a stress-corrosion enhanced crack growth mechanism was responsible (69). Other investigators have reported on slow crack growth in glass where water vapor is credited with enhancing crack growth by a stress-corrosion mechanism (70). The glass studies dealt with externally loaded specimens. The microcracked hafnium oxide, although not externally loaded, did contain internal microstresses necessary for microcrack formation and growth. Thus an analogy can be drawn between the two situations and the stress-corrosion phenomenon considered as a possible mechanism.

Further investigation of this occurrence provided some additional insight. A microcracked specimen was thermally cycled to achieve microcrack healing. On cooling to 400°C the moduli were higher than during the heating. When the specimen was exposed to air at this temperature the moduli dropped abruptly. Therefore it was apparent that the atmospheric effect could take place well above room temperature. Another test performed at room temperature involved exposure of the specimen (after microcrack healing) to dry nitrogen. The effect upon the moduli was the same as when the specimen was

exposed to air.

This suggests that perhaps water vapor is not the key as might be anticipated from the conclusions of the glass/stress-corrosion studies. However, it cannot be assumed that a small amount of water did not accompany the nitrogen into the evacuated system. Whatever atmospheric element was responsible for this effect, it is apparent that only a small amount was necessary as witnessed by the fact that crack formation could occur in as little as a 5 μm vacuum.

Additional evidence of the atmosphere effect was exhibited by the microcracked materials when exposed to the evacuated environment. The Young's modulus increased by as much as 5% simply by changing the specimen environment from air to vacuum ($<10^{-1}$ μm) at room temperature. This situation was not characteristic of all the microcracked specimens, but occurred commonly enough to be considered. No such occurrence had been observed for any of the crack-free specimens. Here it appears that microcracks can be healed without the application of thermal energy. Because the specimen is sonically vibrated during the measurements, there may be some amount of mechanical energy applied to crack healing that works cooperatively with the vacuum environment.

Based upon these observations of the atmospheric effect and with the knowledge that crack healing can be achieved at relatively low temperatures a consistent hypothesis can be

made. If many of the microcracks are formed by stress-corrosion enhanced by an element in the atmosphere, then it can be expected that the crack surfaces thus formed are contaminated with this or other elements from the atmosphere. For complete crack healing to occur it would be necessary for this contaminant to be removed. This could readily take place under vacuum and with increasing temperature. As crack healing can be achieved at relatively low temperatures it is apparent that the crack surfaces must only be brought close enough together so that the surfaces will adhere. If some crack surfaces are already close enough together to adhere, then possibly only the contaminant prevents the actual bonding of the surfaces. The vacuum environment and/or thermal energy may then remove the contaminant allowing the cracks to heal. This hypothesis suggests that the only microcracks that participate in the atmosphere effect are those which lie at or near the surface of the specimen where the atmosphere can readily make contact with the material.

Another effect of interest was that which the grain size produced on the properties of the microcracked material. The critical grain size for microcracking in hafnium oxide is now known, but the effect of further increasing grain size remains in question.

Fig. 23 shows the hysteresis loops generated for the relative Young's modulus (relative to the modulus of a crack-free

Figure 23. Relative Young's modulus as a function of temperature for specimens with average grain sizes of (A) 3 μm , (B) 9 μm , and (C) 16 μm . (Dotted line in (C) represents trend of Young's modulus for crack-free material)

specimen of the same density) during thermal cycling of three microcracked specimens. Several trends can be noted. The starting room temperature moduli lessened with increasing grain size, indicative of increased degrees of microcracking. This was generally true of all the microcracked specimens and was further supported by the internal friction which increased with grain size. The size of the loops increased similarly. This was an obvious consequence of lessening room temperature modulus values. If the relative Young's modulus starts at a low value and increases with heating to a crack-free level and finally forms the hysteresis loop upon cooling, then the loop should be larger than that formed with a higher starting relative modulus.

The plots also show the point at which microcrack formation began during cooling. The largest grain size (16 μm) specimen showed crack formation at 400°C indicated by the decreasing modulus at that point. The intermediate grain size (9 μm) material began cracking at about 250°C and the small grain size material showed no cracking even at room temperature. Only when exposed to air did the latter material show crack formation. This trend supported the conclusion drawn in the Literature Survey from the contentions of Blendell, et al. (39) and Cleveland (33) in that the formation of microcracks occurred at higher temperatures with increasing grain size.

On the basis of the trends in these properties, it appeared that the degree, or severity, of microcracking (reflec-

ted by decreasing moduli and increasing internal friction) was a function of the grain size. These results were consistent with the microcracking theory, but further study revealed that these patterns were not necessarily followed if additional factors were considered.

An example of this was the specimen mentioned in the Grain Size Effects section that was annealed to produce microcracked material. The anneal was carried out at 1400°C and the grain size increased to 3 μm . The internal friction of this specimen was 66×10^{-4} after annealing and was higher than that for the larger grain size specimens. The 60% modulus decrease associated with the microcracking also was excessive. Other microcracked specimens with comparable grain sizes had internal friction values between 13 and 21×10^{-4} and percent modulus decreases from 8 to 40%. Retreating the annealed specimen at 1000°C and slow cooling produced no change in the measured data. The failure of the anneal to bring the modulus and internal friction values into line with the data for the other specimens indicated a significant deviation from the degree of microcracking vs. grain size pattern. The only difference between this annealed specimen and the other specimens was the 1400°C annealing treatment. Thus the effect of thermal treatment became a factor in the degree of microcracking. As long as all the specimens maintained similar thermal histories (the preliminary anneal at 1000°C followed by slow

cooling) the degree of microcracking was fairly consistent with grain size, but additional thermal treatments could change the microcrack system and its apparent dependence on grain size.

