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Abradability and hardness in rare-earth-oxide stabilized hafnia

C. D. WIRKUS, M. F. BERARD
Ames Laboratory and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, USA

The dry abradability and diamond pyramid hardness of HfO_2 fully-stabilized by variable additions of Er_2O_3 were determined on sintered polycrystalline specimens of near-theoretical densities. Measurements on fused silica and on a single crystal of Y_2O_3-stabilized ZrO_2 were included for comparison. In general, the hardness was decreased and the abradability was increased by increasing additions of stabilizing oxide. These effects were attributed mainly to the increase in defect concentration of the anion sublattice with increasing amounts of modifier oxide. Solution of HfO_2 in Er_2O_3 (rare-earth-oxide Type C structure) increased hardness and decreased abradability: effects which also seemed to be related to the defect concentration of the anion sublattice.

1. Introduction

Oxides possessing the fluorite structure (or defective derivatives of it) are among the most refractory oxides known, including UO_2, ThO_2 and solid solutions of ZrO_2 or HfO_2 stabilized* by a solid solution of an appropriate modifier oxide. Among the proven stabilizing modifiers for ZrO_2 and HfO_2 are most of the rare-earth sesquioxides and their close relative Y_2O_3 [1, 2]. In the resulting solid solutions, there is a smooth variation in lattice parameter and, because of the aliovalent modifier cations, there is a variation in the fraction of oxygen sites which are vacant as the modifier content is varied. In many cases, the stabilized defective fluorite-phase prevails over a wide range of composition offering the prospect of considerable lattitude in compounding refractory ceramics with properties tailored by modifier content.

In this study, microhardness and abradability were measured for HfO_2 with varying additions of Er_2O_3 and/or Sc_2O_3 ranging between 10 and about 40 mol% modifier oxide. Sc_2O_3 was included in this study, because, due to its small ionic radius, it alone among the trivalent oxide stabilizers for HfO_2 produces a decrease in average inter-atomic separation distance in the fluorite-phase as modifier content is increased.

2. Experimental procedure

Three series of sintered, stabilized HfO_2 specimens were made with varying amounts of modifier oxide. The modifier in the first series was Er_2O_3, in the second series was Sc_2O_3, and in the third series consisted of blends of Er_2O_3 and Sc_2O_3. In the latter series, compositions were selected to allow variation in total modifier content while maintaining a constant lattice parameter. In addition, a series of sintered Er_2O_3-based specimens were prepared with 0, 7.5 and 15 mol% HfO_2 in solution. These materials were single-phase with the rare-earth-oxide Type C (REOC) structure. Finally, a single crystal of ZrO_2† fully stabilized in the fluorite form with 8.8 mol% Y_2O_3 was included in the study.

All sintered compositions were prepared from precursors made by precipitation or co-precipitation of acidic solutions with 3 M NH_4OH. Erbium and scandium nitrate solutions were

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*Pure ZrO_2 or HfO_2 undergo destructive transformations between monoclinic and tetragonal polymorphs at temperatures of approximately 1200 and 1600° C, respectively. When enough modifier oxide has been added to produce a single-phase defective fluorite solid solution free of polymorphism, the materials are said to be stabilized.
†Ceres Corporation, Waltham, Massachusetts, USA.

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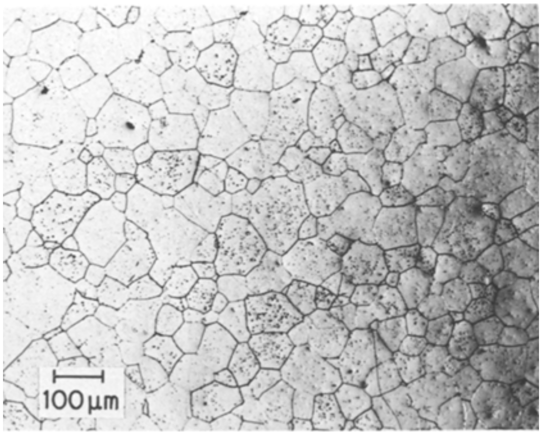

Figure 1 Microstructure of sintered HfO_2 material (etchant: phosphoric acid, 200° C).

