

OXIDATION MECHANISMS OF HAFNIUM CARBIDE AND HAFNIUM DIBORIDE IN THE TEMPERATURE RANGE 1400 TO 2100°C

Two ultra-high-temperature materials, hafnium carbide and hafnium diboride, were oxidized in the temperature range 1400 to 2100°C. The two materials oxidized in distinctly different ways. The carbide formed a three-layer system consisting of a layer of residual carbide, a layer of reduced (partially oxidized) hafnium oxide containing carbon, and a layer of fully oxidized hafnium dioxide. The diboride oxidized into only two layers. For the diboride system, the outer layer, mainly hafnium dioxide, contained several intriguing physical structures.

INTRODUCTION

Materials that can provide protection at temperatures above 1700°C in an oxidative environment are needed for important applications. To be usefully employed as a turbine blade coating, for example, a substance would need to withstand many excursions from normal ambient conditions into the high-temperature regime and back again without cracking, spalling, or ablating. Other applications, such as a combustion chamber liner, might require only one high-temperature exposure. Not only do the chemical properties need to be considered, but the physical, microscopic structure of a candidate material can also determine how well it will function under extreme conditions. To illustrate, a substance fabricated by hot-pressing a powder will generally have micrometer-size pores throughout, which allow hot oxidative gases to diffuse at a significantly higher rate than in a material of the same chemical composition made by chemical vapor deposition (CVD). Carefully manufactured CVD films do not have pores or cracks, so hot gases must diffuse through the lattice of the bulk material, a much slower process than diffusion through pores or openings.

The oxidation mechanisms of CVD films of two important high-temperature materials are discussed in this article. Hafnium carbide and hafnium diboride melt at 3950 and 3250°C, respectively. In an oxygen atmosphere, both form hafnium dioxide, which melts at about 2900°C. In addition to at least one solid oxide, both substances produce other oxidation products. Hafnium carbide yields either CO or CO₂, and hafnium diboride produces boric oxide, which becomes a liquid at 450°C and vaporizes at 1860°C. Obviously the presence of gases and liquids in a protective film can have significant ramifications. Further, a structural phase transition that occurs in hafnium dioxide at about 1700°C should not be overlooked. This transition entails an accompanying 3.4% volume change¹ that can result in cracking or spalling. The work presented here is a selection of various

aspects of research that has been performed over the past four or five years.²⁻⁵

EXPERIMENTAL METHODS

The experimental arrangement for the oxidation process has been described in detail previously.²⁻⁴ An induction furnace consisting of two concentric zirconia tubes with a graphite susceptor between them was used to heat the specimen. (A susceptor is the heating element in an induction furnace.) The specimen temperature was measured with an optical pyrometer through a sapphire window. Gas flow through the furnace of about 20 cm/s was controlled with a system of solenoid valves that maintained a flow of argon until the desired temperature was reached, at which time oxygen, at a partial pressure of 55 torr, was added to the furnace atmosphere. After a specified oxidation time, the atmosphere was switched back to pure argon, the furnace was turned off, and the specimen was allowed to cool to room temperature.

The specimen was then removed from the zirconia tube, photographed at several magnifications, embedded in epoxy, cut to reveal a cross section of the oxidized film, and finally polished using a series of successively finer diamond grit. Normally, samples were sectioned by cutting perpendicular to the surface. Occasionally, however, a specimen was cut at a very small angle to the surface to expose broader sections of oxide and residual material for X-ray diffraction measurements. Thickness measurements of the various layers were made with a calibrated Olympus metallurgical microscope, and cross-sectional photographs were taken. The polished cross sections were also examined by X-ray microanalysis in a scanning electron microscope (SEM).

To characterize certain layers, electrical resistance was measured as a function of temperature. Leads were attached successively to the polished surfaces of the individual layers, and the specimen was then placed in a

cryostat, where the resistance was measured as the temperature was lowered to near 10 K and then returned to room temperature. The hardness numbers were determined for the oxidized hafnium carbide film using standard procedures employing a Knoop indenter. Polished surfaces were also employed for the latter measurements.

RESULTS

A photograph of the hafnium diboride film before oxidation is shown in Figure 1. The polycrystalline film has well-formed crystallites with flat faces and well-defined edges. The overall integrity of the coating is good; only an occasional crack is present. On the basis of the examinations of cross sections revealing the film/substrate interface, the attachment of the coating to the substrate is believed to be excellent. Similar observations were made for the hafnium carbide films.

Figure 2 shows a cross section of the film after exposure to oxygen for 1800 s at 1520°C. At this temperature, a relatively compact oxide forms. Cracks in the oxide between many of the grains were probably formed during cooling or post-oxidation handling. Oxide formed at this temperature appears to adhere to the residual diboride. At higher oxidation temperatures, however, separation between the oxide and diboride is common and is probably caused by different temperature coefficients of expansion for the oxide and diboride.