Three case studies were performed to determine the effects of thermal treatments (thermal cycling and elevated temperature annealing) on the behavioral patterns of the microcracked material.

Case study I

Specimen S-1 was subjected to three thermal cycles, a grain growth anneal, and finally further thermal cycling. Young's modulus and internal friction were monitored during the cycling in order to observe any changes in the nature of the microcracked material.

The Young's modulus vs. temperature data for the first cycle were presented in Fig. 17 and the data for the third cycle are shown in Fig. 24A. The first cycle yielded the typical hysteresis loop. The modulus began rising at just above 300°C and the maximum rate of increase occurred between 700° and 1000°C. Above this point, the modulus decreased linearly to 1400°C.

The second and third cycles gave hysteresis loops of a different nature. As seen in Fig. 24A the modulus did not begin to swing upward until about 500°C. The maximum increase was similar to that in the initial cycle, but the major differ-

Figure 24. Young's modulus as a function of temperature for specimen S-1 (microcracked) for: (A) the third thermal cycle with re-heat, and (B) the thermal cycle after annealing

ence appeared above 1000°C. The modulus leveled off, dropped, and then began to increase again at 1200°C. This suggested a shift upward of the temperature range for crack healing.

The cooling procedure was altered slightly in the third cycle to investigate the crack free state of this specimen. Cooling to 500°C produced no apparent microcracking so the specimen was re-heated from this point. As the microcracks had already been healed by the initial heating, no further healing occurred during the re-heat. The modulus decreased linearly to about 1000°C above which it began to decrease at a greater rate in a non-linear manner. This was the grain boundary sliding effect that had been observed in the crack-free material, but was otherwise masked out by the crack healing effects in the microcracked material. The modulus decrease from grain boundary sliding undoubtedly occurred during the initial heating, but was in competition with the crack healing effects. For this particular cycle the grain boundary sliding apparently caused the small dip in the modulus curve at 1100°C, but further heating resulted in additional crack healing and continued modulus increase. After the re-heat, the specimen was cooled to room temperature with the modulus decreasing from crack formation as the temperature proceeded below 500°C.

Subsequently the specimen was annealed at 1575°C for 15 hours and then at 1000°C for 16 hours and cooled slowly. The

grain size increased from 9 to 14 μm and the density from 86.51% to 88.07% of theoretical density, but the Young's modulus decreased by 78% from 85.5 to 16.9 GN/m^2 . Compared to the empirically determined modulus ($\sim 180 \text{ GN/m}^2$) for a crack-free specimen of equal density, this was a net decrease in room temperature Young's modulus of greater than 90%. Based upon this figure, the degree of microcracking in this specimen was the highest found in any of the hafnium oxide specimens, even though the grain size was not the largest encountered in this study.

Fig. 24B shows the Young's modulus vs. temperature for the annealed specimen. The additional microcracking occurring from the anneal produced a profound effect on the nature of the hysteresis loop. The modulus remained nearly constant up to 1000°C indicating that very little crack healing was taking place. Above 1100°C rapid healing was evident and continued as the temperature rose to above 1500°C where sintering could be expected to contribute to crack healing. It is of interest to note that the modulus did not reach an apparently crack-free level and that to have done so would have required even higher temperatures. As cooling proceeded, the modulus began to decrease at 1200°C and returned very nearly to the starting room temperature value while under vacuum. Exposure to air brought about the final small amount of microcracking necessary to bring the modulus back to that value. Previous to the

anneal, the modulus decrease (crack formation) had started only after cooling below 500°C. Further cycling of the annealed material yielded the same crack healing/modulus increase pattern above 1000°C and the subsequent crack formation/modulus decrease beginning at 1200°C during cooling.

Case study II

Microcracked specimen HP-21 was subjected to a number of thermal cycles in continuance of the study of cycling effects. The Young's modulus vs. temperature for the first cycle is shown in Fig. 25A. The expected modulus increase was present up to 900°C and there was a corresponding internal friction peak. Surprisingly, significant hysteresis did not appear upon cooling as the modulus essentially returned along the same path defined by the heating values. The second cycle (Fig. 25B) was carried out up to 1200°C. The modulus increased, dipped at 1100°C, and then began to rise again. This behavior was very similar to that exhibited by specimen S-1 and shown in Fig. 24A, with the exception that the modulus for HP-21 showed very little hysteresis.