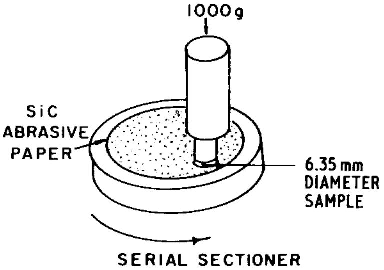

Figure 2 Schematic diagram of apparatus for dry abradability tests.

prepared from Er_2O_3 and Sc_2O_3 produced at the Ames Laboratory as 99.999% purity material. Hafnium oxychloride*, containing less than 100 ppm Zr and less than 100 ppm Ta as the most significant impurities, was dissolved in water to prepare the Hf solution. Solution blends were precipitated by introduction into the NH_4OH solution followed by water washing and decanting to remove dissolved salts. Filter cakes were then treated with acetone and toluene washes [3] to remove the water. This special treatment produces precursor powders which calcine to yield highly sinterable oxides [4].

After pressing to 500 MPa in double-acting dies followed by isostatic pressing to 2070 MPa, most HfO_2-based specimens were sintered in vacuum for 1 to 3 h at 2100° C. The compositions containing only 10 mol% modifier were pre-fired in air to 1550° C and then sintered at 2100° C in vacuum. Pre-firing, in this case, produced the highest sintered densities, but had no beneficial effect for other compositions. Er_2O_3-based compositions were all fired in vacuum to 1850° C. The sintered densities of all specimens exceeded 98% of the theoretical density. Fig. 1 shows the microstructure typical of these specimens.

After sintering, all the specimens were about 0.65 cm in diameter and 5 mm in thickness. A standardized specimen diameter of 6.35 mm was imposed upon every specimen by turning in a small lathe using a diamond wheel for stock removal. Specimens were then cemented† onto brass rods of the same diameter; particular care was taken to insure that the specimen surface was perpendicular to the centre-line of the rod.

Dry abrasion tests were performed with a serial sectioning device normally used in diffusion studies [5], represented schematically in Fig. 2. This device is used to grind thin sections of material from the end of a specimen using abrasive paper. The amount of material removed from the specimen can be determined by carefully weighing the paper before and after grinding. The spindle weight (1000 g), the type of paper (320 grit) and the number of turns of the sectioner (7 turns) were identical for every abrasion test to allow direct comparisons to be made. These testing parameters were set with the guiding principle being that the minimum thickness of material be removed that would still yield good weighing statistics. Therefore, grit-clogging and lubrication of the abrasive by the powder removed were minimized. The abradings performed on the single crystal of Y_2O_3-stabilized zirconia were made on a surface ground parallel to the (1 1 0) plane. The thickness removed, typically 2 to 5 μm, was calculated from the mass of powder removed and the known density and diameter of the specimen. Uncertainty in masses were no greater than 10 μg, although mass readings were recorded to the nearest μg‡. For each specimen, 12 identical abradings were made. The highest and lowest weights obtained were discarded and the remaining 10 weights were averaged. Standard deviations were 4 to 6% of the mean values when all the tests were performed promptly on fresh surfaces. If fresh surfaces were not prepared before abrading, the

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*Wah Chang Corporation, Albany, Oregon, USA.

†Using Duco Cement from E. I. Dupont, Wilmington, Delaware, USA.

‡Cahn Model 25 Automatic Electrobalance from Cahn/Ventron, Cerritos, CA, USA.

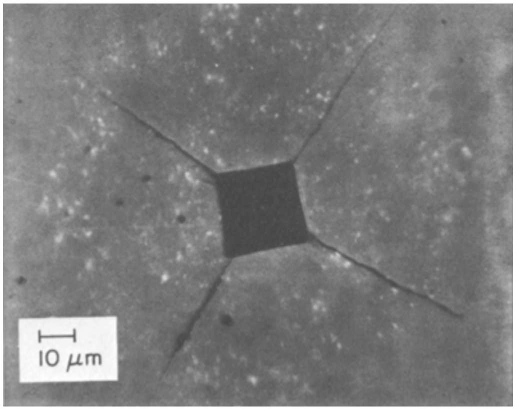

Figure 3 Typical diamond pyramid hardness indentation.

first few sections removed often yielded erratic weights. This effect was probably due to hydrogen embrittlement resulting from contact with moisture in the laboratory air. Hydrogen embrittlement seems to be almost universal in inorganic solid materials, as discussed by Cuthrell [6]. In order to assign a simple numerical abradability to each specimen, a fused silica rod 0.635 cm in diameter was subjected to the standard abrading procedure, and the average thickness removed was used as a normalizing factor for the thickness removed from other specimens. Thus, the abradability of fused silica was given a value of unity, and all the other materials were compared to this standard.

