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DEVELOPMENT OF PROTECTIVE COATINGS FOR TANTALUM BASE ALLOYS

**TASK II - DEVELOPMENT OF TECHNOLOGY APPLICABLE
TO COATINGS USED IN THE 3000 TO 4000 F TEMPERATURE RANGE**

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FOREWORD

This report was prepared by the Research Laboratories of Solar, a Division of International Harvester Company, San Diego, California on Air Force contract AF33(657)-11259, under Project 7312 "Metal Surface Deterioration and Protection", Task 731201 "Metal Surface Protection". The work is administered by the Research and Technology Division, Air Force Material Laboratory, with Mr. Norman M. Geyer acting as Project Engineer.

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Special acknowledgment is given to J. A. Bauer for developing the electrical conductivity versus frequency technique to obtain diffusion data.

This report is an interim summary report on Task II - Development of Technology Applicable to Coatings Used in the 3000 to 4000 F Temperature Range. The contractor's report number is RDR 1360-10.

ABSTRACT

The objective of this program was to develop new concepts and obtain experimental data which would be useful in a solution to the problem of the protection of tantalum from oxidation in the 3000 to 4000 F temperature range. Studies of bulk oxides were made to determine what modifier oxides would be required to form the optimum oxide coating.

Thermal expansion measurements were performed on oxides from 1500 to 4000 F to determine the expansion match with tantalum. Electrical conductivity of an oxide was used as one indication of the diffusion characteristics of an oxide; hence its protective ability. Compatibility tests were also conducted with oxide, reservoir, barrier, and substrate material.

The experimental results indicate that hafnia or hafnia modified with ZrO_2 and Y_2O_3 are suitable for continued investigation as coating materials. Hafnium appears to be a suitable reservoir material with tungsten as a barrier on tantalum.

This technical documentary report has been reviewed and is approved.

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I. INTRODUCTION

Tantalum and its alloys are attractive because of the wide range of temperatures over which they have useful engineering properties. The only other competitor for use at 3000 to 4000 F is tungsten; but this metal and its alloys lack ductility at low temperatures and are of higher density. Tantalum has an extensive solubility for oxygen and oxidizes rapidly at high temperatures so a protective coating must be developed to realize its full potential.

Silicide and aluminide coatings become increasingly sensitive to the environment as the temperature is increased. The life of silicide coatings on molybdenum is strongly pressure dependent (Ref. 1). The aluminum-tin coatings, which appear to require the presence of a liquid metal, are also strongly pressure sensitive (Ref. 2). It is improbable that these systems can be successfully extended much beyond 3000 F for most applications; therefore, new concepts are urgently needed.

The object of the program was to develop new coating concepts which will lead to protection of tantalum alloys between 3000 and 4000 F.

II. TECHNICAL APPROACH

2.1 STATEMENT OF THE PROBLEM

Silica, because of its volatility, will not make a successful coating for use in the 3000 to 4000 F range. That is unfortunate because the wide viscous range of modified silica, excellent wetting properties, low elastic modulus, high strength, and low thermal expansion make it a particularly remarkable material. No other material, with the possible exception of B_2O_3 , has the same combination of properties. Losing silica as a coating means that:

- Expansion match between coating and substrate must be much closer.
- Self healing by a reservoir material will be more difficult to attain because without viscous flow only diffusion or fluid flow are repair mechanisms in crystalline materials.
- The strength-modulus ratio of crystalline material is less favorable than the silica system.

For the preceding reasons, future coatings will be engineered for specific alloys, and will not have the versatility of present coating systems.

Development of successful coatings for tantalum for the 3000 to 4000 F temperature range requires consideration of the following parameters:

- Diffusion
 - Oxygen through the coating
 - Oxygen into the substrate
 - Interdiffusion of substrate and oxygen diffusion barrier
 - Oxygen through the diffusion barrier
- Chemical Stability
 - Thermodynamic equilibrium between coating and substrate
 - Solubility limit of oxygen and reservoir material in the substrate
 - Kinetics of the various diffusion reactions

TABLE 1
VAPOR PRESSURE OF METAL COMPONENTS
OF IMPORTANT PROTECTIVE SYSTEMS(1)

Element	Vapor Pressure (Torr)			
	2500 F	3000 F	3500 F	4000 F
Th	< 0.01	< 0.01	< 0.01	< 0.01
Zr	< 0.01	< 0.01	< 0.01	< 0.01 ⁽²⁾
Hf	< 0.01	< 0.01	< 0.01	< 0.01
Si	0.01	0.4	15	300
Al	3	53	380	> 760
Cr	0.05	1.5	23	152
Ta	< 0.01	< 0.01	< 0.01	< 0.01
W	< 0.01	< 0.01	< 0.01	< 0.01
Sn	0.2	6	76	530
Be	0.08	2 ²	28 ²	-

1. Data for Table 1 extracted from the following sources:

Smithells, C.J., Metals Reference Book. New York: Interscience Publishers, Inc. (1955) Vol. II, p. 613.

Kelley, K.K., "Contributions to the Data on Theoretical Metallurgy III." Bureau of Mines Bulletin 383 (1935).

Hampel, C.A., Rare Metals Handbook. New York: Reinhold Publishing Corp. (1954).

2. Extrapolated data from Smithells

- Vaporization
 - Both of the coating and reservoir material
- Physical Damage
 - Naturally occurring discontinuities from oxide growth, inclusions in coating and substrate, thermal cycling, and handling damage.

Although the list of parameters that must be controlled to develop a protective coating for tantalum alloys is imposing, sufficient background data are available to indicate that several of the parameters do not present serious limitations. It appears that the principal limiting parameters in high-temperature coating development are physical damage and oxygen diffusion through oxides. Interdiffusion of oxygen barriers, such as tungsten and rhenium into tantalum, appear to be tolerably low (Ref. 3).

Oxides appear to be the only candidates for high-temperature coatings (Ref. 4) and the free energy of formation of the refractory Group IV oxides is high enough to minimize reaction with an oxygen barrier such as tungsten. Vaporization also does not appear limiting with the refractory metals (Table 1) and Group IV oxides.

Physical damage results from defects which are initiated in the coating from oxide growth, substrate inclusions, thermal gradients, differential thermal expansion, and lattice parameter mismatch. The damage must be repaired by either oxidation of the reservoir material or self healing. Physical damage is believed to be the principal cause of breakaway (change from parabolic to linear oxidation rates).

2.2 ANALYSIS OF THE PROBLEM

2.2.1 Previous Analysis

General Telephone & Electronics Laboratory has studied the problem of high-temperature protection of tungsten (Ref. 4) and they concluded that with adequate refractoriness, five phenomena would determine the usefulness of a coating:

1. The rate of vaporization
2. Breakaway
3. Diffusion paths in ternary oxygen-metal-metal systems
4. Coating-substrate reactions
5. Rate of diffusion-controlled film growth

Although this analysis is believed to present the reasons for coating failure, it is unsuitable for coating development for several reasons. Foremost is the fact that certain phenomena, such as breakaway, are insufficiently understood so that they cannot be related to measurable quantities. For example, it is suggested that among the factors affecting breakaway are vaporization, solubility in the metal, phase changes, lattice parameter match of oxide and metal, and multiplicity of oxides. In view of the impossibility of relating breakaway to some measurable physical property, it seems that this phenomenon, out of the five listed, is not subject to investigation.

2.2.2 Solar Analysis

Solar's analysis has divided the problem of coating development into four areas:

1. Oxygen transport through the coating
2. Stability of oxide in contact with the substrate
3. Retention of reservoir
4. Physical maintenance of oxide

The problem of control of oxygen transport through the protective oxide requires a continuous oxide film, free from flaws, and a low rate of diffusion of oxygen through the film.

The stability of the oxide in contact with the substrate is extremely difficult to predict. Free energies of formation of oxides are not applicable because the reaction is not between the pure substrate and stoichiometric oxide, but between an oxygen-containing substrate and an oxygen-deficient oxide.

Retention of reservoir means that the layer beneath the oxide that supplies additional ions for growth and repair of the oxide must last throughout the protection period. For example, molybdenum disilicide supplies silicon to maintain the silica layer; similarly, tantalum aluminides may provide a source of aluminum to repair the alumina protective film. These compounds form a "reservoir" to supply silicon or aluminum to the oxide film.

The fourth problem area is the physical maintenance of the oxide. Prevention of any discontinuities within the oxide is a necessary, although not the only, condition for parabolic growth rate laws. The disruptive influences are many:

differential thermal expansion between reservoir and oxide, lattice misfits, surface energy forces, vaporization, chemical interaction, and aerodynamic shear, to name a few. This problem is the most acute of the four types discussed here, but it is followed closely in importance by the problem of oxygen transport through the coating.

2.3 DISCUSSION OF PROBLEM AREAS

2.3.1 Oxygen Transport

The rate of oxygen transport through the oxide controls the life of the reservoir and hence the life of the coating. Surveys such as those reported by Nicholas (Ref. 4) are useful in assessing the best oxides for minimal rates of oxygen transfer. No data are available above 2000 K but at this temperature, alumina and magnesia have diffusion coefficients given by:

$$\begin{aligned}\text{Alumina:} \quad (D)O_2 &= 1.9 \times 10^3 e^{-\frac{152,000}{RT}} \\ \text{Magnesia:} \quad (D)O_2 &= 2.5 \times 10^{-6} e^{-\frac{62,400}{RT}} \\ (D)Mg &= 0.249 e^{-\frac{79,000}{RT}}\end{aligned}$$

Data on chromic oxide, rare earth oxides, Group IV (Zr, Hf, and Th) oxides, and beryllium oxide are generally inadequate. Available data show that acceptable growth rates are possible with oxides, but that the diffusion rate of the cation (e.g., magnesium) may be the controlling factor. Movement of magnesium ions to the oxygen-oxide interface is equivalent to a movement of oxygen ions to the oxide-substrate interface. Review of ionic sizes (Mg^{++} 0.78Å; O^{--} 1.32Å) show that this is a problem to be expected.

Transport through an oxide is determined by several factors according to the theories of Wagner and others. Lattice vacancies increase both the electronic and ionic transport so that approaches to reduce these defect concentrations are desirable. Vacancies result from two mechanisms. One mechanism is the increase in the number of vacancies at equilibrium due to thermal effects, and this increase can be calculated from the entropy of disorder. These vacancies increase with temperature in single component material such as tungsten or graphite. The second origin of vacancies results from chemical equilibrium and is determined by the departure of the composition from stoichiometric composition. Iron oxide, FeO, has a very large

FIGURE 1. PARABOLIC FILM GROWTH CONSTANT FOR HAFNIA WITH EXTRAPOLATION TO HIGHER TEMPERATURE

number of cation defects because the range of composition is from 51 to 54 atomic percent of oxygen. The gradual replacement of iron by nickel probably reduces the range of composition and accounts for the better oxidation resistance of nickel-iron alloy. Doping nickel oxide with lithium causes a further decrease in oxidation rate whereas chromium (in small amounts) raises the oxidation rate by increasing the number of cation vacancies.

Because of the increase in the number of vacancies with temperature, it is unlikely that minor amounts of doping will be significant at 3000 to 4000 F. However, when the range of composition of the protective oxide is extensive, additions should be effective. For example, measurements of hafnia after exposure to a vacuum of 10^{-4} Torr at 4500 F show that the composition approximates $\text{HfO}_{1.985}$ (Ref. 5). This composition shift must be accompanied by a large concentration of anion defects, and the addition of several percent of pentavalent or higher valency cations may succeed in restoring the composition closer to MO_2 .

Figure 1 reproduces data on the parabolic film growth constant for hafnium from work of Simnad and Smeltzer reproduced by Nicholas (Ref. 4). The linear extrapolation from 1100 to 2000 C on the reciprocal temperature plot is dangerous because the concentration of lattice vacancies increases rapidly in this temperature range.

2.3.2 Stability of Oxide in Contact with Substrate

The partial molal free energy of a solid solution approaches infinity for the solution of the first atom because the entropy of disorder is extremely high. With progressive increase in concentration of solute, the partial molal free energy decreases until the solid solution reaches a composition in equilibrium with its surroundings. Kubaschewski and co-workers at the National Physical Laboratory have used this principle very effectively to determine partial molal free energies of solid solutions of oxygen in vanadium by equilibrating with oxides of known free energy of formation such as CaO, BaO, and SrO. It is precisely this phenomenon that prevents the use of oxide coatings directly on tantalum. Studies of compatibility with tantalum have revealed that this problem is acute (Ref. 6).

Experimental determination appears to be the only way to solve this problem. In the case of the work of Kubaschewski, the assumption was made that the free energy of formation of the alkaline earth oxide could be used. This assumption can be justified on the grounds of the narrow range of composition of these oxides at low temperatures.

At high temperatures, however, the range of composition increases in most cases, so that equilibrium is determined by the free energy of formation of the oxygen-defect oxide in equilibrium with tantalum or the substrate. In addition, the loss of oxygen from the original stoichiometric composition provides a readily available source of oxygen. These complexing factors make experimental determinations the best approach to the study of compatibility.

There does not appear to be a major problem in the development of compatible systems of oxides and metallic diffusion barriers such as tungsten for use to 4000 F. Development of stable reservoir-oxide systems may be more difficult because of the inherent high free-energy of formation of solid solutions of oxygen in Group IV metals.

2.3.3 Retention of Reservoir

The problems of retaining a reservoir to replenish the oxide coating are threefold. The reservoir may be lost by diffusion inwards to form lower compounds. For example, diffusion of a disilicide (MSi_2) inwards to form a lower silicide (M_5Si_3) would result in loss of protection because the high metal contact of M_5Si_3 would make the SiO_2 film unstable. A second loss mechanism is evaporation. In this mechanism, the vapor pressure of the active component in the reservoir may lead to both loss of this component and to disruption of the oxide layer. Closely allied to evaporation is loss by interaction. In this case, the product may be volatile as in the silica-silicon reaction to yield the monoxide. The selection of suitable reservoirs does not appear to present too much difficulty if diffusion barriers are employed to reduce the loss by inward diffusion. Work by Passmore et al (Ref. 3) show that tungsten and rhenium form good diffusion barriers for tantalum.

2.3.4 Physical Maintenance of Oxide

Accepting the thesis that an oxide is the only candidate to control the access of oxygen to low rates, then the maintenance of this oxide is the most severe problem facing the developer of coatings. Unless the oxide can be maintained intact, there will be no possibility of obtaining the much desired parabolic growth rate. Factors that may influence maintenance of the oxide are:

- Differential expansion stresses
- Surface tension forces
- Vaporization
- Interactions at substrate boundary
- Aerodynamic shear

Surface tension forces may play a part when films are thin and of low strength or viscosity. The surface tension may cause irregularities in the substrate by surface migration to an equilibrium configuration. Similarly, the oxide may undergo surface migration and, in the limit, ball up. This problem is closely allied to that of aerodynamic shear because mobile oxides may be swept from the surface by this environmental stress. Vaporization of oxides such as silica has been discussed previously and is allied with the analogous problem of substrate-oxide interactions. The classic example is the silica-silicon interaction that can disrupt the silica layer and may be more destructive than the direct vaporization of silica.