The third and fourth cycles were a combination cycle designed to compare modulus changes both with and without the presence of significant crack healing below 1000°C. The results are shown in Fig. 26A and B for the third and fourth cycles, respectively. In the third cycle, crack healing (as shown by the modulus increase) continued up to a temperature

Figure 25. Young's modulus as a function of temperature for specimen HP-21 (microcracked) for: (A) the first thermal cycle, and (B) the second thermal cycle

Figure 26. Young's modulus as a function of temperature for specimen HP-21 (microcracked) for: (A) the third thermal cycle, and (B) the fourth thermal cycle

of 1300°C and most likely some healing was realized as heating continued to 1500°C because the modulus showed only a small decrease from 1300° to 1500°C. During cooling, a reverse hysteresis was exhibited until the heating and cooling curves intersected between 800° and 1000°C. Normal hysteresis, although still minimal, was observed as cooling to room temperature proceeded. The reverse nature of the hysteresis above ~1000°C suggests two things. First, cracks began to form immediately as the cooling started and, second, additional microcrack damage had been imparted to the specimen by the thermal cycle so that the material showed a greater degree of microcracking during cooling than during heating. Some permanent crack healing (under vacuum) did exist during cooling and this resulted in the normal hysteresis below 1000°C.

The specimen was immediately re-heated from room temperature without an intervening exposure to air. This effectively prevented many of the microcracks from forming (and subsequently healing during heating) so that only the most unstable cracks could be observed during the fourth cycle. The modulus remained nearly constant with temperature up to 1300°C indicating only a small amount of crack healing to this point. At 1500°C, however, crack healing obviously was in effect as the modulus rose significantly. The immediate decrease in the modulus as cooling started indicated that this crack healing had little permanent effect. The small amount of hysteresis

on cooling showed that some crack healing occurred in the cycle, but this was substantially less than in the third cycle. After completion of the cycle and exposure of the specimen to air, the room temperature Young's modulus was 68.56 GN/m^2 . The as-fabricated Young's modulus for this specimen was 78.01 GN/m^2 . This 12% decrease in Young's modulus represented an increase in the degree of microcracking caused by the thermal cycling. Overall, the final Young's modulus value was 62% less than the empirically determined value for crack-free material of equal density.

Thermal expansion was measured on this specimen after the thermal cycling and the results are shown in Fig. 27. The expansion was generally linear during heating and cooling. The coefficient of expansion was determined to be $5.68 \times 10^{-6} / ^\circ\text{C}$, substantially lower than that shown by crack-free specimen HP-11.⁹ Comparison of results for specimen HP-21 to those for microcracked specimen HP-1 show some consistent differences.

As mentioned in the Temperature Effects section, the expansion and moduli results for HP-1 indicated crack healing during heating and crack free behavior during cooling. This was apparent from the hysteresis and the different behavior between the heating and cooling data. The results for HP-21 showed hysteresis, indicative of crack healing, but at no point in the temperature range investigated did crack free behavior become apparent. This was because the effect of crack healing

Figure 27. Linear thermal expansion for specimen HP-21 (microcracked)

achieved in heating was counteracted by immediate crack formation as cooling proceeded. As a result little difference was observed between the slopes (expansion coefficients) of the heating and cooling expansion curves. Some of the cracks remained healed during cooling to 400°C. This was indicated by the hysteresis and the abrupt expansion change at 400°C caused by crack formation. However, because cracks formed immediately upon cooling, crack-free modulus values and expansion were not observed as the specimen was cooled from elevated temperatures.

On the basis of these results, it was obvious that specimen HP-21 was extensively microcracked. Judging by comparative degrees of microcracking in the other microcracked specimens, it would be expected that HP-21 would have a relatively large grain size. Contrarily, the grain size was 2.5 μm , only slightly above the critical size for microcracking. This was further evidence that the degree of microcracking is not solely dependent upon grain size.

The two case studies for the microcracked specimens revealed some characteristics of microcracking that were not obvious from the previous measurements. It is apparent that the microcrack system in hafnium oxide can be changed by thermal treatment and the behavior of the material changes accordingly.

The facts that the hysteresis character of the modulus

diminished with thermal treatment and that crack healing shifted to higher temperatures indicated that a more unstable crack system had formed. It can be surmised that the micro-crack system became more extensive by an increase in the number of cracks and/or by an increase in the crack size. An increase in the number of cracks would explain decreasing room temperature moduli with successive thermal cycling, but does not necessarily account for the upward shift in crack healing temperatures and the increasing instability of the cracks.

An increase in the crack size could reasonably necessitate higher temperatures for healing and result in a more unstable crack system. Moreover, larger cracks may require mass transport (sintering) for healing. Crack healing observed at 1500°C in the case studies indicate sintering as a mechanism possibly instrumental in the healing process. Clearly, sintering can occur in hafnium oxide at 1500°C as much of the material was sintered in this range during specimen fabrication. The larger crack size could be achieved by a crack growth mechanism caused by thermal treatments. Alternately, crack growth could result from the combination of smaller cracks into a larger interconnected crack. In this case, both increased crack population and size would work cooperatively.

Interestingly, specimen HP-21 showed many of the exceptional characteristics (limited hysteresis and the unstable

crack system) during the first thermal cycle. Specimen S-1 exhibited these characteristics only after thermal treatments. This suggested that some phase of the thermal treatment of HP-21 prior to the modulus measurements contributed to this behavior.

The fabrication procedure for this specimen perhaps yields the answer. The specimen had been hot-pressed at 1500 °C and 4000 psi for 1 hour. The other hot-pressed specimens were fabricated under similar conditions, but at shorter hold times (2 to 10 minutes). Only HP-1 (also extremely microcracked) had been held for 1 hour, but at a lower pressure. The longer hold time possibly amounted to a thermal treatment that led to the exceptional behavior of this specimen. Definite conclusions cannot be drawn, but this situation suggests that fabrication parameters (in addition to subsequent thermal treatments) may have a profound effect upon the microcrack system.