Near the boiling point of boric oxide ($\approx 1860^\circ\text{C}$), the oxidized hafnium diboride develops some interesting morphology. Figure 3 is a stereopair of photographs of the oxide after exposure to oxygen for 540 s at 1850°C. Many blunt posts protrude from the surface, a few of which have no cover over the top, suggesting that they are hollow, resembling stovepipes. In stereo, one may



Figure 1. Surface of hafnium diboride film showing crystallites with flat faces and well-defined edges.

observe hollow channels in the protrusions. Some of the stovepipes have a height almost equal to the film thickness. The formation of these structures is apparently an intricate process that includes the transport and deposition of hafnium dioxide by liquid or gaseous B_2O_3 . Figure 4 is a stereopair of photographs of one of the stovepipes, revealing in dramatic fashion not only the hollow center of the protrusion but also a large channel going into the oxidized layer at the left of the structure's base.

Two examples of oxide growth morphology formed at 1900°C are shown in Figure 5. The hafnium diboride exposed for 100 s (Fig. 5A) has an interesting growth pattern in which the oxide has periodically separated into thin laminae. The film exposed to oxygen for 300 s (Fig. 5B) provides an example of the formation of large voids. In both examples, the separation of oxide and the remaining diboride is apparent.

Examination of cross sections of hafnium carbide revealed a phenomenon different from that of hafnium diboride in that an additional layer had formed between the residual carbide and the white outer layer of oxide. In the light microscope, the new layer appeared gray (Fig. 6). In the SEM, the interlayer was observed to be compact and fine grained compared with the porous outer oxygen layer shown in Figure 7. This new layer was very intriguing from the point of view of protecting the substrate, since compact layers are expected to allow much slower transport of gases than porous materials. To characterize the interlayer, further analysis was performed.

Figures 8A, 8B, and 8C show X-ray microanalysis spectra of the residual carbide, the interlayer, and the outer oxide layer, respectively. As noted earlier,³ the big change in the oxygen-to-hafnium peak ratio occurs between the residual carbide and the interlayer. In other

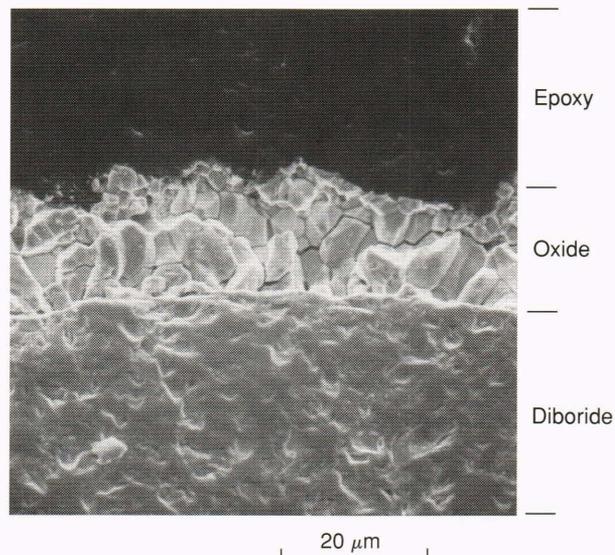


Figure 2. Cross section of film after exposure to 55 torr of oxygen for 1800 s at 1520°C. The oxide is compact but has some cracks between the grains. The cracks probably formed during cooling or post-experimental handling. Oxide formed at this temperature appears to adhere to the diboride in most places.

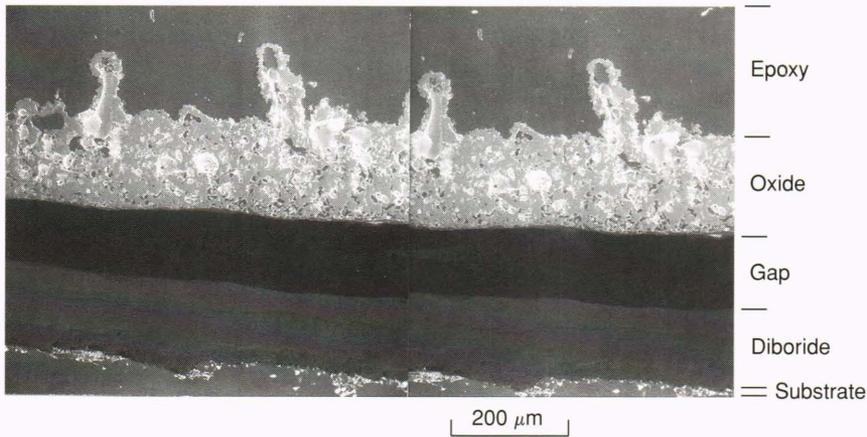


Figure 3. A stereopair of photographs of the cross section of a film oxidized in 55 torr of oxygen for 540 s at 1850°C, showing unusual protrusions from the oxide surface. Viewing in stereo reveals that these structures are hollow (see also Fig. 4), resembling stovepipes, with a well-formed central channel. In fact, many channels occur throughout the films oxidized at this temperature, several of which can be observed in this stereopair. Note also that the oxide is separated from the residual diboride.

