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HIGH-TEMPERATURE X-RAY DIFFRACTION
STUDY OF $\text{HfTiO}_4\text{-HfO}_2$ SOLID
SOLUTIONS

D. A. Carpenter

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HIGH-TEMPERATURE X-RAY DIFFRACTION STUDY OF HfTiO₄-HfO₂ SOLID SOLUTIONS

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ABSTRACT

High-temperature X-ray diffraction techniques were used to determine the axial thermal expansion curves of $\text{HfTiO}_4\text{-HfO}_2$ solid solutions as a function of composition. Data show increasing anisotropy with increasing HfO_2 content. An orthorhombic-to-monoclinic phase transformation was detected near room temperature for compositions near the high HfO_2 end of the orthorhombic phase field and for compositions within the two-phase region (HfTiO_4 solid solution plus HfO_2 solid solution). An orthorhombic-to-cubic phase transformation is indicated by data from oxygen-deficient materials at > 1873 K.

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SUMMARY

Thermal-expansion data have been collected, by high-temperature X-ray diffraction, for $\text{HfTiO}_4\text{-HfO}_2$ solid solutions as a function of composition. The a axis expands by about the same amount, regardless of composition within the single-phase region; b axis expansion decreases and becomes very negative as the high HfO_2 end of the phase field is approached; c axis expansion also decreases with increasing HfO_2 content, but to a lesser extent than b.

An orthorhombic-to-monoclinic phase change was observed near room temperature. This transformation has characteristics in common with martensitic phase changes. The transformation was observed most readily in the high HfO_2 end of the orthorhombic phase field as well as in the neighboring two-phase field. An orthorhombic-to-cubic transformation was observed in oxygen-deficient samples within the orthorhombic phase field at temperatures > 1873 K.

INTRODUCTION

A recent survey of approximately 40 mixed metal oxide compositions was conducted in a search for systems having low thermal expansion and relatively high melting points (> 1600 K).⁽¹⁾ Certain hafnium oxide (HfO_2)-titanium oxide (TiO_2) compositions showed especially interesting properties having relatively high melting points⁽¹⁾ and low thermal expansion coefficients up to at least 1273 K.⁽¹⁻³⁾ The HfO_2 - TiO_2 system appears to be similar to the zirconium oxide (ZrO_2)-titanium oxide (TiO_2) system⁽⁴⁾ in that terminal solid solutions form over relatively large composition ranges.⁽⁵⁾ An orthorhombic (HfTiO_4) compound forms at about 50 mol % HfO_2 , and the compound exists over a large composition range.⁽²⁾

The bulk thermal expansion curves of sintered compacts containing 43.2 to 77.4 mol % HfO_2 have been reported from room temperature to about 1273 K.⁽¹⁻³⁾ X-ray diffraction thermal expansion data have been reported for compositions containing 50 and 63 mol % HfO_2 from room temperature to 1173 K.⁽²⁾ The bulk thermal expansion curves are significantly lower than the average axial expansion curves determined by X-ray diffraction. According to Lynch and Morosin,⁽²⁾ the difference is due to microcracking within the bulk specimens caused by the large anisotropy in the thermal expansion of the individual grains. Bulk thermal expansion data by Simpson⁽³⁾ and by Holcombe and coworkers⁽¹⁾ show that the bulk expansion decreases with increasing HfO_2 content, at least through 66.7 mol % HfO_2 . One possible explanation is that the degree of anisotropy increases with increasing HfO_2 content since the X-ray diffraction data by Lynch and Morosin indicate an increase in expansion along the a axis and a decrease in the expansion along the c axis on going from the 50 to the 63 mol % HfO_2 . Additional X-ray diffraction thermal expansion data from room temperature to approximately 1873 K for five compositions throughout the orthorhombic hafnium titanate (HfTiO_4) composition range are presented and examined in this report to determine the existence of any further trends.

During this study (conducted at the Oak Ridge Y-12 Plant),^(a) an orthorhombic-to-monoclinic phase transformation was detected that is apparently diffusionless. Experimental observations were made of this transformation. Also, an investigation was made of a phase transformation that was reported by Simpson⁽³⁾ to occur at about 2143 K.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Energy Research and Development Administration.

