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Synthesis and Pyrolysis of Metal Alkoxides as Potential Refractory Oxide Coatings for Graphite

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FOREWORD

This project was initiated in the Directorate of Materials and Processes under Project No. 7350, "Refractory Inorganic Nonmetallic Materials", Task No. 735002, "Graphitic." It is part of an investigation of the coating of graphite with refractory oxides.

This report was co-authored by Mr. K. S. Mazdiyasni and Dr. C. T. Lynch of the Ceramics and Graphite Branch, Metals and Ceramics Laboratory, Directorate of Materials and Processes, Deputy for Technology, Aeroanutical Systems Division and encompasses work accomplished from January 1962 to February 1963.

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ABSTRACT

The vapor phase deposition of hafnia and zirconia on graphite substrates by decomposition of the isopropyl and tertiary butyl alkoxides has been investigated.

The infrared spectra of the isopropoxides of zirconium and hafnium have been obtained. Thorium isopropoxide infrared data have also been obtained and the spectra compared with titanium and aluminum isopropoxides.

The tertiary butoxides show more promise for coating applications because of their higher vapor pressures. The vapor pressures and decomposition temperatures of the zirconium and hafnium butoxides have been studied.

Preliminary data on the oxidation resistance to 1600°C of various grades of graphite coated by this method are reported. The results indicate a potential route to more protective refractory coatings than currently available.

This technical documentary report has been reviewed and is approved.

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INTRODUCTION

The increasing demands of aerospace systems for materials with reasonably good physical and mechanical properties at extremely high temperatures have stimulated much recent effort on very refractory materials. The carbides, nitrides, borides, and graphite have thus become of considerable interest. Graphite is particularly interesting because of its resistance to thermal shock, high strength to weight ratio at elevated temperatures, low density, and chemical inertness.

A major limiting factor of graphite in many aerospace applications is its lack of oxidation resistance. The porous nature of graphite and the lack of a protective oxide film formation results in a large surface area being exposed for attack.

There are three approaches to the problem of improving the oxidation resistance of graphite: (1) by making composite bodies where other refractories with good oxidation resistance enhance the oxidation resistance of the composite, (2) by impregnation where a less permeable body is produced, and the added material provides a higher oxidation resistant matrix, and (3) by coating, where an oxidation resistant refractory film is provided, or a film which will oxidize to a protective layer.

The composite structure generally suffers from impairing the physical and mechanical properties of the graphite, impregnation is not enough by itself, and the best coatings presently available are of SiC which forms a glassy protective phase on oxidation. However, it is not effective above 1500°C.

The oxides deposited in this study have definite limitations. The decomposition of organo-metallics in the vapor phase which is employed in the method presented is a flexible and versatile one which deserves serious consideration for the coating of graphite.

In a previous report (ref 1) the synthesis of isopropoxides of zirconium and hafnium by the method of Bradley et al (refs 2 and 3), and the synthesis of the corresponding butoxides were carried out by the Mehrotra method. Bradley (ref 4) has reviewed the synthesis and properties of the alkoxides (ref 5). The vapor phase deposition of the isopropoxides on graphite of varying grades and size was promising enough to warrant a more detailed study of the deposition process and the resultant coatings.

EXPERIMENTAL

General Procedures

Various grades, sizes, and shapes of graphite which have been discussed previously were suspended in the chamber of the apparatus as shown schematically in figure 1 (ref 1).

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The deposition apparatus which includes all of the supporting equipment except the vacuum and the diffusion pump is shown in figure 2. The overall reaction proceeds according to the equation:

$$M(OR)_4 \xrightarrow[0.1\text{-}6.5\text{mm Hg}]{500\text{-}600^\circ\text{C}} MO_2 + ROH + \text{Olefin}$$

where M is the transition metal, Zr, Hf, or Th, R can be the n-propyl, isopropyl, or tertiary-butyl group. The vapor deposition chamber was made of Vycor glass with ground glass joints. The specimen was suspended on chromel-alumel thermocouples and temperature measured on an L and N potentiometer. Circulating oil maintained a constant temperature of 145°C on the chamber walls. The induction coil heated the substrate materials to 500°-600°C. The inlet end of the chamber was connected to the alkoxide compound reservoir, heated to the boiling point of the alkoxide (100°-160°C). A series of cold traps are used on the vacuum line. A McLeod gauge monitored pressures throughout the system. Decomposition of a 0.01 mole of the alkoxides was completed in 30-180 minutes.