Another problem is stresses arising from differential expansion. Exact matching of expansivities is a step to minimize these stresses, but under transient conditions, stresses will arise and can become high if the elastic moduli are high. Silica has a much lower modulus than alumina and beryllia and has performed better, in general, than these other oxides. Not enough information is known of the elastic constants of other oxides to enable a comparison to be made.

Many other mechanisms of oxide disruption might be cited. For example, irregular growth can lead to stresses within an oxide, but irregular growth in turn may be related to a local breakdown of the oxide so that growth rates accelerate. The mechanisms discussed are believed to be important but differential expansion stresses are believed to be the most significant.

2.4 SELECTION OF OXIDES

At the outset of the program, the problem of interaction of oxide, substrate material, and/or oxygen barrier was separated to enable concentration on the principal protective species, i.e., the oxide barrier between the environment and substrate. This separation permitted maximum concentration of effort on modifying selected oxide systems to meet the requirement of a protective overlay.

Selection of potential oxide systems is a relatively simple task when it is considered that the oxide should (1) have a melting point above 4000 F, (2) be essentially nonvolatile, and (3) preferably be an oxide of an element which has a low vapor pressure. Table 2 shows essentially all of the simple oxides melting above 4000 F which can be considered. More complex oxides, e.g., $3\text{BeO}-2\text{ZrO}_2$ (mp 4590 F), $\text{SrO}-\text{ZrO}_2$ (mp 5070 F), and $\text{BaO}-\text{ZrO}_2$ (mp 4890 F), could also be considered candidate oxides, but stoichiometry is very critical in maintaining the high melting point. Complex oxides will be studied only after all simple oxides have been explored.

The list of candidate oxides was reduced further by consideration of the volatility of the metallic element in the compounds and the valence instability. Calcium, barium, strontium, and magnesium boil below 4000 F and beryllium has a vapor pressure higher than 100 Torr at 4000 F, thus eliminating oxides containing these elements. Ceric oxide and UO_2 cannot be maintained in the high melting state due to valence instability and revert to Ce_2O_3 and U_3O_8 , which have inadequate melting points. The list

TABLE 2
SIMPLE OXIDES MELTING ABOVE 4000 F

Material	Melting Point (F)
ThO ₂	5825
HfO ₂	5240
ZrO ₂	4850
Y ₂ O ₃	4370
MgO	5070
CaO	4660
BeO	4620
UO ₂	5200
CeO ₂	5070
Cr ₂ O ₃	4410
SrO	4410
La ₂ O ₃	4180

of candidate oxides was narrowed to three principal materials, ZrO₂, HfO₂, and ThO₂. The list also included several subordinate materials, including Y₂O₃, and several rare earth materials for which little data are available.

The properties of the important oxides included in the study are shown in Table 3. All the oxides have very large free energies of formation and are known to be stable in contact with a potential diffusion barrier, such as tungsten, to at least

TABLE 3
PROPERTIES OF OXIDES

Oxide	Melting Point (F)	ΔF (K Cal/gm Atom Oxygen at 4500 F)	Thermal Exposure (in./in. F $\times 10_6$)	Cation Radius (Å)	Anion Radius (Å)
ThO ₂	5825	-89	5.9	1.10	1.32
HfO ₂	5020	-77	Monoclinic 4.0 (70-2800 F)	0.84	1.32
			Cubic 6.5 (70-4000 F)		
ZrO ₂	4850	-76	Cubic 6.3 (70-4000 F)	0.87	1.32
Y ₂ O ₃	4370	-89	---	1.03	1.32
Ta ₂ O ₅	3700	-47	11.8 (70-1440 F)	0.68	1.32
WO ₃	2680	-27	---	~0.68	1.32

4000 F (Ref. 4). Coefficients of thermal expansion of cubic ZrO₂, HfO₂, and ThO₂ are similar up to 4000 F (Table 3) averaging about 6.2×10^{-6} in./in. deg F which compares with 4.4×10^{-6} in./in. deg F for 90Ta-10W. Monoclinic hafnia has the lowest thermal expansion of the refractory oxides, i.e., 4.0×10^{-6} in./in. deg F (to 2800 F) and, therefore, the best match in expansion.

In summary, the three oxides selected for study as potential protective coatings were HfO₂, ZrO₂, and ThO₂. These oxides were studied in the experimental phase of the program, in the order given, with the greatest emphasis placed on HfO₂.

III. EXPERIMENTAL STUDIES

3.1 RAW MATERIALS UTILIZED IN EXPERIMENTAL STUDIES

The various materials used in the studies described in the following sections are listed in Tables 4 through 9. The tables also give the certified analysis for each oxide and a typical analysis for hafnium. Yttria used in the various experiments was obtained from Kleber Laboratories. The yttria content given was 99 percent pure.

3.2 EXPANSION CONTROL STUDIES

Differential expansion stresses are believed to be the most significant factor influencing physical maintenance of an oxide coating. Physical maintenance of the oxide, in turn, is felt to be one of the critical requirements for parabolic growth rate of a protective oxide coating. Since a parabolic growth rate is desirable, differential expansion stresses must be minimized.

The effect of temperature change on the thermal stress in an oxide coating of infinite plate geometry with an oxide film on both sides of the plate can be expressed as follows (Ref. 7):

$$S_c = \frac{E_c \Delta T (a_c - a_b)}{1 + \frac{2 E_c t_c}{E_b t_b}}$$

where S_c = Coating stress

E_c, E_b = Elastic moduli of coating and base metal

ΔT = Change in temperature

a_c, a_b = Thermal expansion coefficients of coating and base metal

t_c, t_b = Thickness of coating and base metal, respectively

TABLE 4

CHEMICAL ANALYSIS OF HAFNIUM OXIDE; Wah Chang Corp.

Composition	Analysis in ppm		
	Lot RX 106125A Spectrographic	Lot 5-24-61-A Reactor	Lot 1-11-A Reactor
Al	< 25	35	70
B	< 0.2	--	0.2
Cd	< 0.3	< 1	< 1
Co	< 5	< 5	< 5
Cr	< 10	< 75	50
Cu	< 40	< 40	< 40
Fe	< 50	2100	2400
Mg	10	50	10
Mn	< 10	15	15
Mo	< 10	10	< 10
Ni	< 10	40	75
Pb	< 5	10	5
Si	< 40	600	150
Ti	< 20	2000	250
V	< 5	15	5
W	< 50	< 50	50
Zr	150	2.2%	1.25%
LOI	--	0.02%	--
Sn	< 10	---	--

TABLE 5

CHEMICAL ANALYSIS ZIRCONIUM OXIDE; Zircoa, Lot 5576-6568

Element	ppm	Element	ppm
Al	150	Hf	< 50
B	4	Pb	< 10
Ca	650	Mg	350
Cd	< 1.0	Mn	2
Cl	10	Mo	10
Cr	< 10	Ni	50
Co	< 10	Si	1400
Cu	< 10	Ti	< 10
F	< 10	Sn	< 10
Fe	100	V	< 10
Sulfate	1800		

Examination of this equation shows that for a given temperature change, a low coating modulus of elasticity or a small difference in coating and base metal expansion coefficients is desirable to keep the thermal strain at a low value. The thermal stress in the coating must be kept below the tensile strength of the oxide to prevent physical damage and breakaway. Significant control of the elastic modulus does not appear feasible in crystalline systems, but control of the expansion coefficients in certain oxides leading to oxide-metal expansion match may be possible.

Hafnia is an oxide which appears most promising in attainment of an expansion match with tantalum alloys. In its unstabilized form, hafnia has the closest expansion match with tantalum alloys of the refractory simple oxides, but undergoes a rapid volume reduction at the monoclinic to tetragonal phase transformation at

TABLE 6

CHEMICAL ANALYSIS THORIUM OXIDE; Vitro Chemical Co., Lot 232-84

Composition	ppm
SiO ₂	93
TiO ₂	< 30
Fe ₂ O ₃	< 20
CaO	< 100
Al ₂ O ₃	< 100
V ₂ O ₅	< 100
BeO	< 10
Fe ₂ O ₃ (total)	< 100
MnO ₂	< 30
MgO	25
Cr ₂ O ₃	< 20

temperatures of 3100 to 3488 F (Ref. 8). Addition of certain oxides causes a cubic phase of HfO₂ to develop which is stable at all temperatures. Partial stabilization of this cubic phase of HfO₂ and hence a closer expansion match with tantalum may be possible through oxides addition such as Y₂O₃, Ta₂O₅, or ThO₂.

Yttria is known to stabilize the transformation of HfO₂ and ZrO₂. Tantalum oxide may stabilize HfO₂ since the Ta⁺⁵ ion radius is within 15 percent of the Hf⁺⁴ radius. Many other factors influence stabilization, but ionic size is probably the most critical. The effect of ThO₂ additions on the expansion of HfO₂ and ZrO₂ is not well known, but it is interesting because of the extremely refractory nature of ThO₂ and the possibility of combining HfO₂, ZrO₂, and ThO₂ in protective coatings. The ionic size of the Th⁺⁴ ion is about 30 percent greater than Hf⁺⁴ and Zr⁺⁴, so stabilization of HfO₂ or ZrO₂ by small additions of ThO₂ cannot be expected.

TABLE 7
CHEMICAL ANALYSIS TANTALUM OXIDE;
Union Carbide Metals Co., Lot 1035

Composition	Percent
Ta ₂ O ₅	99.90
Cb ₂ O ₅	0.01
Fe ₂ O ₃	0.024
TiO ₂	0.01

Another approach to expansion control of HfO₂ may be possible through addition of ZrO₂. Hafnia and zirconia are reported to form a complete solid solution (Ref. 8), but the effect of ZrO₂ additions on expansion is not known. Zirconia has chemical and physical properties very similar to HfO₂, but undergoes the monoclinic to tetragonal phase transformation at a much lower temperature (2000 to 2200 F). In addition, volume change at transformation of ZrO₂ is 7.5 percent as opposed to about 3.4 percent in hafnia. Zirconia additions to HfO₂ may influence the temperature and temperature range of phase transformation and the magnitude of volume change at inversion. Some control of the expansion of HfO₂ would then be possible by controlled ZrO₂ additions.

Work was undertaken to develop techniques for controlling the thermal expansion of HfO₂ through controlled oxide additions. Initial work involved measurement of thermal expansion of oxides of selected composition. Finally, evaluation of the thermal expansion match of promising oxide composition with potential metal substrates was attempted by bonding the oxide to metal rods.

3.2.1 Thermal Expansion of Oxides

Spectrographic grade and reactor grade hafnia were used as base materials. Yttria, Ta₂O₅, ThO₂, and ZrO₂ were used as additions to the hafnia. Yttria was obtained from Kleber Laboratories and was 99 percent pure. The source and chemical analysis of the other oxides are given in Tables 4 through 7.

TABLE 8
CHEMICAL ANALYSIS NIOBIUM OXIDE;
Fansteel Metallurgical Corp., Lot HP-2

Composition	Percent
Ta_2O_5	0.05
ZrO_2	0.05
FeO	0.005
SiO_2	0.32
WO_3	0.05
Alkali	0.02
LOI	0.29

Procedure

The oxide powders were mixed with 4 weight percent polyethylene glycol binder (Carbowax 4000) and enough distilled water to make a very thin slurry. The slurry was mixed for 10 minutes in a Waring blender (No. 700A) to obtain a homogeneous mixture of components. The mixture was then dried and the resulting cake broken up and sized using Tyler standard sieves. The particles which passed through a 20-mesh sieve but not through a 100-mesh sieve (0.0059 to 0.0331 inch in diameter) were placed in a steel die and pressed at 10 ksi into bars 2.5 inches by 0.4 inch by 0.3 inch.

The binder was burned out of the bars by heating them in air to 1800 F and holding them at that temperature for at least one hour before cooling to room temperature. The bars were then wrapped in tungsten foil, inserted into a tungsten crucible, and placed in position in the resistance-heated graphite furnace shown in Figure 2. The bars were heated in an argon atmosphere at a rate of 40 F/min to 2500 F where they were held for 30 minutes while essentially all the shrinkage occurred. The temperature was then raised at a rate of about 60 F/min to the

TABLE 9
CHEMICAL ANALYSIS HAFNIUM ELECTRON BEAM INGOT;
Wah Chang Corp.

Element	ppm
Al	< 25
B	< 0.5
Ca	< 50
Cd	< 1
Co	< 10
Cr	< 30
Cu	< 40
Fe	50
Mg	< 10
Mn	< 10
N	20
Ni	< 10
O	400
Pb	10
Si	70
Sn	< 20
Ti	< 50
V	< 20
W	< 50
Zr	< 4 %
BHN	155 to 175

sintering temperature of 4000 to 4300 F. The bars were held at the sintering temperature one hour and then cooled at a rate of about 50 F/min to room temperature. This technique allowed fabrication of dense bars without visible external cracks.

Normally, about 15 percent linear shrinkage of the samples would occur during sintering. The color of the sintered bars was black or dark gray throughout. The color was probably due to the oxygen-deficient defect structure formed during sintering

FIGURE 2. EXPANSIVITY FURNACE; Cross-Sectional Drawing

in the reducing atmosphere of the furnace. The color was changed from black to white or amber by heating the bars to 1800 F in air.

The temperatures were determined by a calibrated optical pyrometer sighted on the specimen. The assumption of black body condition in the furnace cavity was based on close agreement of temperature on the surface of the crucible and a black body hole with a 7 to 1 length to diameter ratio in a specimen. In addition, the observed melting point of pure platinum foil placed on the crucible was within 9 F of the reported value of 3227 F.

FIGURE 3. LINEAR THERMAL EXPANSION OF TUNGSTEN

The expansion measurements were made using the apparatus shown in Figure 2. The relative linear expansion of a known room-temperature length of pure tungsten (the sides of the crucible) and the sample bar was measured with a Gaertner model M-353 filar micrometer microscope. The temperature was determined by an optical pyrometer sighted on the specimen. Readings were taken when no change in specimen length occurred at a given temperature. The difference between the sample and crucible wall length was added to the expansion of tungsten for that temperature to obtain the total change in length of the sample. Figure 3 shows the expansion curve of tungsten obtained from the literature.

The expansion measurement apparatus was calibrated by measuring the expansion of an extruded pure tungsten rod relative to the crucible. There was essentially no relative expansion or contraction of the rod and crucible in the temperature range of 1600 to 4000 F. Therefore, it was assumed that the plasma-arc spray-formed tungsten crucible expanded at the same rate as extruded tungsten. In addition, the measured expansion of a pure thoria bar agreed well with the literature.