X-RAY DIFFRACTION STUDY OF SOLID SOLUTIONS

EXPERIMENTAL WORK

Samples with selected ratios of HfO_2 and TiO_2 were prepared by coprecipitation of the mixed hydrous oxides. Spectroscopically pure HfO_2 (99.99%) was dissolved in nitric acid and mixed with an aqueous solution of TiCl_3 oxidized to Ti(IV) with HNO_3 . This solution was poured into dilute (1:5) excess ammonium hydroxide. The resulting precipitate was filtered, dried at 473 K, then fired at 1273 K.

High-temperature X-ray diffraction was carried out, using a commercially available strip heater-type^(b) diffractometer attachment. A Pt/40% Rh heating-element sample support was used. The heating element was annealed at 1173 K for 16 hours after being formed. Samples were painted onto the strip from an alcohol slurry. Care was taken to produce a thin, homogeneous layer on the front of the element in order to minimize thermal gradients. Two Pt-Pt/10% Rh thermocouples were spot welded to the back of the element—one for temperature control and the other for temperature measurement. The latter thermocouple was calibrated against the thermal expansion of spectroscopically pure thorium dioxide (ThO_2). The thermal expansion curve of ThO_2 was calculated by fitting data from four sources⁽⁶⁻⁹⁾ to a second-degree polynomial:

$$y = 1.91 \times 10^{-2} + 8.47 \times 10^{-4}T + 9.5 \times 10^{-8}T^2$$

where:

y represents the percent thermal expansion, and

T the temperature in °C.

Lattice parameters were determined from approximately 17 low-angle reflections (23 to 70° 2 θ) by a least-squares refinement technique. Computations were made by using a lattice-parameter refinement program written by Williams.⁽¹⁰⁾ Each sample was held at 1873 K for about one hour to ensure complete reaction and to sinter the sample so as to increase the thermal conductivity and decrease the thermal gradient through the sample. Runs were made in a helium atmosphere, and some loss of oxygen by the samples was evidenced by the gray color of the specimens after heating. Diffraction scans were made at temperatures below 1873 K after cooling and holding at temperature for one hour.

In using low-angle diffraction lines for thermal expansion measurements, a systematic error may be introduced by the movement of the heating element caused by thermal expansion of the element. A translation adjustment on the furnace was used to compensate for this movement. The amount of heating-element movement from thermal expansion was determined during the calibration of the thermocouple by the following procedure: At each temperature, the position of the furnace was adjusted until the same lattice parameter was

(b) Manufactured by the Materials Research Corporation.

calculated from both a high-angle and a low-angle line of ThO_2 . The amount of adjustment was plotted as a function of temperature and the data least-squares fitted to the straight line. The amount of compensation for the heating-element expansion during a HfTiO_4 thermal expansion run was then determined from this least-squares line.

RESULTS

Figures 1 through 3 present the lattice parameter-versus-temperature curves along the a , b , and c axes of the orthorhombic unit cell for $\text{HfO}_2\text{-TiO}_2$ compositions containing 47.5, 56.4, 63.0, 66.7, and 70.9 mol % HfO_2 . Figures 4 through 6 show the percent thermal-expansion curves for the same compositions. Table 1 lists thermal expansion coefficients along each axis at room temperature. For all compositions except 70.9 mol % HfO_2 , the thermal-expansion curves along a are linear, and the thermal expansion coefficient, α_a , is practically independent of composition. The expansion curves along the b and c axes are more complex. Along the b axis, the expansion curves decrease with composition. At each composition, α_b is initially very low or negative. As the temperature increases, α_b tends to increase, pass through zero, and become positive. The temperature range through which α_b passes through zero is a function of composition. At 47.5 mol % HfO_2 , α_b is approximately zero at room temperature; while, at 66.7 mol % HfO_2 , α_b is approximately zero at 1573 K. Along the c axis, the expansion curves are approximately linear from 47.5 through 56.4 mol % HfO_2 . At 66.7 mol % HfO_2 , the expansion curve along c appears to have some curvature. The expansion coefficient decreases from 47.5 to 66.7 mol % HfO_2 . At 70.9 mol % HfO_2 , the expansion curves along b and c show large deviations from the trends established by the other curves. This departure will be discussed subsequently.