Vapor pressure measurements were made by the gas-saturation method. In an all-glass system the compound was volatilized in a pot contained in a hot bath, the vapor pressure of the system measured with a McLeod gauge, and the products frozen out in a trap and weighed. Using Dalton's Law $p = \frac{gRT/MV'}{1+gRT/MV'P}$ as modified for a non-ideal gas V' is the volume of the pure carrier gas, P is the barometric pressure, p is the vapor pressure of the liquid, and g is the weight of vaporized material in grams.

X-ray data were obtained on a diffraction unit using CuK_α irradiation.

Infrared spectra were obtained using a Baird Infrared Spectrophotometer, Model B. Reference solvents were Mallinkrodt Anal. Reag. CCl_4 and CS_2, except for the thorium isopropoxide which was suspended in a Nujol mull. Extreme care was necessary to avoid prior hydrolysis on handling the samples. A 0.135 mm cell was used for the CS_2 and CCl_4 solutions. In the 8.5 to 9.0 µ range it was run in a capillary film and in a 0.072 mm cell.

Products formed in the synthesis, purification, and decomposition of zirconium isopropoxide were submitted to a commercial laboratory for a series of analyses by routine methods for carbon, hydrogen, oxygen, nitrogen, and in a few cases chloride, phosphorus and sulfur. Zirconium was done spectrophotometrically and ashed as the oxide. Emission spectroscopy was used for the metal impurities. The principal decomposition products of the tertiary butoxide were qualitatively identified by gas chromatography. It was necessary to handle all analytical samples in dry nitrogen to avoid decomposition. When exposed to air the alkoxides initially lose weight while decomposing, due to the replacement of the R groups by water and the formation of volatile products such as propylene and isopropyl alcohol.

A Stanton thermobalance was used for the oxidation studies and thermal degradation of the alkoxides. The furnace is the chromel-alumel wound alumina tube with the balance mechanism sensitive to 0.1 mg. Precision limits weight change determinations to 1 mg or more.

Materials

The substrate graphites used were discs, cones, and cylinders of ATJ, AWG and RT-0029 grades (National Carbon Co.), and AX grade (Great Lakes Carbon Co.). Sizes ranged from ¾ inch in diameter and ¼ inch to 2 inches thick. The graphite specimens shown in figure 3 were machined from bulk pieces to predetermined shapes and sizes. The specimens were then pre-fired at 600°C and quenched in water. The quenching removed loose graphite particles left from the machining operation. A few specimens were polished to compare results of coating on smooth and rough surfaces.

Reagent grade isopropyl alcohol was dried over sodium hydroxide pellets according to the Gilson (ref 6) method. The anhydrous alcohol was distilled from a 70 centimeter-long column packed with Fenske helices. The 82.4°C fraction was collected at a take-off ratio 1:6.

Reagent grade benzene was dried over magnesium perchlorate crystals. Reagent grade zirconium tetrachloride was obtained from Matheson, Coleman and Bell. Hafnium and thorium tetrachlorides were obtained as the highest purity grades of Fairmont Chemical Company.

Tertiary butyl acetate was prepared by the acetic anhydride method (ref 7).

$$(CH_3)_3\ COH + (CH_3CO)_2O \xrightarrow{ZnCl_2} CH_3CO_2C(CH_3)_3 + CH_3CO_2H$$

Eastman Kodak Company's best grade of tertiary butyl alcohol and analytical reagent grade acetic anhydride were used. The acetic anhydride was redistilled, the alcohol dried over soda lime and distilled.

A mixture of 2.1 moles of t-butyl alcohol, 2.1 moles of acetic anhydride, and 0.5 grams anhydrous zinc chloride was refluxed for two hours. The crude product was distilled through a 20-cm Vigreaux column up to 110°C. The crude distillate was washed with two 50-ml portions of water and aqueous (10%) potassium carbonate until neutral to litmus. The product was dried over potassium carbonate and then further dried with calcium sulfate. The anhydrous ester was distilled through a 16-plate Stedman column or a 30-cm Carborundum packed column and the 97.9°C fraction collected. The ester was stored over calcium hydride.

The isopropoxides of zirconium, hafnium, and thorium were prepared according to the procedure of Bradley and co-workers (refs 2, 3 and 5).

$$MCl_4 + 4\ ROH + 4NH_3 \rightarrow M(OR)_4 + 4NH_4Cl$$

R is the isopropyl radical. The n-propyl, n-butyl, and n-amyl alkoxides are also made in this manner. With the exception of the initial reaction of ammonia with the metal halide solutions, all preparative steps were performed in a dry box in an anhydrous nitrogen atmosphere because of the rapid hydrolysis of the alkoxides.