TABLE 10
DENSITY AND AVERAGE LINEAR THERMAL EXPANSION COEFFICIENTS OF BULK
OXIDE SAMPLES

Composition (wt %)	Apparent Density (g/cc)	Linear Thermal Expansion Coefficient (per/F x 10 ⁻⁶)	Temperature Range (F)
99.9 HfO ₂	9.75	3.8 6.9	1600-3250 3500-4300
97 HfO ₂ -3 ZrO ₂	9.32	5.2 4.3	1750-3180 3250-4170
78.4 HfO ₂ -21.6 ZrO ₂	8.27	4.0 6.7	1800-2800 2900-4130
68.6 HfO ₂ -31.4 ZrO ₂	8.02	3.5 6.8	1700-2800 3100-4050
48.9 HfO ₂ -51.1 ZrO ₂	6.95	4.0 7.7	1680-2430 2570-4430
29.3 HfO ₂ -70.7 ZrO ₂	6.40	4.1 8.4	1660-2225 2550-4300
80 HfO ₂ -15 ZrO ₂ -5 Y ₂ O ₃	7.99	5.3	1600-4000
84 HfO ₂ -15 ZrO ₂ -1 Y ₂ O ₃	8.44	3.7 3.9	1700-2950 3250-4000
82 HfO ₂ -15 ZrO ₂ -3 Y ₂ O ₃	8.13	5.2 6.8	1550-2600 3050-4150
94 HfO ₂ -3 ZrO ₂ -3 Y ₂ O ₃	8.62	6.5 4.0 6.9	1500-2800 3200-3700 3700-4200
95 HfO ₂ -3 ZrO ₂ -2 Y ₂ O ₃	8.96	3.9 6.6	1400-2900 3200-4150
97 HfO ₂ -3 Y ₂ O ₃	9.21	3.7 6.7	1400-2900 3100-4100
84.75 HfO ₂ -15 ZrO ₂ -0.25 Ta ₂ O ₅	8.84	Sintering and shrinkage with disintegration at the inversion tempera- ture	1500-4000
84 HfO ₂ -15 ZrO ₂ -1 TaO ₅	8.82		
80 HfO ₂ -15 ZrO ₂ -5 Ta ₂ O ₅	8.84		
100 ThO ₂	9.41	6.9	1640-3800
95 ThO ₂ -5 ZrO	9.29	7.6	1900-4070
90 ThO ₂ -10 ZrO ₂	8.78	8.9	1600-3900
90 Ta-10W	16.8	5.4	2000-3700

FIGURE 4. LINEAR THERMAL EXPANSION OF 99.9 WT % HfO_2 AND 90Ta-10W ALLOY

Results

HfO_2 (Spectrographic grade). The linear thermal expansion of bars of 99.9 percent pure HfO_2 was measured between 1500 and 4300 F. The specimen density as determined by the water immersion method and the expansion coefficients are presented in Table 10. The expansion data are plotted in Figure 4 along with the reported expansion of 90Ta-10W alloy.

$\text{HfO}_2\text{-ZrO}_2$. The linear thermal expansion of $\text{HfO}_2\text{-ZrO}_2$ blends containing from 97 weight percent to 29.3 weight percent HfO_2 was measured between 1500 and 4300 F. The expansion data are plotted in Figures 5 through 9 along with the reported expansion of 90Ta-10W alloy. The densities and thermal expansion coefficients are listed in Table 10.

$\text{HfO}_2\text{-ZrO}_2\text{-Y}_2\text{O}_3$. The linear thermal expansion of blends of $\text{HfO}_2\text{-ZrO}_2\text{-Y}_2\text{O}_3$ was measured between 1400 and 4300 F. The data are plotted in Figures 10 through 14 along with the reported expansion of 90Ta-10W alloy. The densities and average linear expansion coefficients are given in Table 10.

FIGURE 5. LINEAR THERMAL EXPANSION OF 97 WT % HfO₂ - 3 WT % ZrO₂ AND 90Ta-10W ALLOY

FIGURE 6. LINEAR THERMAL EXPANSION OF 78.4 WT % HfO₂ - 21.6 WT % ZrO₂ AND 90Ta-10W ALLOY

FIGURE 7. LINEAR THERMAL EXPANSION OF 68.6 WT % HfO_2 -31.4 WT % ZrO_2 AND 90Ta-10W ALLOY

FIGURE 8. LINEAR THERMAL EXPANSION OF 48.9 WT % HfO_2 -51.1 WT % ZrO_2 AND 90Ta-10W ALLOY

FIGURE 9. LINEAR THERMAL EXPANSION OF 29.3 WT % HfO_2 -70.7 WT % ZrO_2 AND 90Ta-10W Alloy

FIGURE 10. LINEAR THERMAL EXPANSION OF HfO_2 - ZrO_2 - Y_2O_3 BLENDS AND 90Ta-10W ALLOY

FIGURE 11. LINEAR THERMAL EXPANSION OF 84 WT % HfO₂-15 WT % ZrO₂-1 WT % Y₂O₃ AND 90Ta-10W ALLOY

FIGURE 12. LINEAR THERMAL EXPANSION OF 94 WT % HfO₂ - 3 WT % ZrO₂ - 3 WT % Y₂O₃ AND 90Ta-10W ALLOY

FIGURE 13. LINEAR THERMAL EXPANSION OF 95 WT % HfO_2 - 3 WT % ZrO_2 - 2 WT % Y_2O_3 AND 90Ta-10W ALLOY

FIGURE 14. LINEAR THERMAL EXPANSION OF 97 WT % HfO_2 - 3 WT % Y_2O_3 AND 90Ta-10W ALLOY

FIGURE 15. LINEAR THERMAL EXPANSION OF $\text{ThO}_2\text{-ZrO}_2$ BODIES SINTERED AT 4000 F

$\text{HfO}_2\text{-ZrO}_2\text{-Ta}_2\text{O}_5$. Hafnia bars with compositions containing 15 weight percent ZrO_2 and from 0.25 to 5 weight percent Ta_2O_5 were fabricated. The bars did not sinter satisfactorily and extensive cracking and expansion of the specimens occurred when heated and cooled through the transformation temperature. No expansion values are reported for these samples.

$\text{ThO}_2\text{-ZrO}_2$. The linear thermal expansion of thoria-zirconia blends containing 100, 95, and 90 percent thoria was measured between 1600 and 4100 F. The resulting data are plotted in Figure 15. The densities and expansion coefficients of these materials are tabulated in Table 10. Specimens containing more than 10 weight percent ZrO_2 could not be fabricated because of extensive cracking.

FIGURE 16. INFLUENCE OF COMPOSITION ON INVERSION TEMPERATURE IN THE $\text{HfO}_2\text{-ZrO}_2$ AND $\text{ZrO}_2\text{-TiO}_2$ BINARY SYSTEMS

Discussion

HfO_2 (Spectrographic grade). The abnormally low thermal expansion of spectrographic HfO_2 (Fig. 4) was probably the result of internal expansion into cracks and voids during the expansion run (Ref. 11). Upon cooling from sintering, internal cracks developed, and on heating, the cracks tended to close resulting in an abnormally low expansion rate at the lower temperatures. This kind of expansion is observed when poor sintering occurs and the expansion coefficient is markedly different in different crystalline directions. Poor initial sintering of the pure HfO_2 was indicated by the fact that those specimens were easily crushed. On the other hand, $\text{HfO}_2\text{-ZrO}_2$ specimens sintered well and were very difficult to crush. Three 99.9 percent HfO_2 specimens were made and they all showed essentially the same characteristics even when sintering temperatures of 4600 F were used.

Figure 5 shows the expansion data from two specimens of reactor grade hafnia and data from the literature for high purity hafnia. The X-ray data of Grain et al (Ref. 9) were obtained from 99.5 percent pure HfO_2 and connects smoothly with the Solar data. This agreement of expansion of reactor grade HfO_2 bars with literature

expansion values of 99.5 percent pure HfO_2 supports the assumption that the abnormally low expansion of polycrystalline 99.9 percent HfO_2 does not represent the expansion of a well sintered polycrystalline body. The average expansion of a coherent 99.9 weight percent HfO_2 bar would probably be very similar to that measured for 97 weight percent HfO_2 .

In spite of the error discussed above, the expansion of spectrographic grade HfO_2 bars was shown because the temperature of transformation and hysteresis can be accurately obtained from the data. Those properties are of particular interest and are discussed below.

Pure hafnia has been considered a much better refractory than zirconia because unlike zirconia, hafnia does not normally fracture when it undergoes inversion. This ability of hafnia has been attributed to its smaller volume change during phase transformation. The respective transformation volume changes for hafnia and zirconia are 3.4 and 7.5 percent (Ref. 8). Another important consideration may be the higher transformation temperature of HfO_2 , particularly during cooling. Plastic deformation of ceramic bodies may occur at high temperatures to relieve stress caused by the volume change of the phase transformation. If the transformation occurs at lower temperatures, plastic deformation is not possible and fracture occurs.

The transformation temperature of the spectrographic grade hafnia measured in this work agrees well with that reported by Curtis et al (Ref. 8) which was also for oxygen deficient hafnia. Recently, hafnia not previously fired in a reducing atmosphere was reported to undergo inversion about 300 F lower than reported here (Ref. 12). In view of this finding, the use of nearly pure hafnia may be necessary to obtain a transformation temperature high enough for good thermal shock resistance.

HfO_2 - ZrO_2 . The addition of ZrO_2 to HfO_2 lowered the transformation temperature and increased the hysteresis as shown in Figures 5 through 9. When the temperature range of the inversion was plotted against mole percent hafnia as in Figure 16, an essentially linear relationship was found with the temperature increasing from pure zirconia to pure hafnia. Compositions in the ZrO_2 - TiO_2 system are included in Figure 16 to show the interesting trend that apparently exists in the Group IV oxides. Assuming that the temperature of inversion is an important consideration, the high hafnia compositions are more likely to survive thermal shock. A test of this assumption

was made by slowly heating the hafnia-zirconia bars in a furnace to 4000 F and then cooling them to 1800 F at about 700 F/min. Only the bars containing 97 and 99.9 weight percent hafnia did not develop large external cracks. The data indicate the volume change during inversion is not greatly different for all the compositions and, with the exception of 99.9 weight percent HfO_2 , the expansion coefficients are similar. Therefore, temperature of inversion seems to be an important factor in thermal shock resistance.

The thermal expansion coefficient of 97 weight percent HfO_2 below the transformation temperature was about 20 percent greater than shown by the other HfO_2 - ZrO_2 compositions (Table 10). One explanation is that uniform solid solution was not attained in the higher ZrO_2 blends. Small amounts of free ZrO_2 and ZrO_2 compositions containing less HfO_2 than the average calculated for the specimen may have existed. These compositions could have gone through the transformation at a lower temperature than the average composition. The resulting volume change would decrease the expansion rate. This assumption was supported by X-ray diffraction analysis which indicated uniform solid solution was not attained in specimens containing less than 97 weight percent HfO_2 . However, considerable solid solution must have occurred in order to show the pronounced effect of the average composition on the transformation temperature.

Coatings of the HfO_2 - ZrO_2 compositions used in this study, bonded to 90Ta-10W alloy, would go into compression upon cooling through the transformation temperatures as shown in Figures 5 through 9. In place of a perfect expansion match with tantalum, this condition may be acceptable provided the inversion occurs at a high enough temperature. Spectrographic HfO_2 and reactor grade HfO_2 have the highest transformation temperatures, so they are promising in this regard. A lower inversion temperature could be tolerated if the volume change at the inversion were reduced. Partial stabilization of the HfO_2 phase transformation would enhance the expansion match with tantalum alloys provided the linear expansion before and after the transformation was not greatly changed.

HfO_2 - ZrO_2 - Y_2O_3 . Changes in the relative proportions of HfO_2 , ZrO_2 , and Y_2O_3 appear to have a major effect on three parameters which are important in the development of a coating. Those parameters are the amount of volume change at inversion, the expansion coefficient, and the temperature range between the respective inversions which occur when heating and cooling.

Stabilization of the cubic phase will be discussed first. The $\text{HfO}_2\text{-ZrO}_2$ solid solution was evidently completely converted to the cubic phase by 5 weight percent Y_2O_3 addition. This is evidenced by the absence of the monoclinic to tetragonal phase transformation in that composition as shown in Figure 10. On the other hand, three, two and even one weight percent Y_2O_3 partially stabilized the cubic phase as shown in Figures 10 through 14. Brittle materials such as oxides exhibit their maximum strength when in compression. For that reason, the optimum amount of stabilization would cause the oxide coating on an alloy such as 90Ta-10W to always be in a neutral or slight compressive stress.

The expansion coefficient of the coating should be as close as possible to that of the substrate, particularly at low temperatures. It appears that the expansion coefficient increased as the ZrO_2 content was decreased and the Y_2O_3 content increased. Therefore, by judicious balancing of effects, a reasonable expansion coefficient match with the substrate should be possible.

There remains a third parameter to consider, phase transformation hysteresis. All of the compositions which contained Y_2O_3 exhibited a rather large hysteresis. The inversion temperature upon heating was about 3000 F, whereas the volume change of the inversion during cooling occurred in the temperature range of about 2000 to 2500 F. Inversion of unstabilized pure ZrO_2 also occurs in that temperature range. The poor thermal cycling properties of ZrO_2 are probably due to the fact that the material is very brittle at the temperature of the inversion. However, the amount of volume change of pure ZrO_2 at inversion is much greater than that of the partially stabilized $\text{HfO}_2\text{-ZrO}_2\text{-Y}_2\text{O}_3$ compositions. The reduced volume change should improve the thermal cycling properties of the partially stabilized oxides.

From the considerations discussed above, the composition 94 weight percent HfO_2 - 3 weight percent ZrO_2 - 3 weight percent Y_2O_3 whose thermal expansion is shown in Figure 12 appears to have the best overall expansion match with a potential 90Ta-10W alloy substrate.

$\text{HfO}_2\text{-ZrO}_2\text{-Ta}_2\text{O}_5$. All of the specimens showed rather erratic behavior which was probably caused by extensive intergranular cracking. The specimens were relatively porous prior to the expansion runs and after the runs they crumbled easily. A complex reaction evidently occurred in these blends and very little, if any, phase stabilization was realized. These blends did not appear promising with regard to thermal expansion control, so work in this system was not continued.

ThO₂-ZrO₂. Figure 15 shows that 90 and 95 percent thoria stabilizes zirconia. The expansion curves for those compositions are approximately parallel to that of pure ThO₂. Comparison of the expansion of ThO₂-ZrO₂ compositions with tantalum indicates those compositions have expansion coefficients much too high to be of interest. Dense bars containing more zirconia than 10 weight percent could not be fabricated due to extensive cracking. Since HfO₂ and ZrO₂ are chemically very similar, the same results can be expected for HfO₂-ThO₂ composition. Therefore, this work was not extended into the HfO₂-ThO₂ system.