Microhardness tests were performed using a diamond pyramid indenter with a 1000 g load*. Prior to testing, all specimen surfaces were given a series of polishing treatments with a final polish with 0.3 μm alumina powder. Five or more indentations were microscopically measured in the tester and diamond pyramid hardness (DPH) indentation numbers were calculated. Fig. 3 shows a typical indentation. Some cracking usually occurred at the corners of indentations but this did not seem to affect reproducibility of the measurements. The standard deviations of the DPH numbers were less than 3% of the mean for all materials

3. Results and discussion

Fig. 4a and b represents all or portions of the phase equilibrium diagrams for HfO_2–Er_2O_2 [7, 8] and HfO_2–Sc_2O_3 [9] that are of interest in this study. The HfO_2-based compositions containing 10 to 40 mol% Er_2O_3 are all single-phase fluorite materials, which was verified by X-ray diffraction on the sintered specimens. At the lowest Er_2O_3 content, the complete absence of any monoclinic or tetragonal material is important, because incompletely stabilized material can be expected to display increased toughness over fully-stabilized material [10]. In the specimens consisting of Er_2O_3, either pure or doped with up to 15 mol% HfO_2, the structure was single-phase REOC. The HfO_2-based compositions containing

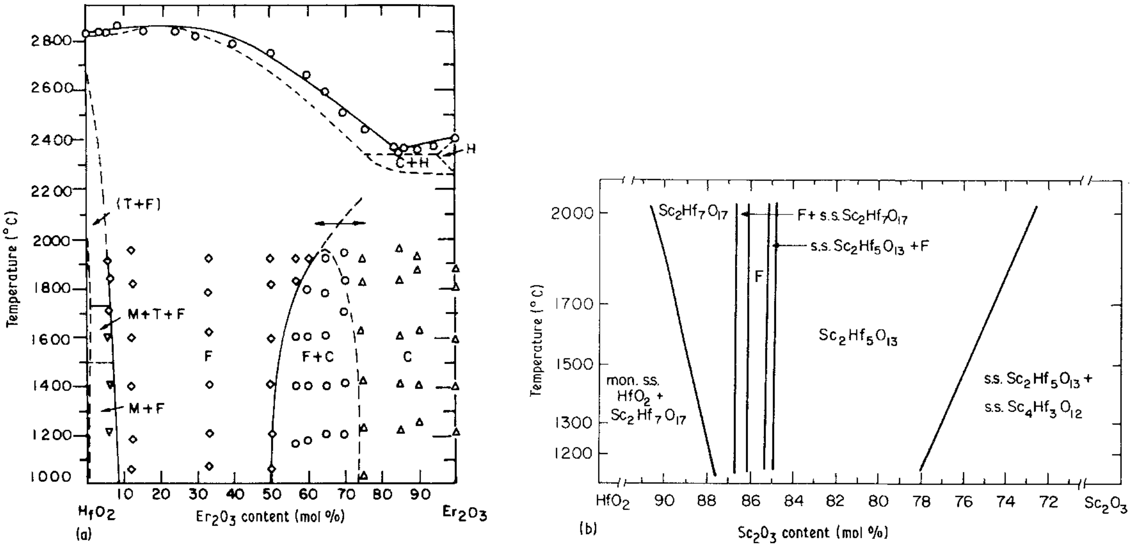

Figure 4 (a) HfO_2-Er_2O_3 equilibrium diagram (after Johnstone [7]), (b) HfO_2-Se_2O_3 equilibrium diagram (after Kalinovskaya *et al.* [9]).

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*Wilson Tukon Tester, New York, NY, USA.