The metal tetrachloride (100 gms) was slowly added to 1000 ml of isopropyl alcohol and 750 ml of benzene saturated with anhydrous ammonia at 5°C. After a two-hour reflux the solution was filtered through a fritted glass funnel at 80.1°C. The residue of NH_4Cl which weighed about 80 grams was discarded. The filtrate was heated under reduced pressure to remove any remaining ammonia, most of the unreacted alcohol and benzene solvent. The filtrate was evaporated to dryness at 80°C under reduced pressure.

The crude zirconium and hafnium isopropoxides were dissolved in boiling anhydrous isopropyl alcohol and cooled to room temperature. The liquid was decanted and the recrystallization procedure was repeated. The purified product was evaporated to dryness under reduced pressure and stored under nitrogen atmosphere in tightly sealed containers.

The thorium isopropoxide is purified in the same manner. It is sparingly soluble in benzene and much more soluble in isopropyl alcohol. It is insoluble in CS_2 and CCl_4 which are good solvents for the zirconium and hafnium isopropoxides. This demonstrates the increased ionic character of the thorium isopropoxide. In the $Zr(OR)_4$ or $Hf(OR)_4$ compounds the metal atom is 10 electrons short of the inert gas configuration. The thorium compound has filled d-orbitals and the empty 5f orbitals exhibit little tendency toward completing their orbitals.

The yields of isoproxides were 75-85%.

The tetra-tertiary butoxide of zirconium was prepared by the Mehrotra method (ref 4) from the isopropoxide and tertiary butyl acetate.

$$Zr(OR)_4 + 4R'OOCCH_3 \longrightarrow Zr(OR')_4 + 4ROOCCH_3$$

R is the isopropyl radical and R' is the tertiary butyl radical. The reaction is pushed to completion since the ester formed in reaction, isopropyl acetate (b. p. 89°C), is more volatile than the reactant, tertiary butyl acetate (b. p. 97.9°).

Crystalline zirconium isopropoxide [$Zr(OR)_4$ X ROH, where R is the isopropyl radical] was refluxed in tertiary butyl acetate at a bath temperature of 140-150°C. After a two hour reflux the products were fractionated in the column as described previously and the 94-95°C fraction was collected. The product was a pale yellow liquid which became colorless on redistillation at reduced pressure (92.5°C at 6.0 mm Hg).

Quantitative yields from this reaction were very poor (approximately 10%), however, further work on this synthesis is currently underway. A small amount of hafnium tetra-tertiary butoxide was obtained from Melpar for comparative tests.

The boiling points of the alkoxides prepared are given in table I. The marked difference in character between the thorium alkoxide and those of hafnium and zirconium is shown in these results.

There is a significant increase in volatility when going from the isopropyl substituents to the tertiary butyl substituents.

TABLE 1

ALKOXIDE BOILING POINTS

Compound	MWT	B.p. (°C)	Remarks
Thorium isopropoxide	468.2		Softens at 80°C, 0.1 mm Hg Sublimes at 200-210°C, 0.1 mm Hg
Hafnium isopropoxide	414.7	170° at 0.35 mm Hg	
Hafnium t-butoxide	470.8	90° at 6.5 mm Hg	
Zirconium isopropoxide	327.3	168-172 at 0.35 mm Hg (168-172 calc from log P=A+B/T + Clog T for P=0.1 & P=0.15)	
Zirconium t-butoxide	383.4	92.5° at 6.0 mm Hg	

DISCUSSION AND RESULTS

Vapor Pressures

The vapor pressures of zirconium and hafnium tetra-tertiary butoxides from 25° to 200°C are given in tables 2 and 3 respectively. The corresponding vapor pressure curves from 25° to 165°C are shown in figures 4 and 5. The vapor pressure results for zirconium tetra-tertiary butoxide are within less than 1% of the results of Bradley and Swanwick (ref 8). They found that the vapor pressure relationship could be represented by the equation

$$\log P_{calc}(\mathrm{mm}) = 51.0296 - 5281.72/_{T} - 13.9703 \log T$$

and the error of a single point was ±1.2%. This equation yields increasingly low values of log P_{calc} above 180°C, probably due to decomposition of its alkoxide.