Case study III

Microcracked specimen S-2 was thermally cycled to 1400°C eight times. Although a change in the character of the hysteresis loop (for the Young's modulus vs. temperature) was not observed, there was a significant change in the room temperature Young's modulus with thermal cycling.

The starting Young's modulus for this specimen was 112.06 GN/m²; ~24% less than the value for a crack-free specimen.

This degree of microcracking was not as large as for the specimens in the two previous case studies. The grain size for S-2 was found to be 2.5 μm .

In the initial cycle, the Young's modulus increased by 8.4% at room temperature simply by putting the specimen under vacuum. This phenomenon was discussed previously in this section. A similar increase of 2.5% occurred at the beginning of cycle 2, but in later cycles this effect either disappeared or was too small to observe.

Plots of the data for the first and final cycles are shown in Fig. 28A and B, respectively. The hysteresis loops show that no major changes from thermal cycling had occurred in the crack healing process. The only notable differences are in the lower temperature heating portion of the loops and in the size of the loops. The heating curve for the initial loop begins its upward shift at 500°C whereas the curve for the final loop begins rising at a lower temperature. This is a result of the room temperature healing noted in the initial cycle facilitated by the vacuum. Because of room temperature microcrack healing in the initial cycle, there was less healing to be accomplished at the lower temperatures. In the final cycle the microcracks were less stable and did not heal under vacuum at room temperature, but required some thermal energy for healing.

The increased size of the final loop is the direct result

Figure 28. Young's modulus as a function of temperature for specimen S-2 (microcracked) for: (A) the first thermal cycle, and (B) the eighth thermal cycle

of the change in room temperature Young's modulus effected through the cycling. After the final cycle, the room temperature modulus was decreased by 13.2% relative to the starting value. This decrease was not continuous as cycling progressed. Decreases with each cycle were observed through the first four cycles with a total decrease of 15.3% being found at the end of cycle 4. The modulus subsequently increased through the end of cycle 7 yielding a new total decrease of 10.1%. The final cycle brought the total decrease to 13.2%.

These results presented additional evidence of permanent crack healing. Between cycles, the specimen was exposed to air until the modulus stabilized so that incompleteness of the atmospheric effect could not be responsible for higher modulus values. Nor did the density of the specimen change during cycling. Thus permanent crack healing could be realized, but the overall effect of cycling was to decrease the modulus. The lowered modulus resulting from cycling was consistent with the results of the two previous case studies.

The specimen had, of course, been annealed at 1000°C in air and cooled slowly before cycling. A similar anneal after cycling brought about a gain in the modulus yielding a final total decrease of ~5% in the Young's modulus. The 5% difference between the "before and after" modulus values represented the change in the degree of microcracking caused by the thermal cycling. The final modulus increase brought about by the

anneal was further evidence that some permanent crack healing could be achieved through proper annealing and sufficiently slow cooling from the anneal temperature.

The constant nature of the hysteresis loops for specimen S-2 was unlike the behavior found in the other case studies. No shift in the crack healing temperature range was exhibited and in every cycle crack-free behavior occurred during cooling resulting in a crack-free modulus at room temperature under vacuum. This indicated that the stability of the crack system had not changed. The low degree of microcracking in specimen S-2 (relative to S-1 and HP-21) might have been the reason behind this. Possibly further thermal cycling would have eventuated a change in behavior indicative of decreasing stability of the microcrack system.

Conclusively, thermal cycling resulted in an increased degree of microcracking. A less stable crack system could be achieved as well, but apparently this occurred only in material with a relatively high degree of microcracking.

CONCLUSIONS

- 1) Monoclinic hafnium oxide undergoes extensive microcracking during cooling from an elevated temperature when the grain size exceeds a critical value between 2 and 3 μm . This condition is attributed to the relatively high thermal expansion anisotropy of the monoclinic form of this material.
- 2) When the grain size is approximately 2 μm or less, sufficient stresses for microcracking do not develop and the hafnium oxide is crack-free.
- 3) The crack-free material yields elastic moduli that give relations with porosity as (in GN/m^2):
$$E = 283.6 \exp(-4.17P)$$
$$G = 109.2 \exp(-3.93P)$$
- 4) Microcracked hafnium oxide exhibits abnormally low elastic moduli. The effects of the microcracking are much more pronounced than the porosity effects on the moduli.
- 5) The internal friction for crack-free material increases with porosity while that for microcracked material is substantially higher and any porosity effects are subsequently masked out. The internal friction measurements are very sensitive to microcracking and thus are instrumental in the determination of the critical grain size for microcracking.

- 6) The elastic moduli for crack-free hafnium oxide decrease linearly with temperature up to about 1200°C; above which grain boundary sliding occurs resulting in non-linear behavior. The linear modulus decrease is $\sim 1\%/100^\circ\text{C}$.
- 7) Microcracked hafnium oxide exhibits hysteresis between the heating and cooling values for the moduli vs. temperature. This is attributed to a crack healing process activated as the material is heated to an elevated temperature. The crack healing results in increased moduli and a crack-free state may be reached at elevated temperatures. Upon cooling, crack-free behavior of the moduli can occur to the point where microcrack formation begins.
- 8) The internal friction for the crack-free material shows no large changes with temperature until the grain boundary sliding range is reached. Internal friction for the microcracked material increases during the healing process and this is attributed to friction between the opposite surfaces of the microcracks. As the healing process nears completion, the internal friction decreases and lower values are maintained during cooling until crack formation begins; thus yielding hysteresis between the heating and cooling values.
- 9) A mechanical model incorporating elastic and viscous components can be used to describe the simultaneous behavior of the modulus and the internal friction during the crack healing process.