Conclusions

Thoria did not appear hopeful, and TaO₅ could not be shown by this work to hold promise as oxide additions to achieve thermal expansion match of HfO₂ and tantalum alloys.

Control of the thermal expansion of HfO₂ and reasonable expansion match with tantalum alloys is possible through controlled additions of Y₂O₃ and ZrO₂.

Three compositions which show promise as coatings are spectrographic grade HfO₂, reactor grade HfO₂, and partially stabilized HfO₂ (94 wt% HfO₂-3 wt% ZrO₂ - 3 wt% Y₂O₃). The spectrographic grade HfO₂ gave indications of poor sintering properties, but that does not exclude it from consideration in coating systems.

3.2.2 Evaluation of Substrate-Oxide Expansion Match

Work on control of the expansion of HfO₂ indicated that tantalum and the 90Ta-10W alloy had a good thermal expansion match with spectrographic grade HfO₂, reactor grade HfO₂ and with the composition 94 weight percent HfO₂ - 3 weight percent ZrO₂ - 3 weight percent Y₂O₃. A measure of the degree of thermal expansion match could be obtained by an evaluation of thermal cycle properties of the selected oxides when bonded to alloys of interest. Plasma spray techniques for coating applications did not seem promising, because in previous experiences at Solar the best possible densities of plasma sprayed oxide coatings has been about 90 percent. A technique was investigated which involved sintering the oxide onto a metal rod at temperatures near the oxide melting point.

Procedure

Oxide powders were mixed in a distilled water slurry and applied with a brush to metal rods. The rods were extruded and ground tantalum, 90Ta-10W alloy (1/8-inch diameter by 10 inches), and two percent thoriated tungsten (1/8 inch diameter by

FIGURE 17. TESTING FURNACE

7 inches). Two oxide compositons were used for initial study; 97 weight percent HfO_2 - 3 weight percent ZrO_2 and 94 weight percent HfO_2 - 3 weight percent ZrO_2 - 3 weight percent Y_2O_3 . The purity and source of the oxides are contained in Table 4. After the slurry was dry, the rod was placed in the furnace (Fig. 17) and resistance heated to about 4000 F in one atmosphere of argon. After five minutes at 4000 F, the specimen was cooled and another coat of slurry applied. This procedure was repeated until a sintered coating about 0.012-inch thick was built up. The rods were then heated to various temperatures between 4000 and 5200 F (measured optically) for 3 to 5 minutes in an attempt to partially fuse the oxide and obtain a firm bond to the metal. The texture and composition of the surface changed with time during the run so that no emittance corrections were made in temperature measurement. The true temperature probably ranged from 100 to 400 degrees higher than optical readings. After the final sintering run, thermal cycling tests were conducted, Thermal cycling consisted of cycling the specimens in the testing furnace (Fig. 17) between room temperature and 4000 F at about 500 F/min.

FIGURE 18. TUNGSTEN ROD WITH A 94 Wt % HfO₂ - 3 Wt % ZrO₂ - 3 Wt % Y₂O₃ COATING; Sintered 4780 F for Four Minutes

Results

A dense adherent oxide coating could not be obtained on the tantalum and 90Ta-10W alloy rods. The coated rods developed locally overheated zones and melted when heated to temperatures near 5200 F. The tungsten rods survived the sintering temperature and achieved an adherent coating.

All of the coatings were cracked and porous. In addition, the coatings sintered at temperatures of 4000 F and above had a metallic luster and negligible electrical resistance. Metallographic examination of tungsten with a 94 weight percent HfO₂ - 3 weight percent ZrO₂ - 3 weight percent Y₂O₃ coating showed considerable migration of tungsten into the oxide (Fig. 18). The appearance of the coatings did not change when subjected to repeated thermal cycles between room temperature and 4000 F. When heated to about 2000 F in air, the coatings rapidly turned to a yellow powder and fell off. The yellow color indicated oxidation of the tungsten in the coating with formation of WO₃.

Discussion and Conclusion

The expansion match of hafnia and 94 weight percent HfO₂ - 3 weight percent ZrO₂ - 3 weight percent Y₂O₃ with tantalum and 90Ta-10W alloy is much better than with tungsten. It was felt that a coating which survived thermal cycling on tungsten

would be even more shock resistant on tantalum or 90Ta-10W alloy. However, the cracked and porous nature of the coatings applied indicated that the application technique was not useful even when sintering temperatures near the melting point of the oxide were used.

The excellent thermal shock resistance of the coating was probably more the result of the extensive metallic phase in the oxide (Fig. 18) than it was good expansion match. Therefore, the thermal cycle test was of no value in studying the shock resistance or bond between the base metal and the oxide. Furthermore, the rapid oxidation of the metal in the coatings precluded consideration of the sintered coatings for oxidation resistance.

A meaningful test of thermal shock properties relies upon the development of a sound coherent coating on a metal substrate. Considerable effort will be needed to develop a suitable coating technique. The problems of coating application need not be of primary interest during the initial work on this program. Further effort on coating application and, consequently, thermal cycle testing were not continued.

3.3 TRANSPORT CHARACTERISTICS OF OXIDES

The oxidation theories of Wagner and Mott both depend on independent movement of cations and electrons in an oxide film. Mott's theory deals with very thin films, i.e., 20 to 50 Å. Wagner's theory is applicable to thick oxides because an even distribution of electric charge in the oxide is assumed, unlike the thin film model of Mott which assumes strong electric fields in the film. Wagner's theory will be used in this program as it is applicable to "thick" films.

Figure 19 schematically represents Wagner's concept of the oxidation of a metal. This figure illustrates the requirement for the mobility of the ions and electrons. The rate of film growth (oxidation) in the simplest form as derived by Wagner is as follows:

$$\frac{dn}{dt} = \frac{(T_c + T_a) T_e \sigma A E_o}{96500 C}$$

where n = weight of film formed
 t = time

FIGURE 19. SCHEMATIC REPRESENTATION OF OXIDATION OF METAL

Tc, Ta, Te = transfer numbers; cation, anion, electronic

C = film thickness

A = Area

σ = Conductivity of film ($\text{ohm}^{-1} \text{cm}^{-1}$)

Eo = emf of cell (decrease in free energy of reaction)

The above relationship may not be rigorously applicable to the oxidation of tantalum with an oxide coating but it does indicate the properties of an oxide which will reduce film growth. An oxide coating to be protective must prevent the transport of charge particles to prevent the reaction between Ta^{+4} and O^{-2} . The above equation shows that a material with low electrical conductivity is required for oxidation protection. A very thick coating also reduces oxidation, but in actual use, a thin coating is generally required. Critical examination of the above equation indicates that aside from thickness, electrical conductivity appears as the most readily studied property. Conductivity of an oxide also lends itself to modification with cation additions.

Measurements of electrical conductivity (σ) were made on possible oxide coating materials in view of the influence of σ on the rate of oxidation as given by Wagner. The experimental procedure and results and a discussion of a procedure to separate ionic and electronic conduction are presented below.

Electrical conductivity is related to diffusion by the Nernst-Einstein equations:

$$D_i = B_i k T$$

$$\sigma_i = n_i Z_i^2 e^2 B_i = \sigma t_i$$

$$D_i = \frac{\sigma t_i k T}{n_i Z_i^2 e^2}$$

where D_i = self-diffusion coefficient of ion i

B_i = absolute mobility of ion i

σ = electrical conductivity

t_i = transfer number

n_i = number of ions per unit volume

Z_i = valence

e = electronic charge

k = Boltzmann constant

T = absolute temperature

The above relationship was verified experimentally by other investigators (Ref. 13 and 14). The essential factor relating diffusion and conductivity is the contribution of the diffusion species on conductivity, i.e., transport number. The determination of transport numbers is by no means an easy task. To circumvent the problem of determining transport number, an attempt was made to determine a diffusion coefficient for the oxides of interest.

A number of techniques of obtaining diffusion data are available (Ref. 15). The method used most often to obtain self-diffusion of oxygen in an oxide utilizes radioactive oxygen (O^{18}). Analysis by this method was beyond the scope of the current program. Simpler methods which relate to oxygen diffusion were used as part of this program.

The methods considered were those dependent on a readily or easily measured factor that was related to oxygen diffusion. Two such factors are color and weight change.

FIGURE 20. ELECTRICAL MEASUREMENT APPARATUS

The oxide selected for study in this section was hafnia. This material was selected on the basis of its low thermal expansion as determined in Section 3.2. The high melting temperature and low vaporization rate also make hafnia attractive as a coating material. In addition, hafnium is the only known metal with a 4000 F melting temperature which yields an oxide with a melting temperature of over 4000 F. This particular feature of melting temperatures makes hafnium attractive as a reservoir material.

FIGURE 21. ELECTROMOTIVE FORCE VERSUS TEMPERATURE FOR Pt-6 % Rh Pt-30% Rh THERMOCOUPLE

3.3.1 Electrical Conductivity

A furnace with necessary electrical leads was constructed to measure electrical conductivity in an oxidizing atmosphere to 3250 F. A schematic of the furnace is shown in Figure 20. The heating element coil was fabricated from 0.094-inch diameter tantalum wire. Power was supplied to the element with water-cooled lead-throughs, insulated from the brass top with ALSIMAG bushings. The heating chamber was operated with a positive pressure of argon. Temperature of the sample was measured with a Pt-6% Rh/Pt-30%Rh thermocouple in contact with the top measuring electrode. The thermocouple output was measured with a Rubicon potentiometer, Model 2745, and the temperature was obtained from the emf vs temperature curve shown in Figure 21. This curve was constructed from data presented by Burns (Ref. 16).

FIGURE 22. INDUCTION FURNACE; Oxidizing Atmosphere

Electrical conductivity of a sample was determined by placing Pt-30% Rh electrodes on either side of the specimen which rested on an alumina plate supported by an alumina rod. The electrodes and specimen were maintained under compression by a spring-loaded alumina tube.

Specimen ac conductivity was determined at 1000 cycles/second with a General Radio Company impedance bridge, Type 1650-A. The following relationship was used to calculate electrical conductivity.

$$\sigma = \frac{L}{A R}$$

$$\sigma = \text{conductivity (ohm}^{-1} \text{ cm}^{-1}\text{)}$$

L = specimen length

A = specimen area

R = measured resistance (ohms)

Sample Preparation

Hot pressing and cold pressing were both explored as methods to fabricate specimens. Samples formed by hot pressing in graphite dies were dark in color indicating partial reduction. The previously described furnace was designed to perform measurements in an oxidizing atmosphere. Prior to measuring the hot pressed samples, they were oxidized at 3200 to 3600 F for one hour. The specimens after oxidation appeared well oxidized as the color changed from black to yellow or brown; however, the specimens were very weak and soft. These samples were not acceptable for conductivity measurements.

Cold pressing and sintering to 3800 to 4000 F in an oxidizing atmosphere proved a satisfactory technique for preparing hafnia samples containing appreciable amounts of Ta_2O_5 , Y_2O_3 , or Nb_2O_5 . Unstabilized or partially stabilized materials cracked when fabricated into specimens by this technique. These cracked samples were crushed, re-pressed, and sintered, and the resultant specimen appeared suitable for conductivity measurements.

An oxidizing atmosphere furnace was designed and built for sintering cold pressed samples and for oxidizing hot pressed samples. The furnace consisted of a ceramic tube, a graphite susceptor, and lamp black insulation. An argon plus 5 volume percent oxygen gas mixture was passed through the tube to maintain the oxidizing environment. A 7.5 kw induction unit supplied the power to heat the furnace to 4200 F. A schematic of the furnace is shown in Figure 22. A useful chamber size of 1-inch diameter by 1-inch high was obtained with this unit.

The unit was used repeatedly to 4000 F. The graphite susceptor had a life of 15 to 30 cycles, and the lamp black insulation required partial replenishment after each cycle.

When the furnace was first constructed, a ZrO_2 plus 8 weight percent Y_2O_3 tube was used. The presence of carbon at the tube's outer surface caused melting and eventually tube failure after 4 to 6 cycles. A thoria tube with a hafnia "wash" had a cycle life equal to or greater than the graphite susceptor.

Test Results

Table 11 is a listing of specimens giving composition and densities. Figures 23 through 26 show the effect of temperature on electrical conductivity for the samples listed in Table 11.

TABLE 11
ELECTRICAL CONDUCTIVITY SAMPLES

Specimen No.	Composition	Source	Temperature (F)	Number of Preparation Cycles (hr)	Density (g/cm ³)
1	ZrO ₂ 85 mol % CaO 15 mol %	a b	Calcined 2500 3800	2 1	4.4
2	HfO ₂	c	Hot pressed ⁽¹⁾ 3200, 4000 psi	1	8.7
3	HfO ₂	d	3700	2	6.5
4	HfO ₂	d	3600	2	7.4
5	HfO ₂	e	3800	2	6.8
6	HfO ₂ 99.95 wt % Nb ₂ O ₅ 0.05 wt %	d f	3500	1	8.3
7	HfO ₂ 99.00 wt % Nb ₂ O ₅ 1.00 wt %	d f	3700		5.7
8	HfO ₂ 96.00 wt % Nb ₂ O ₅ 4.00 wt %	d f	3700	1	7.2
9	HfO ₂ 98.00 wt % Ta ₂ O ₅ 2.00 wt %	e g	3950	1	7.8
10	HfO ₂ 96.00 wt % Ta ₂ O ₅ 4.00 wt %	c g	3800	1	8.5
11	HfO ₂ 96.00 wt % Ta ₂ O ₅ 4.00 wt %	e g	4100	1	7.8
12	HfO ₂ 96.00 wt % Ta ₂ O ₅ 4.00 wt %	d g	3900	3	6.9
13	HfO ₂ 92.00 wt % Ta ₂ O ₅ 8.00 wt %	d & e g	3750	1	8.4
14	HfO ₂ 74.09 wt % Ta ₂ O ₅ 25.91 wt %	d g	3350	1	8.8
15	HfO ₂ 73.59 wt % Ta ₂ O ₅ 26.41 wt %	e g	3800	1	Melted
16	HfO ₂ 70.00 wt % Ta ₂ O ₅ 30.00 wt %	e g	3800	1	Melted
17	HfO ₂ 92.50 mol % Ta ₂ O ₅ 5.00 mol %	d g	3800	1	
18	Y ₂ O ₃ 2.50 mol % HfO ₂ 80.70 mol % Ta ₂ O ₅ 14.30 mol %	h d g	3800	2	7.6
19	Y ₂ O ₃ 5.00 mol % HfO ₂ 96.00 wt % Nb ₂ O ₅ 4.00 wt %	h d f	3700	3	6.6
20	HfO ₂ 96.00 wt % Ta ₂ O ₅ 4.00 wt %	d g	3700	2	5.7 6.7

Source Notes:

- a. Zircoa Lot 5576-6568 (Table 5)
 - b. CaO added as CaCO₃ (Baker)
 - c. Wah Chang, Spectrographic grade (RX106125A) (Table 4)
 - d. Wah Chang, Reactor grade (52461A) (Table 4)
 - e. Wah Chang, Reactor grade (1-11-A) (Table 4)
 - f. Fansteel Metallurgical Corp., HP-2 (Table 8)
 - g. Union Carbide Metals Co., Lot 1035 (Table 7)
 - h. Kleber Laboratories, 99% purity
1. Hot pressed spectrographic HfO₂ showed no color change. Upon completion of conductivity measurements, sample retained same color indicating no reduction in hot pressing.