The vapor pressure curve for the hafnium compound is the same as for the zirconium alkoxide within experimental error at low temperatures. Above approximately, 100°C the vapor pressures are consistently higher for the zirconium tetra-tertiary butoxide. At 200°C there is a 10 mm difference.

TABLE 2

VAPOR PRESSURES OF ZIRCONIUM TETRA-TERTIARY BUTOXIDE

TEMP °C	Pmm	TEMP °C	Pmm	TEMP °C	Pmm
25	0.05	67	1.29	132	40.71
26	0.06	68	1.40	135	45.92
27	0.07	71	1.70	136	46.10
28	0.07	73	2.30	138	49.27
29	0.08	75	2.42	141	52.30
30	0.07	76	2.49	144	56.90
31	0.08	77	2.79	145	62.23
32	0.09	78	2.82	146	62.92
33	0.09	79	2.98	150	70.00
34	0.10	80	3.10	153	84.23
35	0.12	81	3.20	155	89.94
36	0.11	82	3.20	158	98.37
38	0.14	83	3.77	159	99.92
39	0.16	84	4.25	160	101.13
41	0.20	88	4.66	163	111.07
42	0.22	89	5.00	165	118.23
44	0.24	95	6.20	167	121.97
46	0.32	97	7.07	168	130.00
47	0.37	100	9.50	169	139.89
48	0.40	105	12.00	170	149.23
49	0.45	106	12.18	172	157.70
50	0.48	108	12.93	179	173.72
52	0.57	109	14.37	182	197.26
54	0.61	112	17.32	185	213.17
55	0.68	114	19.75	186	218.00
58	0.68	116	18.72	187	235.00
59	0.74	118	21.00	188	266.12
62	0.82	122	23.97	189	289.17
63	0.88	125	27.10	190	292.70
64	0.97	126	32.30	192	310.00
65	1.07	127	32.60	197	335.80
				198	362.10
				200	379.12

TABLE 3

VAPOR PRESSURES OF HAFNIUM TETRA-TERTIARY BUTOXIDE

TEMP °C	Pmm	TEMP °C	Pmm	TEMP °C	Pmm
25	0.05	79	3.00	141	50.20
26	0.06	83	3.78	145	60.36
27	0.07	84	4.30	146	60.79
28	0.07	85	4.30	147	69.08
30	0.07	86	4.50	149	77.35
31	0.08	87	4.54	152	82.44
34	0.11	88	4.62	154	85.72
36	0.12	92	4.87	155	88.10
38	0.13	93	4.92	157	96.55
39	0.17	94	5.38	160	100.87
40	0.20	95	6.00	163	108.31
41	0.20	97	6.87	164	112.42
43	0.25	99	8.20	165	116.10
45	0.29	100	9.10	166	120.01
46	0.32	104	10.99	167	120.99
47	0.38	107	11.70	169	128.84
49	0.47	111	16.64	172	150.75
51	0.55	115	18.87	175	153.42
54	0.63	118	20.07	179	155.43
57	0.66	119	21.44	183	190.47
58	0.69	122	22.10	187	210.32
59	0.75	124	26.00	188	258.44
62	0.86	127	30.93	189	277.44
67	1.40	128	33.71	190	287.51
69	1.52	129	34.88	192	297.88
70	1.64	131	39.41	197	311.12
71	1.98	133	40.20	199	349.89
74	2.37	135	44.75	200	369.88
77	2.70	138	47.97		

Bradley and Faktor (ref 9) have suggested as a means of separation the fractional distillation of the tetra-tertiary butoxides of zirconium and hafnium. The decomposition of these alkoxides at higher temperatures is a major disadvantage. Synthesis of sufficient amounts of the butoxides is now being done to test the separation potential by distillation.

Titanium tetra-tertiary butoxide (refs 8 and 10) is not as volatile as the zirconium and hafnium derivatives.

The vaporization of zirconium and hafnium isopropoxides has not been quantitatively studied because of their low volatility. The very low vapor pressures below 50°C can be seen for the butoxides in figures 4 and 5. The isopropoxides have similarly low vapor pressures below 150°C. At 200°C the vapor pressure of zirconium isopropoxide is only 33 mm with partial decomposition taking place.

Infrared Spectra

The infrared spectra of hafnium and thorium isopropoxide, and the far infrared spectra for zirconium and thorium isopropoxides have been obtained. In figure 6 the reference spectra for the two solvent systems CCl_4 and CS_2 are shown. Figure 7 is the spectrum of zirconium isopropoxide obtained in previous work by Mazdiyasni and co-workers (ref 1).