Figure 7 contains the average axial thermal expansion curves for the compositions studied. The average axial-expansion curves decrease with composition through the 66.7 mol % HfO_2 sample. The 70.9 mol % HfO_2 curve again shows deviations from the lower compositions.

Figure 8 indicates the variation of room-temperature lattice parameters as a function of composition for the compositions used in this study, along with the data of previous investigators.(11, 12)

An orthorhombic-to-monoclinic phase transformation was observed in selected compositions from 63 through 80.7 mol % HfO_2 on cooling to room temperature. Although the exact composition limits were not determined, the transformation was observed in compositions ranging from 63.0 to 80.9 mol % HfO_2 . In the compositions greater than 70.9 mol % HfO_2 , this transformation product (hereafter referred to as the MTP phase for "monoclinic transformation product") was observed in addition to the precipitation of monoclinic HfO_2 solid solution (hereafter referred to as the PSS phase for "precipitated solid solution") from the orthorhombic HfTiO_4 solid solution. For example, a composition containing 75 mol % HfO_2 is single phase (orthorhombic HfTiO_4 solid solution) at temperatures close to 1973 K. On cooling below 1873 K, the monoclinic HfO_2 solid solution (PSS) phase appears, and its X-ray peaks slowly increase in intensity with both time and decreasing temperature. On rapid cooling (about 10 seconds) from 1673 - 1773 K to room temperature, the second monoclinic (MTP) phase appears at the expense of the orthorhombic HfTiO_4 phase. There is very little difference between the diffraction patterns of the MTP phase and the PSS phase. The (111) peaks appear as a doublet, with separation

Figure 1. a_0 AS A FUNCTION OF THE TEMPERATURE FOR SELECTED $\text{HfO}_2\text{-TiO}_2$ COMPOSITIONS. (The Error Bars Represent 95% Confidence Intervals)

from 0.2 to $0.5^\circ 2\theta$ (Cu $K\alpha$ radiation at about $28^\circ 2\theta$), depending upon temperature and composition. Compositions in the approximate range of 63 to 71 mol % HfO_2 showed only the orthorhombic HfTiO_4 phase and the MTP phase on cooling.

The ratio of the MTP phase to the orthorhombic phase was composition dependent, being large at room temperature for a 70.9 mol % HfO_2 composition and very small for a 63 mol % HfO_2 composition. The ratio also appeared to depend upon the cooling rate and previous thermal history. Slow cooling of the 63 mol % HfO_2 composition showed no MTP phase; however, on fast cooling (about 10 seconds to room temperature) after heating at

Figure 2. $\text{AXIS } b$ AS A FUNCTION OF THE TEMPERATURE FOR SELECTED HfO_2 - TiO_2 COMPOSITIONS. (The Error Bars Represent 95% Confidence Intervals)

Figure 3. $\text{AXIS } c$ AS A FUNCTION OF THE TEMPERATURE FOR SELECTED HfO_2 - TiO_2 COMPOSITIONS. (The Error Bars Represent 95% Confidence Intervals)

Figure 4. PERCENT THERMAL EXPANSION ALONG THE $\bar{a}$ AXIS AS A FUNCTION OF TEMPERATURE. (Error Bars Represent 95% Confidence Intervals)

1873° K for about one hour, a small $(11\bar{1})$ MTP peak was detected. Qualitatively, in compositions above about 63 mol %, it is not necessary to cool as rapidly in order to obtain the MTP phase. On reheating, the MTP $\rightarrow$ orthorhombic transformation appears to be primarily athermal, at least at lower temperatures. In other words, in order for the transformation, MTP to orthorhombic phase, to occur, the temperature must be continually changed. If the temperature is kept constant, the transformation stops. At 70.9 mol % HfO₂, the MTP phase has completely disappeared by approximately 1073 K; while, at 75 mol % HfO₂, the MTP phase disappears by about 1373 K.