A comparative analysis to determine loss of additives was performed on hafnia specimens containing 1 and 4 weight percent Nb_2O_5 and 4 weight percent Ta_2O_5 . X-ray fluorescence was used to make the comparative analysis. A slight loss of Nb_2O_5 was detected in each sample ($\sim 3\%$). The results with Ta_2O_5 were difficult to resolve as Ta and Hf interfere with each other. The loss of Ta_2O_5 , however, is believed less than 5 percent.

A sample of high purity, high density alumina, Coors AD-99 was obtained and measured in the test apparatus. The measured conductivity versus temperature plot closely follows other published data (Fig. 23). The data in Reference 10 are an average of the efforts of a number of investigators. The match of Solar data with published data on alumina was taken as an indication of the validity of the experimental technique.

The experimental results on hafnia and $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ were compared in Figure 23 with previous published data. The difference in conductivity between the $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ compositions was probably due to specimen density, electrode resistance, and stoichiometry.

The data for hafnia all appear to be in fairly close agreement. The agreement of the Solar data with previous published data further indicates that the experimental procedure was satisfactory.

A difference in conductivity between the reactor grade hafnia and the spectrographic grade hafnia exists as evident in Figure 24. The spectrographic hafnia showed a desirable low conductivity.

Additions of Ta_2O_5 to hafnia tended to increase conductivity except in an instance of 4 weight percent Ta_2O_5 added to hafnia, Lot 52461A. These particular specimens, numbers 12 and 20, Table 11, were as conductive as spectrographic grade hafnia.

Specimens of $\text{HfO}_2 + \text{Ta}_2\text{O}_5 + \text{Y}_2\text{O}_3$ all showed high conductivity (Fig. 25). Only limited amount of experimentation was performed with these compositions because of their apparent high conductivity. Niobia additions also tended to increase conductivity of hafnia, as shown in Figure 26.

FIGURE 23. ELECTRICAL CONDUCTIVITY VERSUS TEMPERATURE FOR VARIOUS LOTS OF HfO_2

FIGURE 24. ELECTRICAL CONDUCTIVITY VERSUS TEMPERATURE FOR HAFNIA WITH Ta₂O₅ ADDITIONS

FIGURE 25. ELECTRICAL CONDUCTIVITY VERSUS TEMPERATURE FOR $\text{HfO}_2 + \text{Y}_2\text{O}_3 + \text{Ta}_2\text{O}_5$ COMPOSITIONS

FIGURE 26. ELECTRICAL CONDUCTIVITY VERSUS TEMPERATURE FOR $\text{HfO}_2 + \text{Nb}_2\text{O}_5$ COMPOSITIONS

FIGURE 27. SAMPLE PLOT OF CONDUCTIVITY VERSUS FREQUENCY

Transport Number Study

The purpose of this portion of the study was to separate the electronic conductivity from the ionic. When the ionic conductivity is known, the mobility can be calculated (Ref. 18) and, thus, one can arrive at the transport of ions through the material.

An alternating current measurement was used to determine the effect of frequency on conductivity at a particular temperature. If ionic mobility is several orders of magnitude less than electronic, a plot of conductivity as a function of frequency will lead to a spread in values as shown in Figure 27. The capacitive admittance, $Y_c = f \frac{A}{K\epsilon_0}$ is directly proportioned to frequency f and should be negligible up to 50 kc. Furthermore, at 50 kc, the ionic contribution to conductivity should be negligible and the value measured strictly electronic. Below 150 cycles, the ionic contribution will begin to play some role in conductivity. Not only will the ionic contribution to conductivity be determined but because of frequency playing an important role, the ionic mobility can be estimated. Although the slope changes may be exaggerated in Figure 27, some differential technique should allow one to pick up the frequency of the onset of ionic conductivity. The measurement at zero frequency becomes virtually impossible due to $1/f$ noise, but because of the sensitivity of the wave analyzer (10^{-9} volts) and because of its selectivity (3 db at 2 cycles), it is assumed that the onset of

FIGURE 28. BLOCK DIAGRAM OF CONDUCTIVITY SETUP

ionic conductivity can be detected at frequencies from 10 to 100 cycles. The frequency of onset designated by the minimum on Figure 27 will be related to the ionic mobility while the slope (actually the extrapolated value to zero) will give the ionic contribution to conductivity.

Determination of Ionic Mobility in Refractory Oxides

Several attempts were made with some preliminary samples to check the feasibility of the proposed method. The heart of the instrumentation is a Hewlett Packard Model 302A wave analyzer which consists of a synchronous oscillator/narrow band voltmeter. Figure 28 shows a block diagram of the experimental setup. From the wave analyzer, a signal is passed through an isolation transformer and fed into the sample through a sensitive microammeter. A bridge rectifier assures the measurement of rms amperes, while the voltmeter on the wave analyzer measures rms volts. From these measurements, the sample impedance is calculated and plotted as a function of frequency.

For the initial setup, a doorbell transformer was used, but the results were unsatisfactory due to wide variations in gain and impedance. In spite of this defect, there was some indication of ionic mobility, so it was decided to purchase a more

sensitive microammeter and a high-fidelity interstage transformer. The transformer has a 1200 ohm primary which nearly matches the output of the wave analyzer and a 95 K ohm secondary which comes close to the sample impedance. The gain is flat from 30 cps to 20 kc (the 3 db down points). The low frequency minimum is 20 db down at 10 cycles. An unusually long delay was encountered in receiving the microammeter. Consequently, this method of determining transport numbers was not utilized. The majority of measurements was to determine conductivity in an effort to obtain low conductive materials; then transport numbers on promising materials would be determined.

Qualitative Description of the Method

The Einstein relationship between mobility and self diffusion will be the starting point:

$$\mu kT = ZeD \quad (1)$$

where:

Z = valence of the ion

D = diffusion coefficient

μ = ionic mobility

k = Boltzmann's constant

T = absolute temperature (K)

e = electronic charge.

Now consider an ion in a lattice site with a vibrational frequency ω . The probability, ρ , that it will leave the site is related to ω but also depends on the potential well U. The usual manner of expressing this, assuming Boltzmann statistics, is

$$\rho \approx \omega e^{-(U/kT)} \quad (2)$$

Furthermore, the number of atoms crossing unit area per unit time, that is, moving from one plane to another, will be simply

$$D_i = \rho a^2 = \omega a^2 e^{-(U/kT)} \quad (3)$$

where:

"a" is the lattice parameter of the solid.

Now, if n is the number of vacancies and N is the total number of ions per unit volume, then the gross diffusion term becomes

$$D = \frac{n}{N} D_i \quad (4)$$

This simple approach neglects multiple vacancies, disorder, and other changes in the entropy and energy of the solid. Mott and Gurney (Ref. 19) have estimated that for a lattice with predominantly Schottky defects (vacancies), the existence of more complex lattice defects and other factors could be accounted for by a constant C_s of the order of 10^3 to 10^4 .

Following the above argument then, it can be shown that the diffusion can be expressed as

$$D = \omega C_s \frac{n}{N} a^2 e^{-U^*/kT} \quad (5)$$

and this equation will be the basis of this discussion.

The reason for the asterisk on U^* in this equation is that it contains not only the potential energy of the ion, but also the work necessary to remove the ion from its occupied site. If all other terms were constant, a plot of $\log D$ vs $1/T$ would give the value of U^* experimentally. Knowing U^* , one could predict the temperature dependence of the diffusion coefficient and hence the ionic mobility.

The theory is not that simple because the other terms in equation 5 are not constant. For example, " a " is known to increase with T due to the fact that the material has some coefficient of expansion. Expansion coefficients offer no problem, therefore, the behavior of " a " can be quite readily taken into account.

The meaning of the next term can best be illustrated by an example. The chemical formula for zirconia is ZrO_2 when all sites are occupied. At high temperatures, however, this may become $ZrO_{1.98}$ and a certain amount of anion vacancies exist. Here the term n/N can be calculated to be 0.01. It is quite plausible that this term can vary drastically with temperature. The other two terms may vary somewhat, but if the n/N term is controlled, their variation will be relatively small and for the present can be neglected. The variation of ω is related to that of a , and that of C_s is related to n/N .

From previous discussions, it was decided that D should be as low as possible, with the added bonus that its temperature dependence could be predicted. Since it is desirable to have D low, one method is to make U^* as high as possible, thus swamping the exponential effect of T . Intuitively, it is evident that if U^* is large, the temperature dependence of n/N will be small.

FIGURE 29. RESISTANCE OF 80% HfO₂-20% ZrO₂ VERSUS FREQUENCY

Determination of Diffusion

From Einstein's relation and the definition of mobility, one arrives at the equation for ionic conductivity

$$\sigma_{\text{ion}} = \frac{N^* e^2 D}{kT} \quad (6)$$

in the neighborhood of a temperature T . N^* is the ionic concentration which is related to the concentration of vacancies through the Boltzmann equation, e is the charge of the ion, and D is the diffusion coefficient.

Superimposed on this is the electronic conductivity

$$\sigma_{\text{el}} = \sigma_0 e^{-W_g/kT} \quad (7)$$

where W_g is the band gap. There is also impurity conductivity, but at high temperatures this turns out to be nearly constant.

Using an alternating current at high frequencies, the ionic mobility is sufficiently low that ions cannot cross the solid, hence they contribute nothing to the conductivity. At some frequency, however, they do indeed cross the solid and contribute to the conductivity. This frequency is determined solely by the applied voltage and the

specimen thickness. For example, given an applied voltage of 4 volts across a specimen 0.4 cm thick, with a value of $D = 10$, the ionic conductivity will be felt below 250 cps by the definition of the units of mobility. Now the question arises what to measure here. Actually, it is true that when the ionic conductivity is felt, the conductivity will rise. Results of these preliminary measurements are shown in Figure 29.

In Figure 29, resistance is plotted against frequency. The inflections in resistance of 80 cps for 2240 F and at 100 cps for 2375 F show the onset of ionic conductivity.

The only drawback is that the electronic resistance becomes less at higher temperatures by the usual rule. Perhaps then, some other parameter might better be measured. Consider equation 1 and express kT as electron volts. By adjusting the voltage, one can control the field across a sample and keep it uniform. Further, one can so preset the voltage to match the kT relation. Then equation 6 becomes

$$\sigma_{ion} = \frac{N^* e D}{V} \quad (8)$$

or
$$\sigma_{ion} V = I_{ion} = N^* e D \quad (9)$$

Thus, the current through the sample is directly proportional to the diffusion coefficient. Now noticing the frequency of onset and the cross section area of the sample, the current I is, in fact, equal to D within the multiplicative constants ω and C_s . The fact remains that it is the relationship between the variables that will enable the prediction of results. The values can be picked off by experimenting on known samples.

Actually the low frequency magnitude of I will determine N^* while the onset frequency determines D .

Discussion

The electrical conductivity of spectrographic grade hafnia approaches that of alumina. The relatively low conductivity values for spectrographic grade hafnia was attributed to the purity of the material. The reactor grades of hafnia contained considerable amounts of impurities which were believed responsible for the higher conductivity values.

An attempt to reduce the conductivity of spectrographic grade hafnia with a penta-valent cation addition (Ta_2O_5) was not successful. The addition of four weight percent Ta_2O_5 resulted in a significant increase in electrical conductivity. The tantalum oxide in the quantity added appears to affect hafnia as an impurity resulting in an increase in conductivity rather than reduced conductivity as would be expected by theory.

Penta-valent cation additions to the reactor grade hafnia resulted in both an increase and decrease of electrical conductivity depending on the source (lot number) of hafnia. The effect of penta-valent additions to reactor grade hafnia are summarized in Figures 24, 25, and 26. A 4 weight percent addition of Ta_2O_5 to reactor grade HfO_2 , Lot 52461A, lowered the electrical conductivity to a level equal to the spectrographic grade hafnia. Electrical conductivity of reactor grade hafnia, Lot 1-11-A, was not appreciably changed by 2 of 4 weight percent additions of Ta_2O_5 . An 8 percent Ta_2O_5 addition appreciably increased the electrical conductivity of reactor grade hafnia (mixture of Lots 1-11-A and 52461A).

The 26 weight percent Ta_2O_5 addition was an attempt to make the HfO_2 - Ta_2O_5 analogy of the compound 6ZrO_2 - Nb_2O_5 . The electrical conductivity of this material was essentially the same as reactor grade hafnia. The decrease in conductivity from the 8 percent addition indicated that higher Ta_2O_5 (> 26 weight percent) addition may decrease conductivity. Samples with the high Ta_2O_5 additions melted (Table 11) and were not suitable for testing.

The variation of electrical conductivity measurements on the reactor grade hafnia with 4 weight percent Ta_2O_5 was probably a result of the impurities present in each lot of material. The analysis in Table 4 shows significant differences in Zr, Ti, Si, and Fe content of reactor grade HfO_2 . The variation of impurities probably determines the effect of Ta^{+5} on the electrical conductivity of hafnia.

Another variable that appears to affect the electrical measurements is density. The wide range of densities for the Ta_2O_5 reactor grade hafnia compositions also indicates the difficulty in sintering these materials. The low density of the 4 weight percent Ta_2O_5 + HfO_2 (Lot 52461A) samples may be partly responsible for the low conductivity values.

The method of separating ionic conductivity from electronic conductivity by measuring σ versus frequency appears promising. This approach should be utilized with spectrographic grade hafnia.

3.3.2 Vacuum Reduction

Two approaches were attempted to determine the oxygen diffusion rates in oxides. Each approach was based on a physical change dependent on oxygen content.

In the first method, depth of color change of a sintered sample of oxide was to be measured. Experimental studies conducted under contract AF 33(616)-8497 indicated that ThO_2 and HfO_2 could be reduced to a dark color and oxidized back to their normal color. Initial work in this program indicated that the depth of change varied with time. The depth of color change with respect to time is related to diffusion by

$$X = K(Dt)^{1/2} \quad (\text{Ref. 15})$$

where

X = distance of zone to interface

t = time

D = diffusion coefficient

K = constant.