Zirconium isopropoxide as recrystallized from isopropyl alcohol contains some isopropyl alcohol which is not removed on drying. Distillation at reduced pressure was tried to remove final traces of isopropanol. The product was no longer crystalline but a gummy mass. The infrared spectra of this distilled product is shown in figure 8. The peaks have disappeared, evidently due only to adsorbed isopropanol at 10.6 and 12.2 microns.

The infrared spectrum of hafnium isopropoxide is seen in figure 9. The thorium derivative, which is soluble in isopropanol, is not soluble in CCl_4 or CS_2. The spectrum in figure 11 was obtained in a Nujol mull. The far infrared spectra of the zirconium and thorium derivatives has also been obtained. These are shown in figures 11 and 12. The reference spectrum of CS_2 is given in figure 13 for the far infrared region.

The entire Group IVB isopropoxide absorption frequencies are compared in table IV. The data for titanium isopropoxide were obtained from Bell, Heisler, Tannenbaum, and Galdenso (ref 11). The Sadtler spectrum (ref 12) of aluminum isopropoxide is given for reference.

TABLE 4

INFRARED ABSORPTION FREQUENCIES OF ALKOXIDES

$Al(OR)_3$	$Ti(OR)_4$	$Hf(OR)_4$	$Zr(OR)_4$	$Th(OR)_4$
-	-	-	-	3.00
3.41	3.38	3.40	3.40	3.40
-	3.42	3.45	3.45	-
3.52	3.50	3.54	3.54	3.52
3.81	-	3.82	3.82	3.75
-	-	-	-	3.90
-	-	-	-	5.80
-	-	-	-	6.23
-	-	6.55	-	-
6.83	6.84	6.85	6.85	6.85
-	6.89	-	-	-
-	7.02	-	-	-
-	7.19	-	-	7.20
7.27	7.24	7.32	7.32	7.25
7.35	7.30	7.38	7.38	7.30
-	-	7.43	-	-
-	7.53	7.50	7.50	7.77
-	8.01	-	-	-
8.55	8.63	8.58	8.58	8.65
-	8.80	8.80	8.80	8.78
8.90	8.90	-	-	-
9.65	-	-	-	9.20
-	-	9.83	9.83	-
-	10.00	9.95	9.95	-
-	-	10.25	10.25	-
10.55	10.48	10.61	10.61	10.91
11.55	-	-	-	-
-	11.74	11.89	11.89	-
12.00	-	-	-	-
-	-	12.23	12.23	12.42
-	-	-	-	13.85

It is beyond the scope of this report to analyze quantitatively the different vibration frequencies. This is being done however, in a joint effort with infrared analysts and the results will be reported in a separate paper.

Decomposition Data

The decompositions of zirconium and hafnium isopropoxides under various conditions are shown in table 5. A substantial residue is found in each case, amounting to about 60 percent of the original material. The volatile products are those expected from the general reaction:

$$M(OR)_4 \longrightarrow MO_2 + ROH + \text{Olefin}$$

Butylene and tertiary butyl alcohol were analyzed qualitatively by gas chromatography as the major volatile products of the reaction. The theoretical residues for the oxides are 32.1% for zirconia and 44.7% for hafnia from their respective butoxides. The actual residues are much higher (59 to 61% and 69 to 71%). A possible intermediate of $MO(OR)_2$ or a polymeric form $[-Zr(OR)_2 - O - Zr(OR)_2 - O]$ has been suggested by Bradley and Faktor (ref 9). The residue calculated as $MO(OR)_2$ would be 66.1% for the zirconium compound and 73.6% for the hafnium compound. A disproportionation (ref 9) of the type $2MO(OR)_2 \longrightarrow MO_2 + M(OR)_4$ would give the same result. In practice some MO_2 is always found in the pot after vaporization at reduced pressures.