- 10) Thermal expansion for the crack-free material is generally linear up to 1250°C and the coefficient of linear thermal expansion is $6.3 \times 10^{-6}/^{\circ}\text{C}$. Microcracked material shows lower expansion on heating, exhibits hysteresis between the heating and cooling curves and may possess crack-free behavior during cooling. Again this is the result of the crack healing process.
- 11) Crack healing in hafnium oxide achieved at elevated temperatures generally is followed by some crack formation during cooling to room temperature. However, all or part of the healing can be retained at room temperature if the material is kept under vacuum. Exposure to air results in slow crack growth that may require several hours to reach completion. Thus an atmospheric effect is suspected of promoting microcrack formation and growth.
- 12) There is a tendency for the degree of microcracking to increase with grain size in hafnium oxide. This is evidenced by the decrease in room temperature moduli and increase in corresponding internal friction with increasing grain size. Further support of this trend is offered by the fact that increasingly larger-grained bodies tend to exhibit microcrack formation at progressively higher temperatures during cooling.
- 13) Thermal treatments of microcracked hafnium oxide can effect a change in the degree of microcracking that results in a deviation from the grain size vs. degree of

microcracking trend.

- 14) With proper annealing and sufficiently slow cooling from elevated temperatures, it is possible in some instances to obtain permanent microcrack healing that is immune to the atmospheric effect.
- 15) Thermal cycling through the crack healing/formation cycle can result in a greater degree of microcracking without any apparent changes in the grain size or density of the microcracked hafnium oxide. Elevated temperature annealing for promoting grain growth produces similar results. Additionally, it is possible to attain a sufficiently high degree of microcracking to form a more unstable microcrack system that requires much higher temperatures than normal to bring about significant crack healing.
- 16) The presence of microcracking in hafnium oxide may have significant effects on the engineering properties of this material. Of key importance is the possibility of microcrack-enhanced thermal shock resistance in hafnium oxide, which, like many ceramics, can be prone to thermal shock.

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APPENDIX A. SPECIMEN CHARACTERIZATION DATA

Table A1. Mass and dimensions of each specimen

Specimen	Mass (gm)	Thickness (cm)	Width (cm)	Length (cm)
S-1 ^a	17.0516	0.432	0.747	6.04
S-2	14.5445	0.323	0.978	5.31
HP-1 ^b	35.3299	0.304	1.595	7.45
HP-3	33.1222	0.336	1.603	7.28
HP-4	29.0852	0.269	1.575	7.43
HP-5	31.9827	0.363	1.557	7.43
HP-6	17.4678	0.339	0.985	5.85
HP-7	21.2949	0.406	0.972	5.86
HP-8	15.0764	0.277	0.982	5.85
HP-9	15.0835	0.301	0.976	5.81
HP-10	19.3237	0.388	0.990	5.83
HP-11	18.5916	0.340	0.966	5.82
HP-12	19.9471	0.420	0.972	5.77
HP-13	15.8287	0.338	0.987	5.82
HP-14	11.6146	0.212	0.974	5.83
HP-15	16.1157	0.363	0.968	5.13
HP-16	17.4685	0.338	0.980	5.70
HP-17	7.3159	0.173	0.964	5.65
HP-18	9.4287	0.211	0.964	5.70
HP-19	17.7736	0.341	0.966	5.675
HP-20	5.0002	0.186	1.014	3.39
HP-21	15.7760	0.287	1.038	5.95

^aS = sintered.^bHP = hot-pressed.

Table A2. Density, volume fraction porosity and grain size of each specimen

Specimen	Density (gm-cm ⁻³)	Volume fraction porosity	Average grain size (μm)
S-1	8.7483	0.1349	9.2
S-2	8.6709	0.1426	2.5
HP-1	9.7803	0.0329	16.0
HP-3	8.4472	0.1647	~0.6
HP-4	9.2395	0.0864	3.2
HP-5	7.6161	0.2469	<1
HP-6	8.9422	0.1158	3.1
HP-7	9.2084	0.0894	1.8
HP-8	9.4744	0.0631	2.3
HP-9	8.8371	0.1262	<1
HP-10	8.6289	0.1467	<1
HP-11	9.7261	0.0383	2.2
HP-12	8.4681	0.1626	<1
HP-13	8.1525	0.1939	<1
HP-14	9.6481	0.0460	2.3
HP-15	8.9403	0.1090	~0.7
HP-16	9.2521	0.0851	2.3
HP-17	7.7642	0.2322	<1
HP-18	8.1324	0.1958	<1
HP-19	9.5078	0.0598	1.6
HP-20	7.8205	0.2267	<1
HP-21	8.9002	0.1199	2.5