This method is readily adaptable to dense polycrystalline materials and single crystals (Ref. 20). Examination of samples of partially stabilized HfO_2 , sintered in a reducing atmosphere and then oxidized did indicate a sharp color band. However, examination at high magnification revealed that the color change was evident along the many cracks present in the samples. Any diffusion data obtained from a porous and/or cracked sample would not indicate bulk material diffusion, but rather pore and grain boundary diffusion. Difficulty was encountered in fabricating high density samples for this study. Consequently, this method was dropped in favor of the weight change technique.

The technique used in the weight change study was to sinter the powder in an oxidizing atmosphere and then vacuum reduce the samples for various times and temperatures. The weight change in the sample was noted at various conditions.

The powder or spheres were prepared by cold pressing reactor grade hafnia, crushing the compact, mechanically screening through a series of sieves, retaining the -80 +100 mesh material, and recycling the fines. The -80 +100 mesh hafnia contained in a thoria crucible was then sintered in an Ar + 5 volume percent O_2 atmosphere to 3700 to 4000 F using the induction furnace previously described and illustrated in Figure 22. The fired material was again screened and the -100 +140 mesh material was used for the vacuum reduction study.

The carbon tube expansivity apparatus (Fig. 2) was used for reduction of the powder. A known weight of powder was placed in a tungsten crucible and covered with a sheet of tantalum. These two materials also act as a getter for any impurities present in the atmosphere. A thoria rod was placed on the tantalum to act as a target for an optical pyrometer. The chamber with sample was pumped down to at least 40 to 50 microns, purged with argon, and pumped again to 40 to 50 microns. Power to the furnace was adjusted to reach test temperature within 1-1/2 to 3 minutes. The same powder sample was used at each temperature.

A check of the experimental procedure was made to determine what the weight loss actually was, i.e., vaporization of either anion or cation or both. A sample of oxidized sintered hafnia powder was reduced at 3600 F and then reoxidized at 3600 F. The weight change was 0.04 percent, or for all practical purposes, zero. The conclusions from this simple test were that the sample was not vaporizing under the pressure, time, temperature relationships used in these experiments and that the weight loss observed was due to the loss of oxygen.

Experimental Results and Discussion

The weight loss data were treated in the following ways:

The mathematical solution of diffusion from a stirred solution of limited volume of spherical particles is given by Crank (Ref. 21). The solutions given by Crank were particularly useful in determining oxygen diffusion using radioactive traces (O^{18}) by a number of investigators (Ref. 13, 22, and 23). In these experiments, the concentration gradient was constant where in the present study, the gradient varied as more oxygen was removed. Also, the small weight losses resulted in considerable difficulty in utilizing Crank's solutions.

Another approach was to use the following expression given by Oishi and Kingery (Ref. 22).

$$D = \left(\frac{\pi}{36t}\right) a^2 \left(\frac{M_t}{M_\infty}\right)^2$$

where D = diffusion constant

t = time

a = radius of particle

Mt = amount of oxygen lost at time t

M ∞ = amount of oxygen in saturated sample (t = 0)

The above expression is for small changes in oxygen content and was used to calculate a "diffusion" coefficient. The results obtained using hafnia (Lot 52461A) are summarized in Figure 30.

An attempt was also made to fit the weight loss data to the following relationship (Ref. 24):

$$\frac{X_o - X}{X_o - X_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(-\frac{n^2 D t}{R^2} \right)$$

R = radius of sphere

t = time

X = oxygen composition at time t

X_o = oxygen composition at time t = 0

X ∞ = oxygen composition at end of reaction

D = apparent diffusion constant

For large values of t, this equation reduces to the form:

$$\frac{(X - X_\infty)}{(X_o - X_\infty)} = 6/\pi^2 \exp (-Dt/R^2)$$

A plot of log (X-X ∞) against t should be a straight line of slope -D/2.303R².

The diffusion coefficient obtained from this relationship is determined from a changing concentration and should yield a more reliable coefficient from the weight loss data. However, the data from the vacuum reduced studies did not fit the above expression.

FIGURE 30. OXYGEN DIFFUSION COEFFICIENT VERSUS TEMPERATURE

3.3.3 Discussion

Attempts to obtain a quantitative oxygen diffusion coefficient were unsuccessful. A plot of diffusion coefficient against $1/T$ appeared reasonable; however, the data were not corroborated by calculations using another approach. The data appearing in Figure 30 were determined from a mathematical solution where the concentration gradient does not change. In the vacuum reduction studies, the concentration gradient changed continuously, thereby affecting the validity of the data.

An attempt was made to determine the influence of WO_3 on the vacuum reduction of HfO_2 . X-ray fluorescence analyses were made on the $HfO_2 + 1$ weight percent WO_3 sample before sintering, after sintering, and after vacuum reduction. WO_3 losses of 50 percent were observed in the sample after reduction. These weight losses of WO_3 eliminated this technique as a method to determine the effect of WO_3 on hafnia.

3.3.4 Conclusions

Spectrographic grade hafnia appears to warrant continued study as a coating material. The electrical conductivity of this material was equal to that of alumina. Generally speaking, oxides exhibiting low electrical conductivity also exhibit low oxygen diffusion rates. Figure 31 shows the electrical conductivity and diffusion coefficient versus temperature for various oxides. The figure does show that relationship between electrical conductivity for oxides is reflected in the relationship of oxygen diffusion coefficient among the oxides. The low electrical conductivity of hafnia (spectrographic grade) indicates that it would have a low oxygen diffusion coefficient. This trend is observed in Al_2O_3 and MgO .

The oxygen diffusion in hafnia does not appear to be in its proper relationship with the other oxides. The agreement of conductivity measurements on hafnia with published data is good. Therefore, doubt exists as to the validity of the diffusion data on hafnia as determined by the vacuum reduction technique. The diffusion results appear to be on the high side if compared to the conductivity and diffusion in thoria.

Both conductivity and diffusion follow the Arrhenius equation

$$A = A_0 e^{(-E/RT)}$$

FIGURE 31. ELECTRICAL CONDUCTIVITY AND DIFFUSION COEFFICIENT VERSUS TEMPERATURE FOR VARIOUS OXIDES

where A can equal either conductivity (σ) or diffusion (D). Since a low value for either σ or D is desired in this instance, the pre-exponential term A_0 ($A_0 = D_0$ or σ_0) should be as small as possible ($A_0 = 0$ desirable) and E (activation energy) as large as possible. The pre-exponential term is a constant and the activation energy is determined from the slope of plots of σ or D versus $\frac{1}{K}$. The constant, A_0 , is a material characteristic and varies considerably in value. The activation energy term does not vary as greatly as the constant.

TABLE 12

EFFECT OF ACTIVATION ENERGY ON CHANGE IN DIFFUSION
COEFFICIENT WITH TEMPERATURE (Ref. 11)

$$D = D_0 \exp (-Q/\kappa T)$$

D at:		Q				
(C)	(F)	1.0 ev ⁽¹⁾	2 ev	3 ev	4 ev	6 ev
500	932	$3.6 \times 10^{-7} D_0$	$1.2 \times 10^{-13} D_0$	$4.2 \times 10^{-20} D_0$	$1.6 \times 10^{-26} D_0$	$2 \times 10^{-39} D_0$
800	1472	$4.0 \times 10^{-6} D_0$	$1.6 \times 10^{-11} D_0$	$6.2 \times 10^{-17} D_0$	$2.2 \times 10^{-22} D_0$	$4 \times 10^{-33} D_0$
1000	1832	$6.2 \times 10^{-4} D_0$	$1.6 \times 10^{-8} D_0$	$1.8 \times 10^{-12} D_0$	$2.5 \times 10^{-16} D_0$	$3 \times 10^{-24} D_0$
1200	2192	$4.2 \times 10^{-4} D_0$	$1.7 \times 10^{-7} D_0$	$6.7 \times 10^{-11} D_0$	$2.7 \times 10^{-14} D_0$	$4 \times 10^{-21} D_0$
1400	2552	$1.0 \times 10^{-3} D_0$	$1.1 \times 10^{-6} D_0$	$1.1 \times 10^{-9} D_0$	$1.2 \times 10^{-12} D_0$	$1 \times 10^{-18} D_0$
1600	2912	$2.2 \times 10^{-3} D_0$	$4.5 \times 10^{-6} D_0$	$1.0 \times 10^{-8} D_0$	$2.1 \times 10^{-11} D_0$	$1 \times 10^{-16} D_0$
1800	3272	$3.8 \times 10^{-3} D_0$	$1.5 \times 10^{-5} D_0$	$5.7 \times 10^{-8} D_0$	$2.3 \times 10^{-10} D_0$	$3 \times 10^{-15} D_0$
2000	3632	$6.2 \times 10^{-3} D_0$	$4.0 \times 10^{-5} D_0$	$2.5 \times 10^{-7} D_0$	$1.6 \times 10^{-9} D_0$	$6 \times 10^{-14} D_0$
2200	3992	$9.1 \times 10^{-3} D_0$	$8.3 \times 10^{-5} D_0$	$8.5 \times 10^{-7} D_0$	$7.7 \times 10^{-9} D_0$	$6 \times 10^{-13} D_0$

1. 1 ev = 23.05 K cal/mole

Table 12 shows the effect of activation energy on change in diffusion coefficient with temperature. The values for Q (ev) are those generally found for oxides. The table shows the desirability of a high activation energy and low pre-exponential term (D_0) to obtain low diffusion values.

A plot of diffusion coefficient versus time to obtain various percentages of saturation for various thicknesses of material is shown in Figure 32. The curves in Figure 32 were constructed from Figure 33 using saturations of 0.5 and 1.0 for a slab of infinite width and length. Looking at Figure 32, a coating of 0.030-inch thickness would achieve 100 percent saturation with a diffusion coefficient of $10^{-6} \text{ cm}^2/\text{sec}$, or the substrate could dissolve all of the oxygen originally present in the oxide film, and the film in this length of time would have replaced all of the oxygen. The oxide would be protective in a limited sense. The diffusion coefficient in Figure 32, if used for

FIGURE 32. DIFFUSION COEFFICIENT VERSUS TIME; Various Coating Thickness And Percent Saturation

oxygen, is dependent upon the effect of the metal-oxide couple on ionic diffusion rather than self diffusion. Using the diffusion data for hafnia, as determined by vacuum reduction, a D value at 4000 F ($10^3/K = 0.4$) of 5×10^{-7} would give an hour protection if 0.030-inch thick providing the substrate could tolerate the uptake of oxygen.

A layer of tungsten immediately beneath the oxide would have a low solubility for oxygen. This low solubility could result in a low effective oxygen diffusion.

The data obtained by the vacuum reduction method are believed high when compared with conductivity data. On this basis, a diffusion value of 10^{-9} to 10^{-10} cm^2/sec would be expected at 4000 F. If this value matches the diffusion of the composite (metal-oxide-gas), then reasonable protection times with suitable coating thickness can be obtained (Fig. 32).

Future work involving oxygen diffusion will require consideration of the metal-oxide-gas combination so the proper chemical and free-energy gradients can be established.

FIGURE 33. FRACTIONAL SATURATION OF SHEET, CYLINDER, AND SPHERE OF UNIFORM INITIAL CONCENTRATION c_0 AND CONSTANT SURFACE CONCENTRATION c_s , WITH c_m THE MEAN CONCENTRATION AT TIME t

The preceding examples were made to indicate the effect of diffusion coefficient, time, and thickness with each other. Examination of Figure 31 indicates that the lowest diffusion coefficients for oxide that can be expected at 4000 F will be approximately 10^{-10} to 10^{-11} . These values are probably lower than will be realized, but diffusion values of 10^{-10} to 10^{-9} can be expected to provide short time protection. Of course, the other factors such as stability of oxide and substrate, physical maintenance of oxide, and retention of reservoir must be solved for any oxide to be protective at 4000 F.

3.4 COMPATIBILITY STUDIES

A useful coating must survive for periods of time of 1 hour or more at 4000 F. At this temperature, oxide coating systems of unusual stability with respect to metallic substrates are needed. Hafnia has been considered a most promising oxide in this regard. Even the most stable oxide, however, may have a significant range of compositions at temperatures of 3000 to 4000 F. Compatibility of the oxide coating and

metal substrate is then determined by reaction between a nonstoichiometric oxide and an oxygen saturated metal. Loss of oxygen from the original stoichiometric oxide by reaction such as:

where x can be as much as 0.02, provides a source of oxygen for oxidation of a metal substrate (Ref. 5).

A second source of oxygen is the dissociation of the refractory oxide at high temperatures which, in this case of HfO_2 , proceeds by the reaction:

At 4000 F the recession rate of the surface of HfO_2 due to dissociation was calculated to be approximately 10^{-7} in./hr (Ref. 28). In coatings, oxygen generation from this source may become significant because the metal substrate acts as a sink for evolved oxygen. The presence of voids and cracks in the oxide could increase the importance of oxide dissociation because of the greater surface area and channels available for oxygen generation and vapor transport. In view of these complexing factors, experimental determination of compatibility of potential coating oxides and substrate metals is the best approach.

Electrical conductivity measurements were reported in Section 3.3 for HfO_2 composition on which control of anion defects and composition range was attempted. Although several possibilities exist, the hafnia compositions which showed the lowest electrical conductivity at high temperatures should also show the greatest compatibility with a substrate metal. That statement is based on the assumption that lower conductivity is associated with low oxygen diffusion rates. For instance, spectrographic grade HfO_2 should be expected to be somewhat more compatible with a substrate metal than reactor grade HfO_2 .

The solid state diffusion rate of oxygen in the oxide will be the controlling factor in determining reaction rate between a dense oxide coating and metal substrate. Therefore, several HfO_2 compositions, which had been characterized in electrical conductivity studies, were selected for experimental determination of compatibility

with Hf, the main constituent of a potential reservoir. Efforts were made to duplicate as closely as possible conditions which would exist at the oxide-metal interface of a potential coating. Studies were conducted at 3000 to 4000 F at times up to 1 hour in an argon atmosphere.

Depletion of the reservoir metal will cause the HfO_2 to come in contact with the tantalum alloy or tungsten diffusion barrier. Hafnia has been found compatible with tantalum and tungsten for short times at temperatures above 4000 F (Ref. 6). However, longer times at temperature may give a significant reaction. In this program, times up to 1 hour at 4000 F are of interest, therefore, a test of the compatibility of HfO_2 with W, Ta, and 90Ta-10W alloy was made under these conditions.

3.4.1 Material

The oxide powders used were spectrographic and reactor grade HfO_2 and Ta_2O_5 . The sources and purity of those oxides are given in Tables 4 and 7. Reactor grade hafnium, 10 mil sheet, with the typical analysis given in Table 9, was obtained from Wah Chang Corporation. Surface ground high-purity tungsten rod, 1/8 inch in diameter, was supplied by General Electric Company and high-purity tantalum and 90Ta-10W rod, 1/8 inch in diameter, was obtained from Fansteel Metallurgical Corporation.