TABLE 5

DECOMPOSITION OF Zr AND Hf TETRA-TERTIARY BUTOXIDES UNDER STATIC CONDITIONS

Atmosphere	Pressure mm Hg	Bath Temp °C	Time min	Residue-Zr Butx wt %	Residue-Hf Butx wt %
Dry Air	760	250	120	59.4	69.8
Nitrogen	760	250	180	59.7	69.7
Purified N_2	760	250	240	60.1	71.0
Purified N_2	760	250	250	59.9	70.2
Purified N_2	760	250	300	61.0	69.9
Helium	760	250	240	59.8	69.3
Argon	760	250	240	59.2	70.1

Hence the vaporization

$$M(OR)_4 \xrightarrow[\text{reduced pressure}]{\Delta} M(OR)_4 \text{ vapor}$$

is accompanied by decomposition side reactions to produce MO_2

The volatile products of the decomposition of zirconium isopropoxide were cold trapped with liquid N_2, and then the low-boiling propylene allowed to boil off. The residue, analyzed 58.4%C, 13.25%H, 28.16%O, 0.65%N, 0%S, 0%P, 0%Zr. Calculated for isopropyl alcohol, 60.0%C, 13.3%H, 26.7%O, 0%S, 0%P, 0%Zr. The pot material which should be entirely zirconia after pyrolysis was examined. Analyzed: less than 0.3%C, less than 0.2%H, less than 0.3%Cl, 99.9 to 100.3% residue. It is interesting to note that virtually no chloride is present. In the vapor phase oxidation of $ZrCl_4$ to form ZrO_2 coatings, chloride contamination is a major disadvantage. With heat treatment the residual chlorine disrupts the coating continuity.

Thermal gravimetric analysis of the decomposition of zirconium isopropoxide was done in both air and nitrogen atmospheres. The decomposition temperature for complete conversion to the oxide is dependent on the heating rate of the balance and the amount of sample in the sample holder. Reproducible results have been obtained using heating rates of 5°C/min or less and 0.1 to 0.15 gram samples in the Stanton thermobalance. Under these conditions the air decomposition is complete at 300°C. The reaction has an unsymmetrical weight loss curve, indicating more than one reaction is occurring. In N_2 atmosphere as shown in figure 14, there are two distinct breaks and the curves are symmetrical. These breaks correspond to the loss of bound isopropyl alcohol and then the decomposition of the isopropoxide to zirconia.

$Zr(OR)_4$ 1 i-PrOH — Theoretical wt loss 15.5%
Actual wt loss 16.8%

$\downarrow$

$Zr(OR)_4$ — Theoretical wt loss 52.7%
Actual wt loss 59.0%

$\downarrow$

ZrO_2 — Total Theoretical wt loss 68.2%
Total Actual wt loss 75.8%

The higher than theoretical weight loss is caused by partial sublimation of the isopropoxide before decomposition takes place. The final product was confirmed by X-ray diffraction.

Emission spectrographic analysis was used to determine the purity of the zirconium isopropoxide as first made and as distilled. These results are shown in table 6. The raw material zirconium tetrachloride (Matheson, Coleman, and Bell) was reported by the vendor to be 97.2% $ZrCl_4$ and 1.5% $HfCl_4$. The preparation of the isopropoxide by distillation has resulted in a significant reduction in the hafnium content of the isopropoxide. As a means of separation of hafnium and zirconium this is encouraging. No further effort was devoted to this problem since small amount of HfO_2 should not be deleterious to a ZrO_2 coating.

TABLE 6

EMISSION SPECTROGRAPHIC ANALYSIS OF ZIRCONIUM ISOPROPOXIDE

Element	As Made ppm	As Distilled ppm	Element	As Made ppm	As Distilled ppm
Al	180	5	Mo	ND<10	ND<10
B	ND<10	50	Na	20	20
Ca	70	50	Ni	ND<10	ND<5
Cd	ND<10	10	Pb	ND<10	10
Co	10	ND<5	Si	1900	700
Cr	ND<10	25	Sn	ND<10	ND<10
Fe	160	10	Ti	20	ND<10
Hf	>10000	5000	V	ND<10	ND<10
Li	1	1	W	ND<100	ND<100
Mg	200		Cu	ND<5	5
Mn	ND<5	ND<5	Zn	ND<20	ND<20

ND< = Not Detected, less than

Recrystallized zirconium isopropoxide was distilled (160°C at 0.1 to 0.15 mm Hg) and the remaining "pot" material and the distillate analyzed by conventional combustion techniques for C-H and residue determination. The zirconium content was done both as ash-oxide and colorimetrically. Analytical samples required complete handling in a controlled atmosphere.

Analytical samples were dried over P_2O_5 in vacuo at 120°C for 18 hours prior to analysis. All samples were weighed and transferred for final analysis in dry nitrogen. Analytical results for zirconium isopropoxide as distilled and the residue left in the still are given in table 7. Several determinations were made in each case.