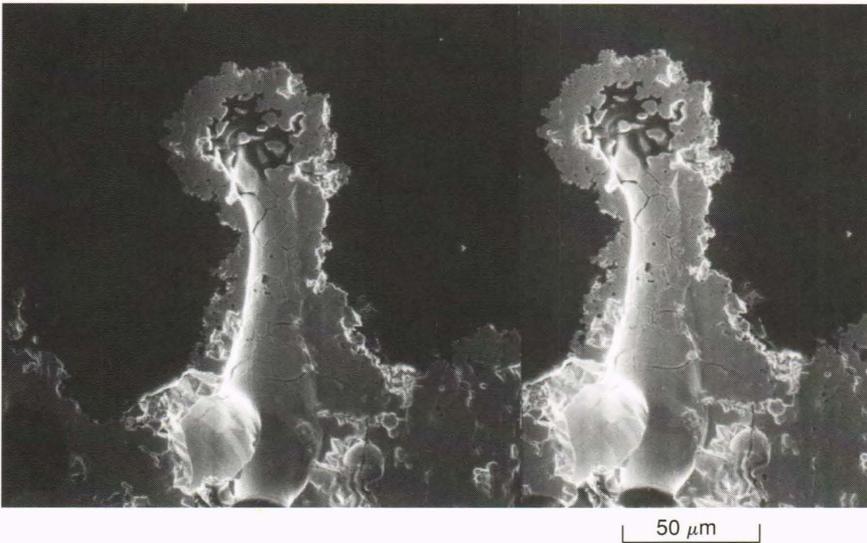


Figure 4. A higher-magnification stereopair of photographs of the stovepipe on the left in Figure 3. Viewing in stereo reveals a hollow, smooth-walled central tube leading out of the oxide. The cracking in the wall is probably due to post-experimental handling. Near the base of this protrusion on the left side, a large secondary channel exists in which one can see well-formed crystallites on the wall.

words, the oxygen-to-hafnium peak ratio is much the same in the interlayer and the outer oxide layer. The peak ratio of carbon to hafnium changes most in the interlayer/outer oxide interfacial region. To summarize, the microanalysis results indicate that the interlayer is an oxide with carbon impurity rather than a carbide.

X-ray diffraction analysis indicated that the hafnium carbide had the usual cubic structure with a lattice constant of $4.60 \pm 0.01 \text{ \AA}$. As shown in Table 1, the outer oxide layer had the known monoclinic structure. It was surprising, considering the sharply delineated interfaces of the oxidized film (Figs. 6 and 7), that the interlayer structure (also in Table 1) matched that of the outer oxide layer as closely as it did. Why should this be so? If the interlayer and the outer oxide have the same crystal structure, one would expect the amount of oxygen to change gradually from the carbide/interlayer interface through the interlayer into the outer oxide, with no visual interface between the two layers. It seems likely, therefore, that although the crystal structures are similar at room temperature, they are not the same at the elevated temperature; otherwise, the observed sharp boundary between the two materials would not be expected.

The results of the electrical resistance determinations are shown for the interlayer in Figure 9 and for the residual carbide in Figure 10. The outer oxide had high electrical resistance; no results are shown for that layer. The residual carbide layer and the interlayer have rather metallic-like resistance values above 50 K. Below 50 K, however, the resistance of both layers increases, indicating that both materials more probably fall in the category of degenerate semiconductors. The upswing in resistance is especially apparent for the interlayer.

Knoop hardness numbers were 970 and 986 kg/mm^2 for the residual carbide and interlayer, respectively, whereas the outer layer had a value of 297 kg/mm^2 , or about one-third of the hardness of the other two. This ratio is consistent with handbook hardness numbers for hafnium dioxide and hafnium carbide.