An attempt was made to investigate a phase change reported by Simpson⁽³⁾ at about 2143 K. Samples containing 56.4 and 75% HfO₂ were heated to the maximum use temperature of the Pt/40 Rh sample support (~ 2073 K), and only the orthorhombic phase was observed in each case. A tungsten strip coated with Pt/30W was then used as sample support in an effort to extend the temperature range. This time, a reversible orthorhombic-to-cubic phase transformation was detected between 1873 and 1973 K for both compositions. Further study indicated that the cubic phase is associated with oxygen deficiency. In extreme cases of oxygen deficiency, the cubic phase occurs mixed with a monoclinic baddeleyite structure phase and is stable down to room temperature.

Figure 5. PERCENT THERMAL EXPANSION ALONG THE b AXIS AS A FUNCTION OF TEMPERATURE. (Error Bars Represent 95% Confidence Intervals)

Figure 6. PERCENT THERMAL EXPANSION ALONG THE c AXIS AS A FUNCTION OF TEMPERATURE. (Error Bars Represent 95% Confidence Intervals)

Figure 7. AVERAGE PERCENT AXIAL THERMAL EXPANSION ($E_a + E_b + E_c/3$) AS A FUNCTION OF TEMPERATURE FOR SELECTED HfO₂-TiO₂ COMPOSITIONS. (Several Typical Error Bars, Representing 95% Confidence Intervals, are Given; E Represents Percent Thermal Expansion; eg, Along a: $E = a_T - a_{25}/a_{25} \times 100$)

Table 1
ROOM-TEMPERATURE THERMAL-EXPANSION COEFFICIENTS
FOR SELECTED HfO₂-TiO₂ COMPOSITIONS
(From X-Ray Diffraction Data)

HfO ₂ Composition (mol %)	Thermal Expansion Coefficient			Average Value, $\bar{\alpha}$
	α_a	α_b	α_c	
47.5	+ 11.2 (0.5) ⁽¹⁾	+ 0.6 (1.0)	+ 6.6 (0.5)	+ 6.1 (0.5)
56.4	+ 11.7 (0.5)	- 2.4 (1.0)	+ 5.5 (0.5)	+ 4.9 (0.5)
63.0	+ 11.3 (0.5)	- 6.8 (1.0)	+ 3.9 (0.5)	+ 2.8 (0.5)
66.7	+ 11.0 (0.5)	- 11.9 (1.0)	+ 1.2 (1.0)	+ 0.1 (0.5)
70.9	+ 15.6 (2.0)	- 11.1 (1.0)	+ 5.8 (1.0)	+ 3.4 (1.0)

(1) Numbers in parentheses are estimated errors from repetitive slope measurements on the thermal-expansion curves.

Figure 8. ROOM-TEMPERATURE LATTICE PARAMETERS OF $\text{HfO}_2\text{-TiO}_2$ COMPOSITIONS WITH $\alpha\text{-PbO}_2$ STRUCTURE. (Error Bars Represent Standard Deviation)

DISCUSSION

Thermal Expansion

The thermal expansion data presented in this report agree generally with that reported by Lynch and Morosin from 293 to 1173 K⁽²⁾ for the 50 and 63 mol % HfO_2

compositions. Although both sets of data show an increasing degree of anisotropy with increasing HfO_2 content, the data from this study show the expansion along the a axis remaining constant with changing HfO_2 content, and the expansion along the b axis decreasing with increasing HfO_2 content. The same decreasing trend is observed along the c axis in both sets of data.

The conclusion that microcracking or internal fracture accounts for the low thermal expansion observed in hafnium titanate ceramic bodies is supported by these data. Internal fracture is a mechanism which has been proposed to account for the fact that the thermal expansion curves observed in ceramic bodies of some materials are significantly lower than the average axial expansion determined by X-ray diffraction.(13 - 15) A system of complex stresses results when a material with a highly anisotropic thermal expansion is cooled from the sintering temperature. Microcracks form in grains joined along directions of high thermal expansion when the tensile strength is exceeded during cooling. As a result, at room temperature, the ceramic body is held together primarily along directions of low or negative expansion. On reheating, the thermal expansion of the body is low and initially tends to follow the expansion of the low expanding directions. During the heating process, the microcracks recombine, and the reformed grains impart their greater thermal expansion to the body. However, the recombination process imparts a negative component to the thermal expansion so that the overall expansion remains relatively low. At higher temperatures, when most of the microcracked surfaces are healed, the bulk expansion coefficient tends toward the average axial expansion coefficient.