TABLE 7

DISTILLATION AND DECOMPOSITION OF ZIRCONIUM ISOPROPOXIDE

Sample	Det'n	%C	%H	%Residue C-H	Zr Colorimetric	Zr Ash-Oxide
Pot (Batch 1)	1	24.7	5.0	54.7	41.2	
	2	26.4	5.1	54.1	43.2	
	3	28.5	5.6	60.4	41.5	
	Avg	26.5	5.2	56.4	42.0	
Pot (Batch 2)	1					50.6
	2					50.3
	3					45.8
	Avg					48.9
Distillate (Batch 1)	1	37.6	7.1	44.9	32.0	
	2	40.6	7.6	40.3	33.5	
	3	40.1	7.7	44.7	32.4	
	Avg	39.4	7.5	43.3	32.6	
Distillate (Batch 2)	1					34.3
	2					35.1
	3					35.1
	Avg					34.9

For $Zr(OR)_4$, theoretical: C, 44.0%; H, 8.6%; C-H residue (ZrO_2), 37.6%; Zr, 27.9%. Found (in distillate) C, 39.4%, H, 7.5%; Residue, 43.3%; Zr, 32.6%. In separate batch, Zr, 34.9%.

For $ZrO(OR)_2$, theoretical: C, 29.9%; H, 4.7%; C-H residue, 51.1%; Zr, 37.8%. Found (in distillation pot) C, 26.5%; H, 5.2%; residue, 56.4%; Zr, 42.0%. In separate batch, Zr, 48.9%.

The evidence demonstrates in the distillate that only a small amount of the material is not in the form of the isopropoxide. This could be ZrC_2 or a polymeric $(Zr(OR)_2O)$ type material in the gummy product mass. Only the recrystallized $Zr(OR)_4 \cdot 1$ iPrOH exists as fine crystals. The material left in the pot has substantially decomposed to the $ZrO(OR)_2$ form. This can be represented simply as the equimolar mixture of ZrO_2 and $Zr(OR)_4$. Since the material disproportionates rapidly to these products, ZrO_2 should be present in the residue. The pot-residue partially dissolves in isopropyl alcohol with ZrO_2 remaining in the pot. The observations of this remaining ZrO_2 have not yet been quantified.

The batch-2 result of 48.9% Zr compares with a theoretical value of 50.05% for the reaction

$$2Zr(OR)_4 \longrightarrow ZrO_2 + ZrO(OR)_2$$

Zirconium isopropoxide samples dried in vacuo over P_2O_5 immediately lose weight when exposed to air. Two samples of zirconium isopropoxide exposed to the air for one hour lost 41.6% and 31% of their original weight. After further drying over P_2O_5 in vacuo at 120°C for another 18 hours the weight losses of 5.7% and 5.1% respectively were observed. This suggests the displacement of the isopropyl radical with the H_2O, O_2 or CO_2 molecules from the atmosphere. The reaction with H_2O is likely (ref 1).

$$M(OR)_4 + H_2O \longrightarrow MO(OR)_2 + 2ROH$$

The disproportionation of $MO(OR)_2$ is suggested by Bradley and Faktor (ref 9).

$$2MO(OR)_2 \longrightarrow MO_2 + M(OR)_4$$

This regenerates the previous reaction and if continued, produces only MO_2 as the final product. The theoretical weight loss for $Zr(OR)_4 \rightarrow ZrO(OR)_2$ is 31.15%; for $Zr(OR)_4 \rightarrow ZrO_2$, 62.36%, assuming complete vaporization of ROH formed after one hour exposure to air. a mixture of $ZrO(OR)_2$ and ZrO_2 is present.

Deposition Studies

The deposition reaction has been shown to be first order (ref 1) with the reaction rate proportional to the concentration of the starting material. if this is correct and all other factors are equal, the coating thickness is time dependent. Using the methods previously described, the coating thickness on graphite was varied in thickness from 0.5 to 2.0 mills by varying the time from 30 to 180 minutes.

The coatings obtained when using zirconium and hafnium isopropoxide were grayish white and sometimes black in color as deposited on the substrate graphite. The coatings were conductive and when heated in air, became white, powdery, and insulative. The coatings obtained from zirconium and hafnium tetra-tertiary butoxides were grayish white, or white in color, and also insulative; firing in air to 1000°C did not change the appearance of these coated specimens. Generally the adherence of these coatings to graphite was better than for coatings obtained from the isopropoxides. Coatings were scraped off the graphite and analyzed by X-ray diffraction. Only ZrO_2 and HfO_2 were found.