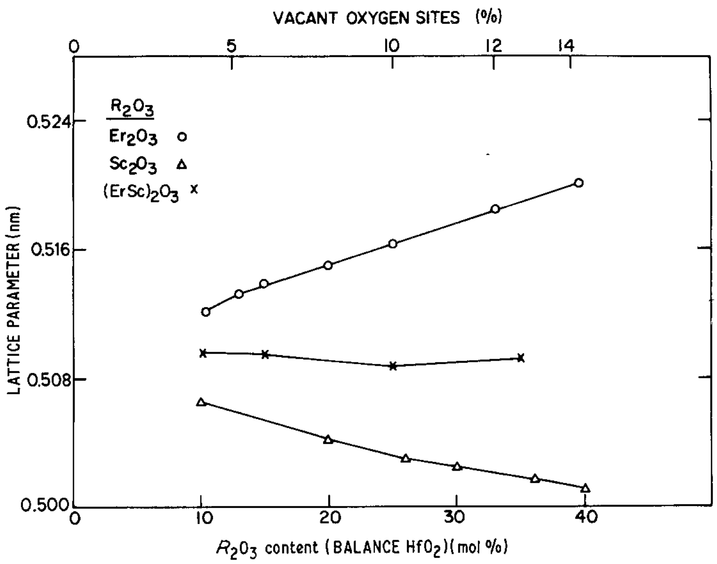

Figure 5 Variation in lattice parameter with modifier oxide content for stabilized HfO_2.

10 to 30 mol% Sc_2O_3 would, under equilibrium conditions consist of several different phases having non-cubic symmetry, but being closely related to the defective fluorite phase through defect ordering and shear [9]. In this study, however, specimens were cooled rapidly from 2100° C and showed little evidence of any of these ordered phases, generally consisting only of the defective fluorite phase. Some oxygen-vacancy ordering may have been present, but escaped detection by ordinary X-ray diffraction techniques. The structure of HfO_2-based compositions using a blend of Er_2O_3 and Sc_2O_3 modifiers was fluorite in every case. The blends of the two modifier oxides were compounded to produce varying total modifier content with essentially constant lattice parameter. Table I includes compositions and lattice parameters for the mixed-modifier series of compositions and Fig. 5 shows the variation in lattice parameter with total modifier content for all HfO_2-based materials studied. Also included in Fig. 5 is the percentage of oxygen sites in the structure which are made vacant by the use of trivalent modifier oxides.

Fig. 6 shows the results of abradability tests plotted as a function of R_2O_3 content, where R is

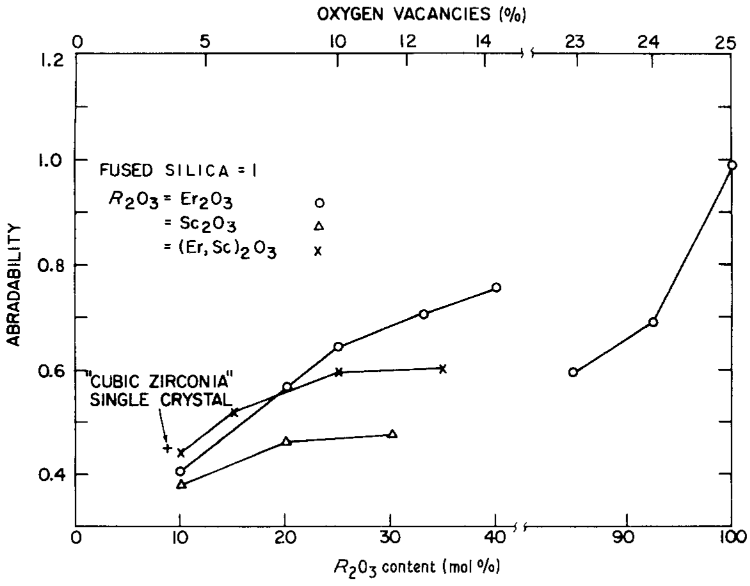

Figure 6 Composition dependence of abradability of fluorite and REOC compositions (fused silica taken as a standard).

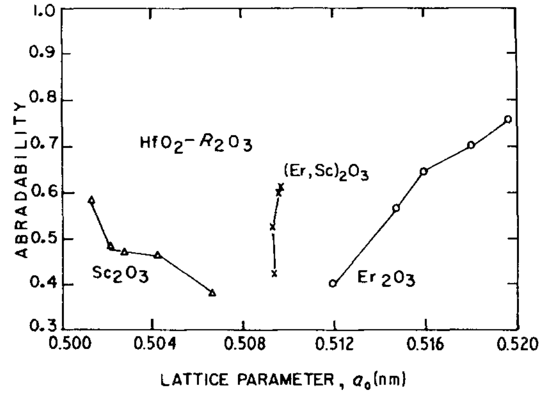

Figure 7 Abradability plotted as a function of lattice parameter for fluorite compositions.