Data from this study show that the thermal expansion curves of $\text{HfO}_2\text{-TiO}_2$ compositions within the orthorhombic phase field are highly anisotropic, and the average axial expansion curves are significantly higher than the bulk expansion curves(1 - 3) at least for temperatures less than 1273 K, as would be expected if internal fracture is the cause of the low bulk expansion. In addition, as the HfO_2 content is increased, the increasing degree of anisotropy would result in the development of higher stress levels in the bulk specimens on cooling; and, thus, more extensive internal fracturing would be expected in those specimens toward the high HfO_2 end of the phase field. This feature would account for the decrease in the bulk thermal expansion coefficient with increasing HfO_2 content.

At temperatures greater than about 1500 K, it could be predicted that the bulk expansion coefficients would be almost independent of concentration and relatively high. This condition follows from the fact that, at these temperatures, a significant amount of recombination has probably already occurred, and the expansion coefficient of the body is approaching the average axial expansion coefficient, which is relatively high. Also, the average axial expansion coefficient is almost independent of composition at these temperatures (Figure 7), at least at compositions up to 66.7 mol % HfO_2 .

Deviation in the thermal expansion trends at 70.9 mol % HfO_2 was initially thought to result from the crossing of the phase boundary into the two-phase region, since this behavior would explain the curvature of the expansion along the a axis, at least to about 1300 K. Thus, on passing through the phase boundary into the two-phase region, orthorhombic lattice parameters would tend to follow the curvature of the phase boundary due to the continually changing composition of the orthorhombic phase. However, no monoclinic HfO_2 (PSS) lines were detected down to about 400 K, even after relatively long soaking

times, although the amount of HfO_2 precipitated may be below the detection limits. Also, no significant isothermal component was detected in the lattice-parameter changes (as would be expected with precipitation from solid solution), although further study with longer soaking times might be necessary. At room temperature, monoclinic (MTP) lines appeared, almost instantaneously due to the low temperature orthorhombic-to-monoclinic transformation. The cause of the thermal expansion deviation is still not clear, although it may be related to the stress generated by the low-temperature transformation.

Orthorhombic-to-Monoclinic Phase (MTP) Change

The most important observations to note about the phase change are:

1. It occurs at relatively low temperatures compared with the probable temperatures at which the liquid phase begins to form. Assuming the phase diagram is similar to that of the $\text{ZrO}_2\text{-TiO}_2$ system, the liquid phase would not be expected to form until temperatures much greater than 2300 K have been reached. In most materials, appreciable diffusion usually does not occur until temperatures of about half the melting point are obtained.
2. The transformation is primarily athermal and occurs rapidly at each temperature.

The speed with which the transformation occurs is an indication of an apparent diffusionless nature. A possible mechanism for the transformation might be the same as that proposed by Lynch and Morosin for the orthorhombic-to-monoclinic transformation observed in HfTiO_4 , $\text{Hf}_{1.26}\text{TiO}_{0.74}\text{O}_4$, and ZrTiO_4 at high pressures.⁽²⁾ The orthorhombic $\alpha\text{-PbO}_2$ structure may be transformed to the monoclinic baddeleyite structure by a twisting and kinking of the octahedral chains, coupled with a shear along the orthorhombic c axis.

The diffusionless and athermal nature of the transformation are characteristics common to most martensitic transformations.^(16, 17) A martensitic transformation is one in which coordinated movement of many atoms of the parent structure occurs in such a way as to form the product structure.⁽¹⁷⁾ The atoms move only a very small amount so that no diffusion is involved and no compositional changes occur. There is a difference in shape between the parent and product grains, and this difference results in a relatively large elastic strain which opposes further transformation. Reducing the temperature increases the free-energy difference between parent and product and induces further transformation. The transformation continues until halted by the stress build up. Since the transformation is very fast, it appears to be athermal. Although the orthorhombic-to-monoclinic transformation appears to be martensitic, further study would be necessary to establish the shape change and crystallographic orientation relationships before making a definite classification.