DISCUSSION

Exploiting information obtained experimentally, we can deduce the oxidation mechanisms of hafnium carbide and hafnium diboride. It seems clear that hafnium carbide dissolves oxygen into its lattice. From our data, Figure 8A shows a small oxygen X-ray peak for the residual

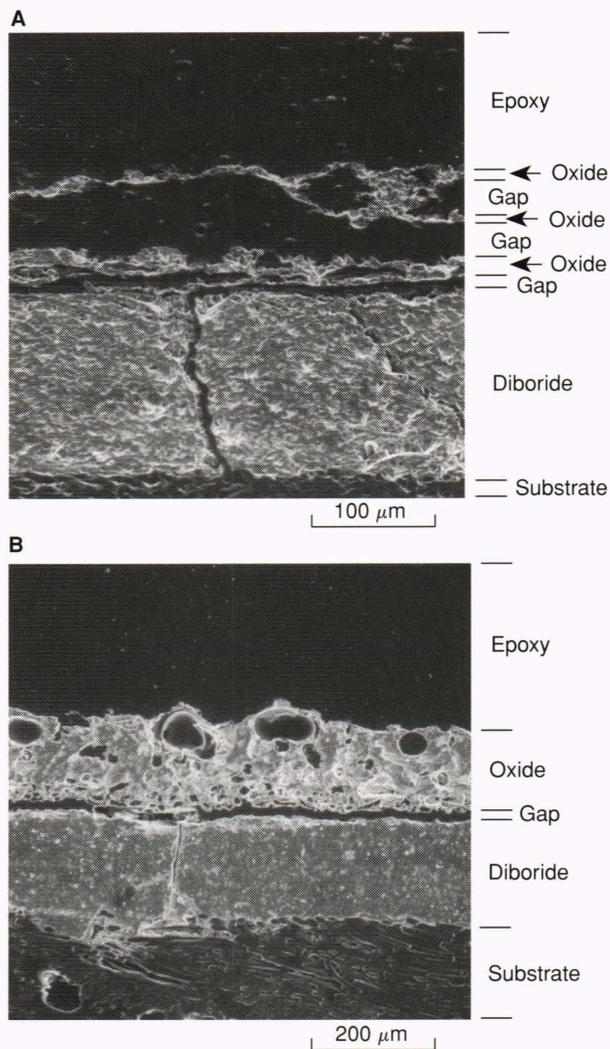


Figure 5. Two examples of oxides grown in 55 torr of oxygen at 1900°C. **A.** A film exposed for 100 s, where the oxide has separated into thin laminae. **B.** A film exposed for 300 s, which has large voids in several places. Apparently, at this temperature, conditions are no longer favorable for the stovepipe growths in Figures 3 and 4. Again, the oxide and residual diboride have separated.

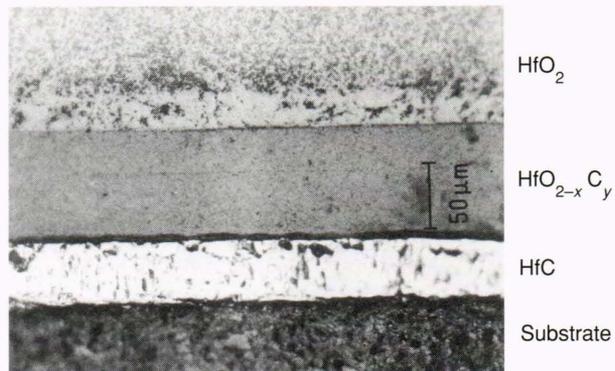


Figure 6. Light micrograph of a cross section of oxidized hafnium carbide film showing a multilayer structure with well-defined interfaces. The adhesion between all layers appears to be excellent with no signs of spalling or separation. Oxidation was for 600 s at 1865°C in an atmosphere of 93% argon and 7% oxygen.

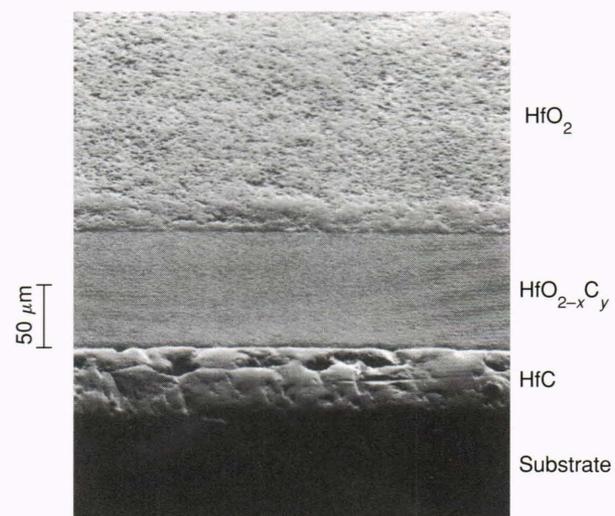


Figure 7. Scanning electron micrograph of a cross section of hafnium carbide film oxidized at 1865°C for 600 s in 7% oxygen and 93% argon. The compactness and lower porosity of the $HfO_{2-x}C_y$ (interlayer) are apparent.