3.4.2 Procedure

Material Preparation

The oxide compositions selected for study were spectrographic grade HfO_2 , both as-received and mixed with 4 weight percent Ta_2O_5 , and reactor grade HfO_2 , Lot 5-24-61-A and Lot 1-11-A, both as-received and mixed with 4 weight percent Ta_2O_5 . Mixtures of HfO_2 with Ta_2O_5 were made by placing the weighed powders in a glass jar and dry blending with a vibrating mixer for 30 minutes. The mixture was pressed into a bar and sintered for 30 minutes in an induction furnace at about 3800 F in argon plus 5 percent oxygen. The sintered bar was then crushed to pass through a 150-mesh screen.

The 10 mil hafnium metal sheet was cut into 1/8 inch by 1/8 inch pieces which were then degreased and pickled in a bath of 2 percent HNO_3 -2 percent HF in water. The tungsten, tantalum, and 90Ta-10W alloy was prepared by a light surface polish with silicon carbide polishing paper followed by washing in distilled water.

Specimen Fabrication and Test

Compatibility specimens containing Hf were fabricated by hot or cold pressing the selected hafnia powders into pellets with the Hf piece in the center. The pellets were about 1/4-inch diameter by 1/4-inch high after cold pressing at 10 ksi. Hot pressed pellets were 1/8-inch high by 1/2-inch diameter after pressing at 4000 psi at 3000 F for 15 minutes in an inductively heated graphite die.

After the pressing operation, the pellets were placed in a tungsten crucible and heated in a graphite tube furnace in flowing argon (Fig. 2) for 30 and 60 minutes at temperatures between 3000 and 4000 F.

The relative purity of the furnace atmosphere was established by placing a 1/8 inch by 1/8 inch piece of 10 mil Hf in a tungsten crucible with a HfO_2 pellet and heating for 30 minutes at 3340 F. Observable reaction, weight gain, or increase in microhardness would indicate any impurities such as oxygen or water that were present in the argon. The Hf subjected to this test had a bright, shiny surface upon removal from the furnace. Accurate weight change could not be measured because of slight sintering between Hf and the tungsten crucible, but the microhardness increased from 189 DPH to 299 DPH, using a 100 grain load. The microhardness of Hf has been reported to vary from 50 to 1220 DPH (Ref. 29) with increasing oxygen content. Therefore, the oxygen impurity in the furnace atmosphere must have been relatively low in view of the small increase in Hf hardness.

Compatibility specimens containing W, Ta, and 90Ta-10W were fabricated by cold pressing reactor grade hafnia powder into a 2 inch by 1/4 inch by 1/4 inch bar with 1/8-inch long pieces of metal rod placed at intervals within the bar. The bar was then placed in a tungsten crucible and heated in a graphite tube furnace for 60 minutes at 4000 F in flowing argon.

The apparent density of the specimens was determined by the water displacement method after sintering. The extent of reaction between metal and oxide was determined by metallographic examination of the sectioned specimens. Particularly interesting specimens were sent to Materials Testing Laboratories, Los Angeles, for electron microprobe analysis of reaction products.

TABLE 13
COMPOSITION AND TREATMENT OF COMPATIBILITY SPECIMENS

Specimen No.	Specimen Composition (wt %)	Metal	Specimen Density (g/cc)	Pressing Technique	Temperature of Test (F)	Time at Temperature (min)
1	Spectrographic grade HfO_2 (99.9 HfO_2) + 4 wt % Ta_2O_5	Hf	9.1	Hot press	3400	30
2	Spectrographic grade HfO_2 (99.9 HfO_2) + 4 wt % Ta_2O_5	Hf	9.3	Hot press	3400	60
3	Reactor grade HfO_2 (Lot 5-24-61A)	Hf	8.4	Cold press	3100	30
4	Reactor grade HfO_2 (Lot 5-24-61A)	Hf	8.7	Cold press	3100	60
5	Reactor grade HfO_2 (Lot 5-24-61A)	Hf	8.5	Cold press	3370	30
6	Reactor grade HfO_2 (Lot 5-24-61A)	Hf	8.5	Cold press	3370	60
7	Reactor grade HfO_2 (Lot 5-24-61A)	Hf	8.5	Cold press	4100	30
8	Reactor grade HfO_2 (Lot 5-24-61A)	Hf	7.9	Cold press	3370	30
9	Spectrographic grade HfO_2 (99.9 HfO_2)	Hf	7.9	Cold press	3370	30
10	Spectrographic grade HfO_2 (99.9 HfO_2)	Hf	8.1	Cold press	3370	60
11	Spectrographic grade HfO_2 (99.9 HfO_2)	Hf	9.1	Cold press	4100	30
12	Spectrographic grade HfO_2 (99.9 HfO_2)	Hf	9.3	Cold press	4100	60
13	Spectrographic grade HfO_2 (99.9 HfO_2)	Hf	9.5	Hot press	3300	30
14	Spectrographic grade HfO_2 (99.9 HfO_2)	Hf	9.6	Hot press	3300	60
15	Spectrographic grade HfO_2 (99.9 HfO_2)	Hf	10.1	Hot press	3600	30
16	Spectrographic grade HfO_2 (99.9 HfO_2)	Hf	9.7	Hot press	3600	60
17	Spectrographic grade HfO_2 (99.9 HfO_2)	Hf	9.1	Hot press	4000	30
18	Spectrographic grade HfO_2 (99.9 HfO_2)	Hf	9.3	Hot press	4000	60
19	Reactor grade HfO_2 (Lot 5-24-61-A)	(Ta, 90Ta-10W, W)	9.6	Cold press	4060	60

FIGURE 34. RODS OF TUNGSTEN, 90Ta-10W AND TANTALUM IN HAFNIA; Sintered One Hour at 4060 F

3.4.3 Results

General

The compositions, pressing, heat treatment, and apparent density of the compatibility specimens are given in Table 13. The experimental results are described in the following paragraphs.

HfO₂-Ta, 90Ta-10W, W

Considerable porosity was present near all the metal inserts because of uneven pressure distribution during pressing and, in some cases, reaction between metal and oxide. Shrinkage during sintering also caused cracks in the oxide around the metal.

Tungsten did not react with hafnia after 1 hour at 4060 F, but 90Ta-10W alloy and tantalum reacted extensively, as shown in Figure 34. The tantalum appeared slightly less reactive than the 90Ta-10W alloy. The reaction zone extended about 1/16 inch into the oxide for both metals. Figures 35, 36, and 37 show the interface of hafnia and the metals tantalum, 90Ta-10W alloy, and tungsten. Movement of metal from tantalum and 90Ta-10W alloy into the oxide is evident.

Magnification: 75X

FIGURE 35. INTERFACE OF HAFNIA AND TANTALUM; Sintered
One Hour at 4060 F

HfO₂ (Reactor Grade) -Hf

Dense, coherent specimens were made from reactor grade HfO₂ (Lot 5-25-61-A) and Hf by cold pressing and sintering at 3100, 3370, and 4100 F for 30 or 60 minutes. Photomicrographs of the reaction interface of the Hf and HfO₂ are shown in Figure 38. The metallic, nodular deposits which remained unreacted at 4100 F were identified by microprobe as Hf, with detectable quantities of Fe and Zr impurities. Breakdown of the electron microprobe prevented more quantitative analysis. Thin surface deposits of bright metal formed around cracks in specimens made of reactor grade HfO₂ as shown in Figure 39. Chemical tests indicated the major constituent of the deposits was tungsten.

HfO₂ (Spectrographic Grade) -Hf

Dense, coherent specimens were made by both cold and hot pressing. Cold pressed specimens were sintered at 3370 and 4100 F for 30 or 60 minutes. Useful specimens could not be made at lower temperatures because of poor sintering of the oxide. Hot pressed specimens were sintered at 3300, 3600, and 4000 F for 30 or 60 minutes. Photomicrographs of the reaction interface of the Hf and oxide are shown in

Magnification: 75X

FIGURE 36. INTERFACE OF HAFNIA AND 90Ta-10W ALLOY;
Sintered One Hour at 4060 F

Magnification 75X

FIGURE 37. INTERFACE OF HAFNIA AND TUNGSTEN; Sintered
One Hour at 4060 F

The lower edge of the photomicrograph is approximately the center of the 10 mil Hf sheet

Magnification: 250 X

FIGURE 38. REACTION INTERFACE OF REACTOR GRADE HfO_2 -Hf

Magnification: 10 X

FIGURE 39. TOP SURFACE OF REACTOR GRADE HfO_2 -Hf
COMPATIBILITY SPECIMEN; Sintered One Hour at 4100 F in Argon

Figures 40 and 41. The metallic nodules at the original oxide-metal **interface** and in the original HfO_2 were identified by electron microprobe as Hf with detectable amounts of Fe and Zr impurities.

HfO_2 (Reactor Grade) -4 Weight Percent Ta_2O_5 -Hf

Attempts were made to fabricate compatibility specimens from blends of 4 weight percent Ta_2O_5 with reactor grade HfO_2 of both Lot 5-24-61A and Lot 1-11-A. The specimens made from these blends were very porous and powdery after hot pressing and sintering at 3300 F for 30 minutes. The specimens could not be examined metallographically, but the metal appeared extensively attacked and crumbled easily. Several mixing, pressing, and sintering variations were not successful in achieving a dense specimen.

HfO_2 (Spectrographic Grade) -4 Weight Percent Ta_2O_5 -Hf

Dense, coherent specimens were made from a blend of spectrographic grade HfO_2 and 4 weight percent Ta_2O_5 by hot pressing and sintering at 3400 F for 30 or 60 minutes. It was possible to examine those specimens metallographically and photomicrographs of the reaction interface of the oxide and Hf are shown in Figure 42. The metallic nodules at the original oxide-metal interface and in the original oxide were identified by electron microprobe as Hf with impurities of Ta, Fe, Ni, and Zr.

30 minutes - 3370 F

30 minutes - 4100 F

The lower edge of the photomicrograph is approximately the center of the 10 mil Hf sheet.

60 minutes - 3370 F

60 minutes - 4100 F

Magnification: 250 X

FIGURE 40. REACTION INTERFACE OF SPECTROGRAPHIC GRADE HfO_2 - Hf; Cold Pressed and Sintered

The lower edge of the photomicrograph is approximately the center of the 10 mil Hf sheet

Magnification: 250 X

FIGURE 41. REACTION INTERFACE OF SPECTROGRAPHIC GRADE HfO_2 -Hf; Hot Pressed and Sintered

30 minutes - 3400 F Magnification: 250 X 60 minutes - 3400 F

The lower edge of the photomicrograph is approximately the center of the 10 mil Hf sheet.

FIGURE 42. REACTION INTERFACE OF SPECTROGRAPHIC GRADE
HfO₂ + 4 WT % Ta₂O₅-Hf

3.4.4 Discussion

HfO₂-Ta, 90Ta-10W, W

Extensive reaction occurred when tantalum and the 90Ta-10W alloy were in contact with hafnia at 4060 F for 1 hour (Fig. 34 through 36). The large amount of metal in the oxide around both tantalum and the 90Ta-10W alloy indicated surface melting of the metal. At the sintering temperature, there was a large thermodynamic driving force for the dissolution of oxygen in the metal. Hafnia and impurity oxides around the tantalum and 90Ta-10W alloy were probably reduced to metal of high oxygen content. The reduced metals could then alloy with the tantalum and the 90Ta-10W alloy to form a melt. The major impurities in the hafnia (Zr, Ti, and Fe), all form relatively low-melting alloys with tantalum and tungsten, but the formation of Ta-Hf and W-Hf alloys probably dominated the reaction.

The Ta-Hf phase diagram is shown in Figure 43. Tantalum and hafnium are completely miscible above 3200 F, and at 4000 F alloys containing about 40 weight percent hafnium or more could produce a liquid phase. Furthermore, at the hafnia/90Ta-10W alloy interface, the formation of molten W-Hf alloy is a distinct possibility.

Data for Figure 43 extracted from:
 English, J. J., Binary and Ternary Phase Diagrams
of Columbium, Molybdenum, Tantalum, and Tungsten.
 DMIC Report 152 (28 April 1961)

FIGURE 43. TANTALUM-HAFNIUM SYSTEM

The W-Hf diagram contained in Figure 44 shows that alloys with more than 35 weight percent hafnium could produce a liquid phase at 4000 F. The more extensive reaction around the 90Ta-10W alloy, as compared with pure tantalum, was probably a result of the lower melting point of Hf-W alloys and ternary Ta-W-Hf alloys as compared with Hf-Ta alloys.

Unlike tantalum and 90Ta-10W alloy, tungsten was inert toward hafnia at 4060 F (Fig. 37). Tungsten has an extremely low oxygen solubility and low free energy

Data for Figure 44 extracted from:
 English, J. J., Binary and Ternary Phase Diagrams
of Columbium, Molybdenum, Tantalum, and Tungsten.
 DMIC Report 152 (28 April 1961)

FIGURE 44. TUNGSTEN-HAFNIUM SYSTEM

of formation of oxide so the tendency to reduce the hafnia was negligible. Production of metallic hafnium would have resulted in the formation of low melting alloys as observed for Ta and 90Ta-10W alloys.

A tungsten diffusion barrier has been proposed to prevent oxygen diffusion into the base metal. Tungsten could also serve as a barrier to interaction of a tantalum substrate with an oxide coating. On the basis of this study, such a barrier will be necessary in coating systems on tantalum for use at 4000 F. However, the interaction of tungsten with the reservoir metal, from which the oxide grows, may be extensive at high temperatures and must be considered.

FIGURE 45. HAFNIUM-OXYGEN SYSTEM

HfO₂ (Reactor Grade) -Hf

As shown in Figure 38, the Hf metal was almost completely oxidized after 30 and 60 minutes at temperatures greater than 3100 F. The amount of reaction at 3100 F was much more than could be tolerated in a coating system. The average composition of all the compatibility specimens were within the oxide single phase field of the Hf-O diagram (Fig. 45). The thermodynamic driving force, therefore, resulted in oxidation of the hafnium when the temperature was high enough to cause HfO₂ dissociation and oxygen diffusion into the metal to proceed rapidly.

The metallic nodules which remained unreacted after one hour at 4100 F (Fig. 38) were alpha Hf in equilibrium with the suboxide of HfO₂ (Fig. 45). That assumption was based on the similar appearance of specimens sintered at 4100 F (Fig. 38) and the equilibrium microstructure of Hf containing about 62 atomic percent oxygen (Ref. 30). The quantities of Fe and Zr which were found in the nodules were impurities originally present in the HfO₂ and Hf metal. Quantitative analyses of impurity content were not received in time for the final report because of the electron microprobe breakdown at the Material Testing Laboratory. However, significant influence from the impurities is not anticipated since other workers (Ref. 30) have found the equilibrium structures in the Hf-O systems are not affected by the minor quantities of impurities in reactor grade HfO₂ or Hf.