The orthorhombic-to-monoclinic transformation observed by Lynch and Morosin at high pressures (< 10 kbars) in the 50 and 63 mol % HfO_2 materials⁽²⁾ is probably the same transformation as that observed in this study. The approximate composition dependence observed in this study indicates that the transformation might occur in the 63 and 50 mol % compositions at relatively low temperatures in the absence of external stress. The applied pressure could raise the transformation temperature to room temperature by not only

partially neutralizing the internal stress; but, also, as suggested by Satyanarayan and Miodownik,⁽¹⁸⁾ by altering the basic free energy of each phase in the high-pressure environment.

Lynch and Morosin suggest that the free-energy difference between the α -PbO₂ structure and the baddeleyite structure in the Group IV B oxides is small,⁽²⁾ and the observation of the orthorhombic-to-monoclinic phase change in the present study supports this conclusion.

HfO₂-TiO₂ Phase Diagram

A few comments may be made about the HfO₂-TiO₂ phase diagram from the data gathered in this study. The orthorhombic phase field is broader than previously suspected since compositions from 47.5 to 66.7 mol % HfO₂ have the single-phase α -PbO₂ structure from room temperature through at least 1873 K. At higher temperatures, the orthorhombic phase field extends to even greater HfO₂ contents. At 75 mol % HfO₂, the material transforms from the two-phase mixture, monoclinic HfO₂ (solid solution) plus orthorhombic HfTiO₄ (solid solution) to single-phase orthorhombic HfTiO₄ (solid solution) at about 1900 K.

Observations of the cubic phase suggests that the transformation observed by Simpson⁽³⁾ was an orthorhombic-to-cubic transformation. A cubic phase has been observed in pure ZrO₂ at > 2558 K;⁽¹⁹⁾ and, presumably, HfO₂ exists as a cubic phase at very high temperatures due to its similarity to ZrO₂. In the HfO₂-TiO₂ system, the cubic phase field could conceivably be relatively extensive. Although the transformation was not observed using a Pt/40 Rh sample support, it was observed with a W/30 Pt-on-tungsten support. Ruh and Garrett found a reduction in the tetragonal-to-cubic transition temperature in ZrO₂ due to oxygen deficiency.⁽²⁰⁾ If the tungsten acted as a mild reducing agent, this action might explain why the transformation was observed at about 200 K lower than that reported by Simpson.

CONCLUSIONS

X-ray diffraction thermal expansion data for HfTiO₄-HfO₂ solid solutions show increasing anisotropy with increasing HfO₂ content. Thermal expansion along the a axis does not change significantly with composition. Thermal expansion along the b axis decreases with composition through about 1500 K, being very negative for high HfO₂ compositions; c axis thermal expansion also decreases with composition, approaching zero at higher HfO₂ contents. Data support the internal-fracture theory as the cause for low bulk thermal expansion in HfTiO₄-HfO₂ ceramics.

These data, as well as the literature data for bulk samples,^(1 - 3) indicate that a desired thermal expansion coefficient may be obtained by simply choosing the proper HfTiO₄-HfO₂ composition. Although the thermal shock resistance would be expected to increase with increasing HfO₂ content from the decreasing thermal expansion, the more extensive internal fracture resulting from the greater anisotropy would tend to reduce the strength of the body and thus reduce thermal shock resistance. Another factor which could affect the strength of the body and the thermal shock resistance is the formation of the monoclinic phase (MTP), particularly at the high HfO₂ (> 67 mol % HfO₂) end of the HfTiO₄ phase field where the monoclinic-to-orthorhombic ratios can be relatively high at room temperature.

The high-temperature phase change observed by Simpson⁽³⁾ is probably an orthorhombic-to-cubic transformation. It appears that the transformation temperature may be lowered in environments which cause oxygen loss from the material, resulting in lower maximum-use temperatures for $\text{HfTiO}_4\text{-HfO}_2$ ceramics because of the thermal expansion and dimensional changes.

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