APPENDIX B. ROOM TEMPERATURE ELASTIC MODULUS AND
INTERNAL FRICTION DATA

Table B1. Room temperature elastic moduli of each specimen

Specimen	Young's modulus (GN/m ²)	Shear modulus (GN/m ²)	Bulk modulus (GN/m ²)
S-1	91.54	37.83	52.60
S-2	112.06	43.63	86.55
HP-1	63.29	25.90	37.93
HP-3	148.08	59.36	97.66
HP-4	121.44	50.86	66.14
HP-5	100.58	40.98	61.45
HP-6	141.89	57.11	91.75
HP-7	198.57	78.57	140.05
HP-8	216.20	85.33	154.59
HP-9	161.83	65.31	103.32
HP-10	147.88	59.88	92.91
HP-11	239.55	92.00	201.58
HP-12	146.14	58.97	93.33
HP-13	138.10	54.57	98.11
HP-14	234.85	90.10	198.94
HP-15	181.17	71.59	128.68
HP-16	182.94	72.30	129.83
HP-17	102.80	41.78	63.50
HP-18	121.68	49.14	77.45
HP-19	213.78	83.88	157.86
HP-20	103.05	43.06	56.59
HP-21	78.01	35.62	32.11

Table B2. Poisson's ratio, internal friction and microcrack status of each specimen at room temperature

Specimen	Poisson's ratio	Internal friction $\times 10^4$	Status
S-1	0.2100	35.98	MC ^a
S-2	0.2840	-	MC
HP-1	0.2219	44.90	MC
HP-3	0.2473	-	OK ^b
HP-4	0.1940	21.19	MC
HP-5	0.2272	3.32	OK
HP-6	0.2423	20.14	MC
HP-7	0.2637	1.56	OK
HP-8	0.2669	8.42	OK
HP-9	0.2390	1.39	OK
HP-10	0.2347	0.98	OK
HP-11	0.3019	0.55	OK
HP-12	0.2390	2.20	OK
HP-13	0.2654	5.67	OK
HP-14	0.3033	5.90	OK
HP-15	0.2654	1.95	OK
HP-16	0.2652	13.51	MC
HP-17	0.2302	12.29	OK
HP-18	0.2381	5.46	OK
HP-19	0.2743	4.66	OK
HP-20	0.1965	-	OK
HP-21	0.0951	-	MC

^aMC = microcracked.^bOK = crack-free.

APPENDIX C. ELEVATED TEMPERATURE ELASTIC MODULUS AND
INTERNAL FRICTION DATA

Table C1. Elevated temperature elastic moduli and internal friction for specimen HP-1

Temperature (°C)	Young's modulus (GN/m ²)	Shear modulus (GN/m ²)	Internal friction (x10 ⁴)
25	63.29	25.90	44.90
99	63.07	25.76	53.43
204	64.72	26.30	63.93
323	67.83	27.37	88.44
415	71.05	28.47	77.37
506	77.53	30.71	70.06
618	89.19	34.77	110.73
721	133.96	52.40	176.84
762	148.19	58.45	298.60
819	180.73	65.05	456.24
879	187.82	66.88	385.36
968	197.35	70.12	286.60
1018	206.60	72.63	301.76
1112	212.18	74.10	237.62
1215	201.59	71.79	-
1302	189.97	67.65	-
1407	182.02	65.95	-
1449	177.95	64.39	-
1497	174.94	-	-
1232	178.74	64.40	-
790	225.88	79.42	83.39
669	229.77	81.45	32.39
522	234.01	83.25	32.18
359	231.68	82.95	33.76
25	175.52	67.93	57.32
25(in air)	63.29	25.90	44.90

Table C2. Elevated temperature elastic moduli and internal friction for specimen HP-11

Temperature (°C)	Young's modulus (GN/m ²)	Shear modulus (GN/m ²)	Internal friction (x10 ⁴)
25	239.55	92.00	0.55
99	237.26	90.93	0.22
171	235.38	89.99	0.22
253	233.10	89.16	0.31
295	231.96	88.61	-
324	231.26	88.44	0.31
404	229.07	87.46	1.22
472	227.28	86.51	0.61
556	225.09	85.62	0.46
630	222.92	84.92	0.34
698	220.63	84.21	0.46
777	218.16	83.22	0.43
853	215.09	82.05	0.70
921	211.71	80.78	0.86
1011	208.36	79.17	0.77
1089	205.34	77.92	0.81
1207	198.86	75.67	1.98
1293	191.64	73.70	-
1405	173.43	71.50	-
1506	156.03	69.28	-
1227	195.96	74.94	2.00
1006	207.77	78.29	1.30
529	223.33	85.16	0.49
25	235.53	90.15	0.57
25(in air)	234.49	90.18	0.55

Table C3. Elevated temperature bulk modulus for specimen HP-11

Temperature (°C)	Bulk modulus (GN/m ²)
25	201.58
99	202.44
171	204.16
253	201.50
295	202.32
324	200.22
404	200.50
472	203.14
556	202.16
630	198.25
698	193.52
777	192.04
853	189.39
921	186.08
1011	188.56
1089	187.64
1207	178.11
1293	159.78
1405	100.61
1506	69.53
1227	169.56
1006	200.05
529	197.20
25(in air)	195.53

Table C4. Elevated temperature elastic moduli and internal friction for specimen HP-19

Temperature (°C)	Young's modulus (GN/m ²)	Shear modulus (GN/m ²)	Internal friction (x10 ⁴)
25	213.78	83.82	4.66
218	207.99	81.31	3.75
405	204.31	79.68	3.12
605	200.38	78.27	3.95
811	196.44	76.54	3.37
1009	191.88	74.50	5.07
1203	185.44	72.12	9.21
1395	177.71	68.94	14.09
1501	173.67	66.78	-
25	213.78	83.82	-

Table C5. Elevated temperature elastic moduli and internal friction for specimen HP-19 (after grain growth anneal).