Table 1. X-ray diffraction parameters.

X-ray diffraction parameter	HfO ₂ (Ref. 6)	HfO ₂ (Ref. 7)	HfO ₂ (Ref. 8)	White outer oxide	Gray interlayer
<i>a</i> (Å)	5.1156(5)	5.119	5.12	5.10(1)	5.14(1)
<i>b</i> (Å)	5.1722(5)	5.169	5.18	5.16(1)	5.19(1)
<i>c</i> (Å)	5.2948(5)	5.290	5.25	5.27(1)	5.27(1)
β (deg)	99.18(8)	99.25	98	99.1(1)	99.2(1)
<i>V</i> (Å ³)	138.20	138.15	137.9	136.9	138.8

Notes: All X-ray diffraction results indicate monoclinic structures. The values *a*, *b*, and *c* are unit cell dimensions; β is the angle between edges *a* and *c*; and *V* is the unit cell volume. Our results for the outer oxide and interlayer were determined by a weighted fit of 23 and 28 diffraction lines, respectively, obtained with a Read camera using filtered Cr radiation. Polycrystalline aluminum foil placed on the surface of the target oxides was employed as a reference to calibrate the camera. The aluminum, which had a slit in it, also served as a mask so that data were collected from only one layer at a time. The numbers in parentheses are the uncertainties in the least significant digits.

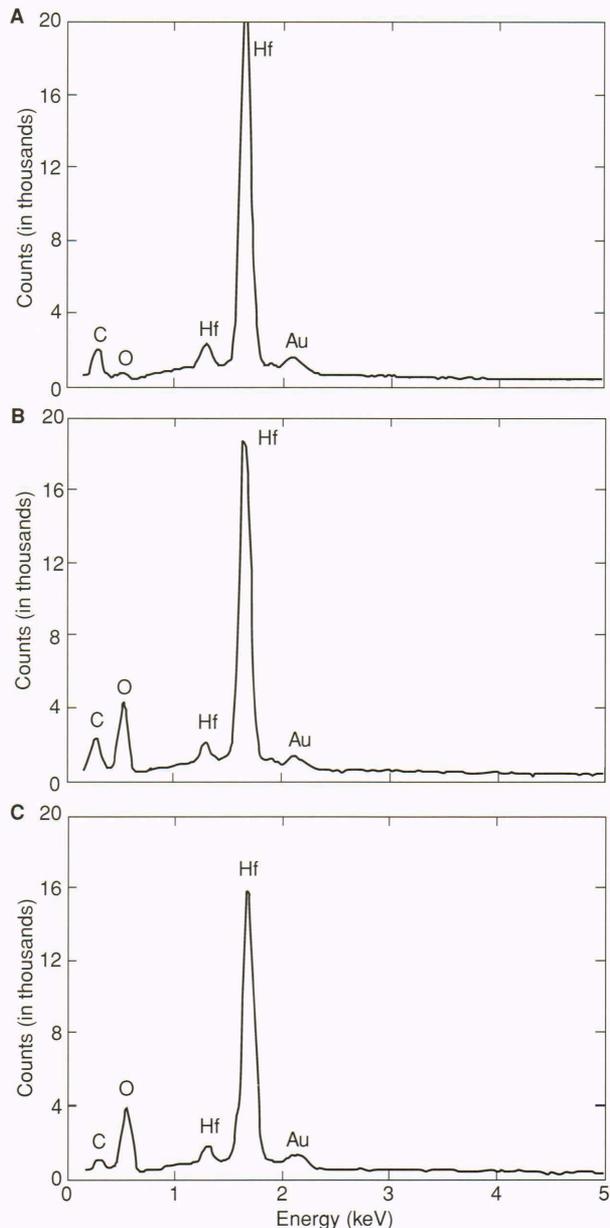


Figure 8. A. X-ray spectrum of the residual hafnium carbide layer, indicating the presence of oxygen. The gold peak is a result of a coating applied to the specimen to prevent charging in the scanning electron microscope. The hafnium carbide film was oxidized at conditions described in the Figure 6 caption. B. X-ray spectrum of the interlayer. C. X-ray spectrum of the outer oxide layer.

hafnium carbide. Further, in an extensive study of materials made from various mixtures of hafnium carbide, hafnium dioxide, and hafnium nitride, Constant et al.⁹ showed that the hafnium carbide can maintain a single-phase, cubic lattice with as much as 25% of the atomic carbon being replaced by atomic oxygen at 1600°C, and that the percentage increases to 30% at 2000°C. In other words, one can synthesize a composition of $\text{HfC}_{1-x}\text{O}_x$ where $x \leq 0.25$ at 1600°C and $x \leq 0.30$ at 2000°C. When the limit on x was exceeded, multiphase materials resulted. The capacity to dissolve oxygen into the bulk is not uncommon; metallic hafnium and titanium both behave