TABLE I Compositions and lattice parameters for the mixed-modifier series of compositions

HfO_2 (mol %)	Er_2O_3 (mol %)	Sc_2O_3 (mol %)	Lattice parameter, (nm)
90	4	6	0.5096
85	6	9	0.5094
75	10	15	0.5090
65	15	20	0.5093

Er or Sc, and percentage of vacant oxygen sites[*]. Each point represents the mean of 10 standard abradings. The abradability of the HfO_2-rich (fluorite) phase is seen to increase with increasing amounts of modifier oxide: the effect being strongest with Er_2O_3, weakest with Sc_2O_3, and intermediate for the blend of modifiers. The abradability of the single crystal of Y_2O_3-stabilized ZrO_2 is about the same as for polycrystalline R_2O_3-stabilized HfO_2 of similar modifier content. In general, all of the fluorite compositions investigated were significantly more resistant to abrasion than the fused silica. The abradability of pure Er_2O_3 (REOC structure) is about the same as fused silica, but it is considerably reduced by the addition of HfO_2 in solid solution. There appears to be a general correlation between abradability and the degree of defectiveness of the fluorite anion sublattice, i.e., the greater the fraction of oxygen sites which are unoccupied, the more readily the material abrades. If the REOC structure is considered to be a highly anion-deficient version of the fluorite structure, the same argument seems to hold for this phase. While the average interatomic distance, or average bond length, may have an effect on abrasion behaviour, Fig. 7 shows that it cannot be a dominating factor. Abradability seems to be inversely proportional to lattice parameter for Sc_2O_3 modification, directly proportional to lattice parameter for Er_2O_3 modification, and multi-valued for the blend of modifiers compounded to hold lattice parameter constant.

Fig. 8 shows the variation of DPH with total modifier oxide content and fraction of the fluorite oxygen sites which are vacant. Within the HfO_2-

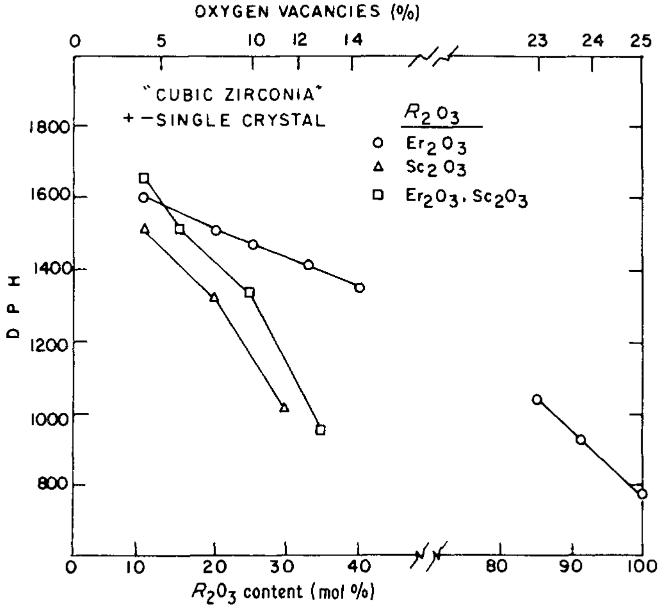

Figure 8 Composition dependence of the diamond pyramid hardness of fluorite and REOC compositions.

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[*] In the case of the high Er_2O_3-content compositions, which have the REOC structure, these empty oxygen sites are not true vacancies, but rather are a special type of interstitial site.

rich (fluorite) materials, hardness decreased with increasing modifier content. As was the case for abradability, there is not a direct correlation between hardness and lattice parameter. The single crystal of Y_2O_3-stabilized ZrO_2 displayed a DPH of 1800, a value somewhat higher than polycrystalline HfO_2 materials of similar modifier content. The hardness of Er_2O_3 (REOC structure) was increased by the addition of HfO_2 in solid solution.

The results of abradability and hardness tests are in general agreement; i.e., as hardness decreases, abradability increases in both the fluorite and REOC phases. At a given modifier content, the hardness of the Er_2O_3-stabilized HfO_2 always exceeded that of the Sc_2O_3-stabilized material and the abradability of the Er_2O_3-stabilized material was always lower than for the Sc_2O_3 material. The reasons for this consistent difference is not known, but may be related to the greater tendency toward anion-vacancy ordering in the Sc_2O_3-modified HfO_2, as shown in the complexity of the Sc_2O_3–HfO_2 phase diagram.

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