Temperature (°C)	Young's modulus (GN/m ²)	Shear modulus (GN/m ²)	Internal friction (x10 ⁴)
25	173.14	69.76	50.60
254	165.33	66.33	24.75
511	163.42	65.25	19.37
724	169.55	67.39	24.67
808	177.65	70.37	25.85
856	183.14	72.26	26.22
1023	196.66	76.06	23.79
1153	193.18	74.56	25.12
540	213.72	82.09	16.94
25	222.77	87.99	19.59
25(in air)			

Table C6. Elevated temperature Young's modulus for specimen S-1

Temperature (°C)	Young's modulus (GN/m ²)
25	89.43
121	88.01
255	86.71
439	96.50
584	99.23
713	102.32
821	118.74
942	132.24
1013	134.22
1079	131.42
1213	127.48
1348	120.89
1416	116.78
1100	126.87
879	145.74
528	154.50
272	156.30
25	136.00
25(in air)	85.40

Table C7. Young's modulus as a function of time at room temperature in air for specimen HP-19

Time	Young's modulus (GN/m ²)	Relative modulus (%)
0	213.78	100.0
2	209.72	98.1
5	208.65	97.6
10	207.15	96.9
15	205.87	96.3
20	204.37	95.6
25	203.30	95.1
30	202.24	94.6
35	201.38	94.2
40	200.74	93.9
45	199.88	93.5
50	199.03	93.1
55	197.96	92.6
60	197.11	92.2
65	195.82	91.6
75	194.75	91.1
85	193.90	90.7
95	193.04	90.3
105	191.97	89.8
115	191.33	89.5
125	190.48	89.1
135	189.62	88.7
165	187.27	87.6
195	184.92	86.5
225	183.00	85.6
265	180.64	84.5
285	179.79	84.1
315	178.29	83.4
345	177.01	82.8
470	172.95	80.9
585	170.60	79.8
705	167.60	78.4
925	165.47	77.4
1465	161.19	75.4
1525	160.55	75.1
1630	160.12	74.9
1705	159.91	74.8
1925	159.91	74.8
1965	159.91	74.8
2050	159.91	74.8
5870	158.62	74.2

Table C8. Elevated temperature Young's modulus and internal friction for specimen S-1 with re-heat data

Temperature (°C)	Young's modulus (GN/m ²)	Internal friction (x10 ⁴)
25	85.40	35.98
434	83.03	45.71
609	87.35	43.54
691	91.33	50.04
730	93.77	56.42
773	103.05	85.36
803	111.88	83.72
842	123.21	101.25
867	128.74	115.57
918	136.42	150.12
956	138.82	204.87
1004	139.40	272.10
1095	135.83	295.16
1199	137.93	207.31
1255	137.36	290.24
979	154.01	248.78
885	159.81	89.76
728	163.19	88.40
503	166.76	66.72
<u>Re-Heat</u>		
714	161.59	80.25
843	159.35	84.82
909	158.09	100.31
959	156.52	143.92
1003	154.44	197.89
1071	149.49	290.24
1094	147.41	322.49
1156	144.54	238.55
1197	143.48	232.19
1254	139.72	272.10
1311	138.47	272.10
25(in air)	85.50	-

Table C9. Elevated temperature Young's modulus and internal friction for specimen S-1 (after grain growth anneal)

Temperature (°C)	Young's modulus (GN/m ²)	Internal friction (x10 ⁴)
25	16.92	144.69
145	14.60	123.23
283	14.25	115.04
400	13.48	72.76
541	12.89	53.65
615	13.08	51.55
704	13.66	36.17
800	14.19	34.29
897	15.50	54.65
992	17.21	50.93
1088	19.90	63.03
1202	32.76	78.27
1310	57.55	45.96
1406	80.63	86.03
1533	86.99	-
1375	93.39	-
1221	94.94	87.81
1112	92.04	98.95
1050	87.37	176.8
931	77.30	155.27
803	64.52	85.45
574	42.94	97.94
385	31.29	71.93
182	26.50	46.30
25	21.62	34.60
25(in air)	16.92	-

Table C10. Elevated temperature Young's modulus and internal friction for specimen HP-21 (first cycle)

Temperature (°C)	Young's modulus (GN/m ²)	Internal friction (x10 ⁴)
25	78.01	44.80
243	82.10	22.30
526	111.37	39.90
606	116.85	132.60
696	123.79	70.70
762	127.61	65.20
836	131.00	57.90
889	131.53	54.00
943	131.66	-
726	130.46	56.10
531	109.10	32.10
168	84.12	12.80
25	82.46	11.60
25(in air)	78.01	-

Table C11. Elevated temperature Young's modulus and internal friction for specimen HP-21 (second cycle)