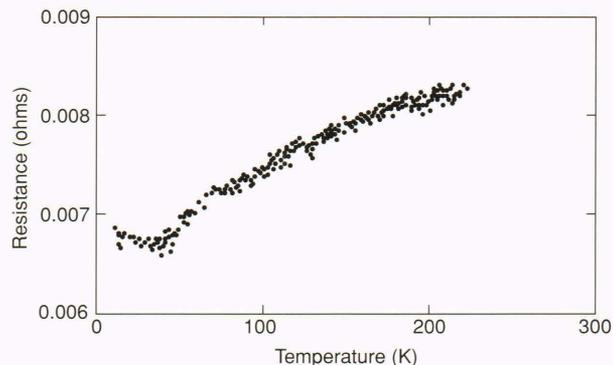


Figure 9. Resistance versus temperature for the reduced hafnium oxide interlayer. The upswing in resistance below 50 K suggests that this new material is a degenerate semiconductor. The units of the ordinate are sheet resistance (ohms). Sheet resistance is the electrical resistance of a material with the dimensions of a unit square and unspecified thickness.

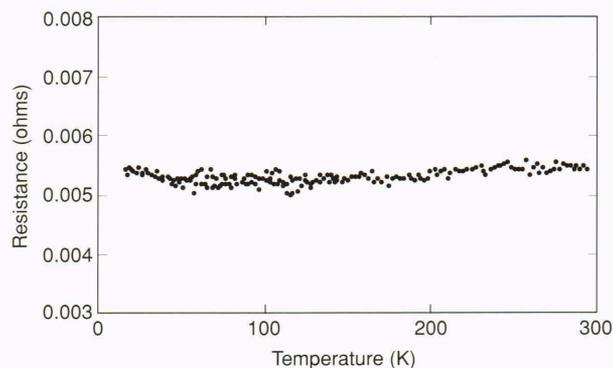


Figure 10. Resistance versus temperature for the residual hafnium carbide layer. The slight increase in resistance below 50 K is possibly suggestive of a degenerate semiconductor. The units of the ordinate are sheet resistance (ohms). Sheet resistance is the electrical resistance of a material with the dimensions of a unit square and unspecified thickness.

in this manner. Therefore, as the carbide encounters oxygen, it first absorbs it into the bulk lattice.

As the oxygen concentration increases in the carbide, it reaches a saturation level, as discussed in the preceding paragraph. Even though a percentage of the carbon has probably left the carbide lattice, considerable carbon still is present in the carbide lattice when saturation is attained. Thus, as the new material forms, a considerable amount of carbon is entrained in it. From our microanalytical measurements, the new material has the form of $\text{HfO}_{2-x}\text{C}_y$, where x is small compared with 2 and y is less than the formula value that carbon possessed at the last instant in the carbide. The carbon diffuses outward as oxygen continues to move inward. Eventually, the carbon level is low enough and the oxygen level high enough that a second interface forms between the outer oxide, which has a general formula of HfO_2 . At temperatures above 1700°C, which is the transition point between the tetragonal and monoclinic forms of hafnium dioxide, the outer

layer possesses the tetragonal structure. Either the carbon or the reduced amount of oxygen, or both, in the interlayer must prevent the interlayer and the outer oxide from having the same structure at elevated temperatures. If this were not so, no reason would exist for the interlayer/oxide interface to form as experimentally observed.

Thus, as hafnium carbide oxidizes, three distinct layers form in a dynamic system with moving interfaces and with each layer possessing a unique density (inferred from Fig. 7 in conjunction with other evidence). Several years ago, Danckwerts¹⁰ solved the diffusion equation for a two-layer system with a moving boundary.¹¹ Our model, depicted in Figure 11, extends his treatment to include a third layer.⁴ Locations in each of the three layers are given by x_0 , x_1 , and x_2 , respectively. Each of the three coordinate systems is fixed in its particular medium as shown. Thus, during oxidation, the systems are in relative motion to one another. Interfaces are denoted by $X_i(t)$, where $i = 0, 1, 2$ refers to coordinate systems and t represents time. In general, two interfaces are associated with each layer; these are distinguished by superscript + and - signs. The initial position of an interface is $X_i(0)$. The indices $i = 0, 1$, and 2 refer to the outer oxide, the interlayer oxide, and the residual carbide, respectively. The positions $X_1(0)$ and $X_2(0)$ are indicated by dotted lines because they are not seen in the cross section after oxidation. We know where $X_2(0)$ is located by measurement before oxidation. The total thickness of interlayer formed, $X_1^+(t) - X_1(0)$, is a quantity necessary to solve the overall diffusion system and is estimated by (1) noting that all of our photographs suggest that the interlayer oxide is dense (i.e., without voids or pores); (2) knowing from X-ray microanalysis and diffraction that it is an oxide-type medium; and (3) obtaining, by subtraction, the amount of carbide depleted. Thus, (1) and (2) suggest that