Porosity of the oxide, visible in the photomicrograph (Fig. 38), probably contributed to the speed of the reaction by allowing vapor phase oxygen transport to the metal surface. In addition, Ti and Fe impurity oxides in the reactor grade HfO₂ may have acted as additional oxygen sources since they are much less stable than HfO₂ and would have decomposed in the reducing environment. It seems reasonable that an improvement in oxide purity and increased density would, therefore, improve the compatibility of HfO₂ and Hf.

The thin metallic surface deposits as shown in Figure 39 probably result from the formation of a low melting alloy of impurities at the Hf-HfO₂ interface and its consequent migration along cracks and pores to the specimen surface. Significant amounts of tungsten were present in the film since it oxidized rapidly in air at 1800 F to a bright yellow-green powder which could be dissolved by boiling in a 10 percent NaOH solution. The reason for the large tungsten concentration in the film was not obvious in view of the low tungsten impurity in the specimens; however, the film was very thin and only

a trace of metal would be needed to give the observed results. The surface deposits did not occur in the specimen made of spectrographic grade HfO_2 so they evidently were the result of a complex interaction of impurities in the reactor grade HfO_2 and Hf metal.

HfO_2 (Spectrographic Grade) -Hf

Cold Pressed and Sintered Specimens. The density of the cold pressed and sintered specimens made with spectrographic grade HfO_2 varied from 7.9 to 9.3 g/cc which was comparable to the densities of specimen made from reactor grade HfO_2 . However, the spectrographic grade HfO_2 had a much smaller amount of impurity than the reactor grade. The increase in HfO_2 purity evidently led to a slight decrease in reaction of the Hf at 3370 F (Fig. 40) since detectable amounts of metal remained as platelets in the specimens. When the temperature was increased to 4100 F, complete reaction occurred in 30 minutes. The similar appearance of specimens heated 30 and 60 minutes at each temperature suggests an approach to equilibrium was made after 30 minutes.

The preferential oxidation of the Hf, which left oriented platelets of metal, suggests the platelets may be rich in segregated impurities which had a lower oxygen solubility and oxide stability than pure Hf. More information concerning their composition would be necessary to fully explain the observation.

The metallic nodules which concentrated at the original metal-oxide interface were alpha phase Hf containing detectable amounts of Fe and Zr impurities. The precise cause of the concentration of the Hf at the original interface could not be determined with the information available.

Hot Pressed and Sintered Specimens. Densities of from 9.1 to 10.1 g/cc were obtained by hot pressing the specimens prior to the sintering treatment. This was a significant increase in density over that obtained in the cold pressed and sintered specimens of reactor grade and spectrographic grade HfO_2 . The increase in densities was accompanied by decreased open porosity on the order of 5 to 10 percent. Total porosity could not be calculated because the theoretical density of the reaction products was unknown. The less porous hot pressed specimens reacted much less with Hf at each temperature than those which were cold pressed. For instance, the hot pressed specimen sintered 30 minutes at 4000 F (Fig. 41) had about the same appearance as

observed in cold pressed specimens sintered 30 and 60 minutes at 3370 F (Fig. 40). Further evidence of reduced oxygen transport relative to cold pressed specimens was that the reaction with Hf had not approached equilibrium after 30 minutes at 3300 F and a continuous metal phase existed even after 60 minutes at 3300 F. In the specimen sintered 60 minutes at 3300 F (Fig. 41), the parallel platelet pattern of unreacted metal can be seen extending from the continuous metal phase into the oxide. Oxidation at Hf generally proceeded around or terminated at the platelets which is evidence of their relative oxidation resistance, but even they were almost entirely reacted after 60 minutes at 4000 F.

Metallic nodules of alpha Hf containing Fe and Zr impurities developed at the metal-oxide interface. There was little change in specimens sintered at 3600 and 4000 F when time was increased from 30 to 60 minutes (Fig. 41). Therefore, the nodules appear to be primarily alpha phase Hf essentially in equilibrium with HfO_2 . The metal-oxide structures in Figure 41 resemble equilibrium microstructures of Hf containing about 62 to 65 atomic percent oxygen (Ref. 30).

HfO_2 -4 Weight Percent Ta_2O_5 -Hf

Spectrographic grade HfO_2 blended with 4 weight percent Ta_2O_5 was hot pressed and sintered at 3400 F to densities of 9.1 to 9.3 g/cc. The densities were comparable to the densities of cold pressed spectrographic grade HfO_2 specimens (Table 13). After 30 and 60 minutes at 3400 F, the Hf was completely converted to oxide, as shown in Figure 42. The concentration of metallic nodules at the original oxide-Hf interface was identified by the electron microprobe as Hf with impurities of Ta, Fe, and Zr. The inability to achieve specimens as dense as hot pressed spectrographic grade HfO_2 probably allowed considerable vapor transport to occur and contributed heavily to the higher reaction rate of those specimens. The decompositions of Ta_2O_5 which is less stable than HfO_2 may also have contributed to the reaction.

Attempts to fabricate specimens of reactor grade HfO_2 blended with 4 weight percent Ta_2O_5 were not successful because of their poor sintering properties. Complex reaction between Ta_2O_5 and impurities in HfO_2 provide the most reasonable explanation for the poor sintering, since spectrographic grade HfO_2 mixed with 4 weight percent Ta_2O_5 sintered under similar conditions to relatively dense coherent specimens. Extensive porosity in these specimens enhanced vapor transport of oxygen and meaningful analysis of the effect of Ta_2O_5 on oxygen diffusion rates was impossible. Therefore, work on this system was discontinued.

3.5 CONCLUSIONS

Tantalum and 90Ta-10W alloy are not compatible with HfO_2 for 1 hour at 4000 F. Tungsten is compatible with HfO_2 under identical conditions. Use of a barrier between the oxide and the Ta substrate may be required. Tungsten is the logical candidate at temperatures up to the W-Hf eutectic (3500 F).

Oxidation of Hf in contact with HfO_2 was extensive in all specimens between 3000 and 4000 F at times of 30 and 60 minutes. However, under similar conditions, spectrographic grade HfO_2 appeared more compatible with Hf than reactor grade HfO_2 or spectrographic grade HfO_2 containing 4 weight percent Ta_2O_5 . The relative compatibility is in agreement with assumptions based on electrical conductivity measurements. This agreement may be only fortuitous since there was evidence that vapor transport of oxygen through voids in the oxide was more significant than solid state diffusion. Under these conditions, spectrographic grade HfO_2 was probably more compatible because of its lower dissociation pressure at high temperature relative to Ta_2O_5 rather than a lower solid state diffusion coefficient for oxygen. In either case, spectrographic grade HfO_2 appears to be the most promising oxide tested.

Reactor grade Hf metal (96 percent pure) was used in the hafnia compatibility tests. In view of the improvement in compatibility with increased oxide purity, a further improvement may be achieved with the use of spectrographic grade (99.9 percent pure) Hf metal.

Voids within the oxide of compatibility specimens provide surfaces for oxygen evolution, and allow vapor transport to occur. Elimination of essentially all voids from refractory oxides is difficult with standard pressing and sintering methods. Nevertheless, a technique should be developed to test compatibility of essentially 100 percent dense oxides in intimate contact with substrate metals. The requirement that the technique be applicable to all oxides and metals of interest at temperatures up to 4000 F and times of 1 hour makes the development task difficult and part of a long range effort.

IV. CONCLUSIONS

For HfO_2 compositions considered as coatings for Ta alloys, expansion match, temperature of oxide phase transformation, and volume change at transformation are important to physical maintenance of the oxide. Thoria and Ta_2O_5 additions to HfO_2 did not improve the expansion match with Ta alloys. Control of HfO_2 expansion and reasonable expansion match with Ta alloys was possible with Y_2O_3 additions. Compositions showing the most promise as coatings were partially stabilized HfO_2 , reactor grade HfO_2 , and spectrographic grade HfO_2 .

Diffusion controlled metal oxidation requires the movement of ions and electrons in the oxide formed. If the oxide is a good electrical insulator, a protective coating may develop which prevents further oxidation. Hafnia has shown promise as an insulator which may make a protective coating. Electrical conductivity measurements versus temperature were made on a series of hafnia and hafnia plus additive samples. The results indicated the impurities present in the starting hafnia affected the conductivity of the samples. Spectrographic grade hafnia had a desirably low value of electrical conductivity.

Tantalum and 90Ta-10W alloy were not compatible with HfO_2 for times of 1 hour at 4000 F in argon. Tungsten was compatible with HfO_2 under identical conditions. The use of HfO_2 in a coating for tantalum may require an intervening tungsten diffusion barrier to prevent contact of HfO_2 and tantalum at high temperatures.

Reaction between Hf and pure HfO_2 or HfO_2 containing small amounts of ZrO_2 and Ta_2O_5 was extensive in argon between 3000 and 4000 F at times of 30 and 60 minutes. However, for similar conditions, spectrographic grade HfO_2 -Hf was the most compatible couple. There was evidence of vapor transport of oxygen through voids in the oxide to the metal. Elimination of vapor transport by the use of dense oxides caused the slower solid-state diffusion to control reaction rate. Study of HfO_2 -Hf compatibility under those conditions would show the systems to be much more compatible. Further study, particularly of the spectrographic grade HfO_2 -Hf interaction, seems warranted.

V. FUTURE WORK

Work will continue on development of concepts which will lead to oxidation protection of Ta and Ta alloys at 3000 to 4000 F. The first year's work indicated spectrographic grade HfO_2 was the most promising oxide considered for use as a coating. Therefore, a thorough examination of the transport properties of pure HfO_2 and compatibility of pure Hf and HfO_2 will be conducted.

Transport properties of spectrographic grade HfO_2 will be studied by use of electrical conductivity measurement techniques developed during the first year. Emphasis will be placed on the determination of ionic mobility at high temperatures by use of an alternating current of varying frequencies as discussed in Section 3.3.

Compatibility of spectrographic grade Hf and HfO_2 will be examined. In previous tests, reduction of impurities in HfO_2 increased compatibility with reactor grade Hf. The use of ultra pure Hf in a HfO_2 -Hf couple may further improve compatibility. At least a qualitative measure of the importance of impurities will be obtained.

Flaws in the oxide significantly influence experimental measurement of electrical conductivity and metal-oxide compatibility. An effort will be made to fabricate oxides of theoretical density for experimental use. Development of hot pressing or fusion techniques will be necessary for this work.

In addition to the work on spectrographic grade HfO_2 , exploration of new concepts and materials will continue. Emphasis will be on selection and evaluation of alloys and intermetallics which form effective oxide diffusion barriers with associated low oxidation rates.

In considering low-diffusion oxides, two factors appear to indicate the ability of the material to transport oxygen. The factors are atom density (number/cu cm) and single-bond strength (Kcal/mole). Oxides with a high bond strength and atom density appear to possess low diffusion or conductivity. Table 14 lists selected oxides with their atom density and bond strength. The single oxides of beryllium, magnesium, aluminum, and silicon have high atom density, or bond strength, or both. These

TABLE 14
MELTING TEMPERATURE, DENSITY, ATOM DENSITY,
SINGLE-BOND STRENGTH AND THERMAL EXPANSION OF OXIDES

Compound	Melting Point ⁽¹⁾ (F)	Density ⁽¹⁾ g/cu cm	Atom Density (No/cu cm)10 ²²	Single-Bond ⁽²⁾ Strength Kcal/Mole	Thermal Expansion ⁽³⁾	
					Coefficient (F ⁻¹)10 ⁻⁶	Temperature Range (77 F to temperature)
BeO	4585	3.01	14.5	63	6.2	3630
MgO	5070	3.58	10.7	37	8.8	3270
Al ₂ O ₃	3660	3.97	12.2	79-101	5.2	2730
CaO	4660	3.37	7.0	32	8.5	2730
SiO ₂	3110	2.2 - 2.3	6.9	106	0.3	1830
ZrO ₂	4920	5.6	8.2	81	5.3	2900
HfO ₂	5090	10.02	8.6	-	2.5	4170 (Ref. 1)
ThO ₂	5825	10.0	6.8	64	6.4	4000 (Ref. 1)
Sm ₂ O ₃	4170	7.23 - 7.24	6.4	-	5.8	1830
BaO	3490	5.72	4.5	33	-	-
Cr ₂ O ₃	3614	5.21	10.3	-	4.9	2730
SrO	4400	4.7	5.5	32	7.8	2190
La ₂ O ₃	4190	6.51	6.0	58	-	-
CeO ₂	4712	7.3	7.6	-	5.0	1830
Y ₂ O ₃	4370	4.84	6.4	50	-	-
UO ₂	4136	10.96	7.3	-	6.7	2190
Gd ₂ O ₃	4230	7.63	6.4	-	5.8	1830
ZrO ₂ + 5wt % CaO	4712	5.55	8.6	-	4.4	2730
Zr _{0.85} Ca _{0.15} O _{1.85}	-	5.48	8.7	-	-	-
CaO - Cr ₂ O ₃	3940	4.80	9.7	-	-	-
CeO - Cr ₂ O ₃	4420	-	-	-	-	-
CaO - HfO ₂	4480	6.50	7.3	-	4.0	1830
BaO - ThO ₂	4170	4.59	3.2	-	-	-
BaO - ZrO ₂	4870	6.26	6.8	-	4.7	1830
CaO - ZrO ₂	4250	4.51	7.6	-	6.0	2190
SrO - ZrO ₂	5070	5.48	7.8	-	5.4	1830
ThO ₂ - ZrO ₂	5070	-	-	-	-	-
MgO - Al ₂ O ₃	3875	3.59	10.6	-	5.1	2730

1. Reference 31
2. Reference 32
3. Reference 32

are generally considered as protective against oxidation when used as coatings. A class of complex oxides that possess a high atom density are the spinels ($RO-R_2O_3$). The implication is that a high-melting spinel or a special type of compound formation might also result in a material with a low oxygen permeability. In general, the complex and single oxides of interest have similar atom densities, as is evident in Table 14.

Oxide compositions indicating low oxygen transport will serve as a base for alloy development. The oxidation of these reservoir alloys will then be studied as a function of composition time and temperature. Examination will be made on the effect of pre-oxidation of reservoir metals under controlled conditions of pressure, temperature, and atmosphere and subsequent oxidation in air. Systems which appear promising to this point will be considered for coatings. Alloy coatings will be applied to Ta and 90Ta-10W alloy by a suitable technique such as plasma arc spraying or chemical vapor deposition and subject to further oxidation testing.

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