Temperature (°C)	Young's modulus (GN/m ²)	Internal friction (x10 ⁴)
25	80.59	42.70
162	81.60	64.60
269	86.54	68.50
399	100.66	41.30
516	111.03	60.10
708	127.20	41.90
899	132.41	77.60
1000	130.21	63.30
1097	127.40	58.40
1211	135.99	57.10
1029	138.31	71.50
25	94.08	34.80
25(in air)	78.01	-

Table C12. Elevated temperature Young's modulus and internal friction for specimen HP-21 (third cycle)

Temperature (°C)	Young's modulus (GN/m ²)	Internal friction (x10 ⁴)
25	78.01	36.90
162	76.61	31.80
258	76.41	34.70
346	76.30	33.00
432	76.34	35.20
512	77.61	38.10
604	79.86	40.20
692	84.62	43.20
796	91.87	50.50
892	106.73	55.00
949	112.60	49.50
998	113.73	48.60
1076	118.47	41.60
1146	120.89	35.20
1223	121.26	35.60
1305	122.53	36.80
1390	121.42	44.70
1491	119.59	85.50
1504	119.57	93.60
1546	118.11	143.10
1282	104.72	30.50
1012	104.19	34.30
795	105.81	106.10
457	106.09	76.70
184	104.95	76.70
25	104.31	74.90

Table C13. Elevated temperature Young's modulus and internal friction for specimen HP-21 (fourth cycle)

Temperature (°C)	Young's modulus (GN/m ²)	Internal friction (x10 ⁴)
25	104.31	74.90
693	98.48	59.50
1004	99.01	54.00
1305	101.11	34.10
1539	115.67	454.70
1497	112.35	318.30
1389	108.17	73.50
1289	105.94	32.30
1105	106.01	27.60
1019	105.29	31.40
858	105.59	18.50
687	105.90	16.90
463	106.37	20.90
278	106.09	22.40
173	105.72	-
25	105.50	-
25(in air)	68.56	-

Table C14. Elevated temperature Young's modulus for specimen S-2 (first cycle)

Temperature (°C)	Young's modulus (GN/m ²)
25	121.51
127	119.46
254	116.12
361	113.67
492	112.00
572	113.67
607	115.25
682	117.55
758	120.49
831	121.26
894	121.51
999	125.23
1090	133.05
1199	142.03
1305	140.00
1409	137.22
1224	143.17
1036	147.99
862	151.73
679	155.32
466	158.43
284	159.91
85	161.41
25	162.56
25(in air)	110.26

Table C15. Young's modulus for specimen S-2 at end of each cycle at room temperature in air

Cycle	Young's modulus at end of cycle	% change in Young's modulus relative to initial value
Initial value	112.06	-
1	110.26	1.6
2	107.36	4.2
3	98.63	12.0
4	94.97	15.3
5	-	-
6	97.66	12.9
7	100.78	10.1
8	97.27	13.2

Table C16. Elevated temperature Young's modulus for specimen S-2 (eighth cycle)

Temperature	Young's modulus (GN/m ²)
25	101.44
246	97.66
384	97.11
520	97.64
620	98.46
700	100.61
796	102.75
882	109.54
993	121.39
1094	133.56
1187	141.66
1305	139.46
1406	135.32
1216	142.25
1018	147.79
868	151.51
699	155.10
302	159.09
25	160.98
25(in air)	97.27

APPENDIX D. THERMAL EXPANSION DATA

Table D1. Percent linear thermal expansion of specimens HP-1 and HP-11 (heating and cooling)

Temp. (°C)	HP-1 (Microcracked)		HP-11 (Crack-free)	
	Heating	Cooling	Heating	Cooling
25	-	-	-	0.060
50	0.014	0.043	0.014	0.069
100	0.030	0.038	0.039	0.090
150	0.051	0.032	0.064	0.118
200	0.077	0.027	0.097	0.154
250	0.098	0.025	0.126	0.171
300	0.119	0.019	0.155	0.201
350	0.139	0.019	0.187	0.234
400	0.165	0.030	0.224	0.265
450	0.179	0.049	0.254	0.300
500	0.193	0.078	0.286	0.335
550	0.219	0.115	0.327	0.370
600	0.241	0.138	0.369	0.402
650	0.261	0.182	0.404	0.436
700	0.279	0.216	0.436	0.468
750	0.300	0.248	0.471	0.503
800	0.318	0.276	0.511	0.535
850	0.332	0.305	0.541	0.567
900	0.344	0.329	0.574	0.596
950	0.368	0.350	0.607	0.642
1000	0.392	0.372	0.639	0.654
1050	0.416	0.390	0.667	0.678
1100	0.434	0.404	0.697	0.702
1150	0.453	0.409	0.726	0.728
1200	0.487	0.436	0.760	0.765
1250	0.525	0.493	0.810	0.811

Table D2. Percent linear thermal expansion of specimen HP-21 after thermal cycling

Temperature (°C)	Heating	Cooling
25	0.000	0.000
50	0.022	-
100	0.050	-
150	0.083	-0.027
200	0.120	-0.016
250	0.150	-0.009
300	0.178	0.007
350	0.205	0.029
400	0.237	0.058
450	0.259	0.090
500	0.285	0.124
550	0.312	0.161
600	0.343	0.192
650	0.372	0.223
700	0.400	0.251
750	0.429	0.283
800	0.464	0.313
850	0.493	0.347
900	0.523	0.379
950	0.557	0.405
1000	0.590	0.435
1050	0.619	0.469
1100	0.644	0.513