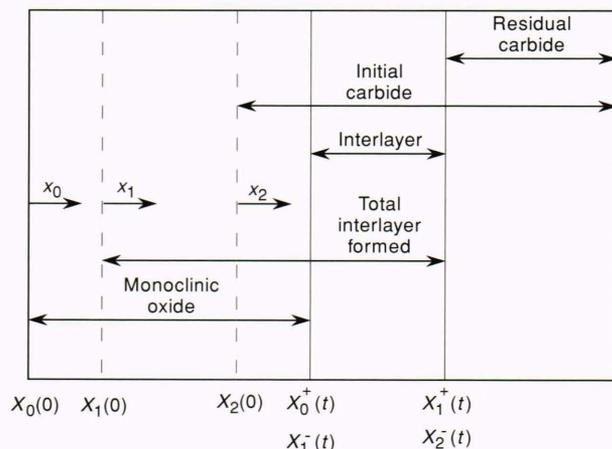


Figure 11. A schematic diagram of the hafnium carbide oxidation model. Lowercase x_0 , x_1 , and x_2 indicate coordinate systems that are fixed in each of the respective media. During oxidation, these systems move with respect to one another because of volume changes due to structural transformation taking place at the interfaces. Uppercase X 's indicate the positions of various interfaces in the cross section of the oxidized film. Solid interfacial lines are observable in the cross section. Dashed lines represent original interfaces that no longer exist because of layer depletion. See the text for further details of this model.

we employ theoretical densities of $\rho_1 \equiv 10.1 \text{ g/cm}^3$ and $\rho_2 = 12.7 \text{ g/cm}^3$ in the equation $f_2\rho_2[X_2^-(t) - X_2(0)] = f_1\rho_1[X_1^+(t) - X_1(0)]$, from which we solve for $[X_1^+(t) - X_1(0)]$. In the preceding equation, f_1 is the weight fraction of Hf in HfO_2 , and f_2 is the weight fraction of Hf in HfC ; thus, the equation conserves Hf atoms. Implicit in our scheme is the growth of the outer oxide at $X_0^+(t)$, the depletion of the interlayer oxide at $X_1^-(t)$, the growth of the interlayer oxide at $X_1^+(t)$, and the depletion of the carbide at $X_2(t)$. We neglect all complications due to the outward (i.e., in the negative direction in Fig. 11) diffusion of carbon. We consider only the inward diffusion of oxygen and recognize that at our working temperatures, 20 to 30% of the carbon sites in the hafnium carbide lattice must be occupied by oxygen before the structure transforms to an oxide.⁹

Because coordinate systems are not moving relative to their own medium, the diffusion equations can be written simply as

$$\partial C_i(x_i, t)/\partial t = D_i \partial^2 C_i(x_i, t)/\partial x_i^2, \quad i = 0, 1, 2 \quad (1)$$

where $C_i(x_i, t)$ is the concentration of the diffusate in the i th medium at point x_i and D_i is the diffusion constant. At each interface, the diffusate is conserved according to

$$\begin{aligned} D_i \partial C_i(x_i, t)/\partial x_i \Big|_{x_i=X_i} + C_i(X_i, t) dX_i/dt \\ = D_{i+1} \partial C_{i+1}(x_{i+1}, t)/\partial x_{i+1} \Big|_{x_{i+1}=X_{i+1}} \\ + C_{i+1}(X_{i+1}, t) dX_{i+1}/dt \end{aligned} \quad (2)$$

for $i = 0$ and 1. The first term on either side of the equation represents the diffusate flux across the interface, whereas the second term takes into account growth and depletion, resulting in moving boundaries.

The solutions of Equation 1 are well-known error functions that depend on the diffusion constants D_i , parabolic rate constants obtained from experiment, and concentrations based on the results of the X-ray microanalysis. The diffusion constants are determined from the boundary conditions given by Equation 2. The interested reader will find further details in Ref. 4. The diffusion constants obtained in this manner are given in Table 2.

The diffusion constants in the table indicate that the interlayer oxide is a diffusion barrier for oxygen under our experimental conditions. With regard to the diffusion constants for the outer oxide, we know from thickness measurements that this layer is much thicker (and therefore less dense) than it would be if the oxide possessed its theoretical density. The lower density probably contributed to a larger diffusion constant in this layer, and our results for the outer oxide should not be applied to fully densified hafnium dioxide. At the higher temperature, the outer oxide layer should possess the tetragonal structure during the oxidation.

The interlayer oxide is composed of only three elements (Hf, C, and O). From our micrographs, this new material appears to adhere extremely well to both the residual carbide and the outer oxide. Specifically, we have seen no cracking, spalling, or separation at any of

Table 2. Oxygen diffusion constants for different layers at various temperatures.

Layer	Temperature (°C)	Diffusion constant (cm ² /s)
Outer oxide	1400	8.1×10^{-8}
	2060	3.0×10^{-6}
Interlayer oxide	1400	7.9×10^{-9}
	2060	1.1×10^{-7}
Carbide	1400	2.6×10^{-7}
	2060	1.6×10^{-5}

its interfaces with either of the other two layers. In addition, we have not observed cracks or voids within the material itself. Our observations of this new material suggest that it might be a very useful and protective high-temperature substance. Currently, no reasons are known why the material could not be produced as a monolithic protective film.

It is instructive to compare our results with those of others who have investigated the oxidation of hafnium carbide. Only two groups of investigators will be mentioned here. Berkowitz-Mattuck¹² used arc-melting techniques to make samples. She observed grain boundary oxidation in her specimen, which often fell apart during oxidation at temperatures up to 1730°C, which was her maximum value. In this instance, it seems that grain boundary impurities, probably carbon, were oxidizing much faster than the bulk. Recently, Prater et al.¹³ published their research on hot-pressed powders of hafnium carbide. In their paper, curiously, they do not mention the formation of an interlayer at all. In the Ph.D. dissertation of Holcomb,¹⁴ however, who is one of the authors of Ref. 13, the interlayer is mentioned rather often, and speculation is presented about its possible nature. It is likely that the interlayer was not as prominent in the specimens of Prater et al.¹³ because the hot-pressed samples had micrometer-size pores that allowed greater oxygen diffusion to the critical region and, thus, oxidized the interlayer at a greater rate, keeping it thin.

In regard to the oxidation of hafnium diboride, no evidence seems to indicate that hafnium diboride dissolves oxygen into its bulk. In addition, near and above the boiling point of boric oxide, large voids and stovepipes form in the oxide layer, indicating a prominent gaseous presence in the film, even though the oxygen was maintained in the initial gas stream at the same level as during the oxidation of hafnium carbide. The large voids and other paths through the oxide mean easier access to the interface where the oxidation takes place, creating additional gaseous products that then must be disposed of. Evidence indicates that B₂O₃ is released from the oxidizing film. After the higher-temperature ($\geq 1850^\circ\text{C}$) hafnium diboride tests, one finds a water-soluble, white powder deposited downstream on the walls of the fur-

nace. In qualitative chemical analysis, the white powder tests positively for boron. Boric oxide melts at about 450°C, so at 1675°C it is present in the oxide as a liquid, in which form it probably acts to seal any porosity or cracks and contributes to the slower oxidation rate.

Therefore, in the oxidation of hafnium diboride, no oxygen is absorbed into the bulk, culminating in a phase change when a saturation level is reached. Instead, a chemical reaction takes place directly at the interface, releasing gaseous products that form large pathways through the oxide. This result allows additional oxygen to reach the interface more expeditiously, thus beginning the cycle again.

Our work has shown that hafnium carbide and hafnium diboride films oxidize in quite different ways at elevated temperatures. The carbide forms a fine-grained, compact protective interlayer that slows the diffusion of oxygen. In contrast, the diboride forms gaseous products at the interface, creating voids and easy oxygen access. The formation of the interlayer during the hafnium carbide oxidation also has the apparent benefit of matching materials together better, probably with respect to both interfacial chemical adhesion and coefficients of thermal expansion, such that they do not separate from one another during broad temperature excursions.

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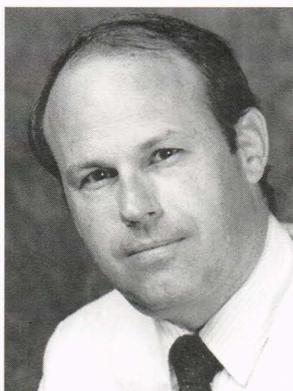


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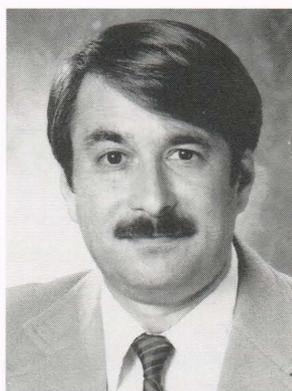


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