An example of the black coating is shown in figure 15. This is RT-0029-grade graphite with a white coating of ZrO_2 on the base of the solid cone and black coating near the tip. In figure 16 a white coating is shown. An uncoated specimen of RT-0029 is shown on the left. In the center is a very lightly coated specimen of RT-0029-grade graphite. On the right the graphite has a 1.5-mill coating of ZrO_2. An adhesion test was made by simply sticking scotch tape to the surface and pulling it off. The coating remained intact.

The principal difference between using isopropoxides and tertiary butoxides for coating purposes is the higher vapor pressures of the butoxides. The butoxides can be decomposed at atmospheric pressure rather than at reduced pressure. It is highly disadvantageous to lay down an oxygen-deficient or carbonaceous coating since subsequent oxidation disrupts the coating. The blackness and conductivity of the coating can be attributed to several possibilities, none of which can be completely ruled out at the present time:

1. Incomplete degradation of the isopropoxides or degradation of by-product alcohol and olefin in the coating.

2. Oxygen deficiency from reduced pressures and presence of an excess of carbon.

3. Random cleavage to the carbide in the degradation of the isopropoxides. The latter point is worth noting because the reaction mechanism depends on the M-O bond strength being greater than the M-C bond strength. The M-O bond for Group IV B metals is very stable. At the high temperatures of degradation to the oxide (500-600°C) the possibility of random cleavage to the carbide cannot be ignored. The more stable butoxides degrade to the oxides and the evidence of this is being white non-conductors as deposited.

Since the X-ray data shown only the oxide phase, the second phase is probably not present in concentrations over a few per cent. By lowering the pot temperature of hafnium isopropoxide from 160°C (0.1 mm Hg) to 140°C the deposition rate was much slower. An all-white very uniform coating 3 mils thick was obtained after ten hours. This coating is shown in figure 17 after an oxidation test at 1000°C. The coating cracked upon cooling. This is expected due to the difference in coefficient of thermal expansion of HfO_2 and RT-0029 graphite.

A very important application of the deposition reaction is its use to produce fine particle high purity oxides.

The purification achieved during the distillation of zirconium isopropoxide (see table 6) is very good. During the decomposition reaction a sizeable amount of the fine particle oxide deposits on the walls of the reaction chamber, on the thermocouple shield, and in the trap. Electron micrographs of this material show that a particle size of 250 to 500 Å is common, with speroidal shaped particles. Even the agglomerates found were less than 0.5μ in diameter. Some of the fine particle oxide specimens have appeared almost amorphous to X-ray diffraction. An approximation of particle size by line-broadening techniques gives a range of 100-500 Å. These initial results indicate that this method has great potential for producing fine particle high purity zirconia, hafnia, thoria, and other refractory metal oxides. Because of their sinterability, fine particulates in general are of great interest to the field of refractory inorganic materials.

Oxidation Tests

The oxidation weight loss at 1000°C in still air of various graphite specimens, coated and uncoated, is given in table 8. The 3-mil coating of HfO_2 (figure 17) had the lowest oxidation loss (<5 mg/cm^2 for one hour at 1000°C). By contrast, the weight loss of 180 mg/cm^2 in 20 minutes at 1000°C occurred with unprotected RT-0029-grade graphite. A specimen of the uncoated RT-0029 coating after oxidation at 1000°C for 20 minutes is shown in figure 18. The results indicate the degree of protection that the substrate graphite has at 1000°C. For ultimate use temperatures at 1800°C or higher, zirconia and hafnia would have to be stabilized in the cubic form to avoid the shock of the monoclinic-tetragonal phase transformation, and any oxide coating would have to be pre-sintered.

TABLE 8

OXIDATION WEIGHT LOSS-COATED AND UNCOATED ATJ, AX AND RT-0029 GRADES OF GRAPHITES

No.	Grades	Oxidation Temp C°	Oxidation Time Min.	ZrO_2 HfO_2 thickness mill	wt loss mg/cm^2
4	ATJ	1000	20	1 --	20
3	ATJ	1000	20	1.5 --	15
1	ATJ	1000	20	2.00 --	10
1	ATJ	1000	20	no coating	72.8
2	AX	1000	20	no coating	60
2	AX	1000	20	1 --	17.5
3	AX	1000	20	1.5 --	15.0
1	AX	1000	20	2 --	9
4	RT-0029	1000	20	1 --	22
3	RT-0029	1000	20	1.5 --	17.5
2	RT-0029	1000	20	2.00 --	10
1	RT-0029	1000	20	no coating	180
1	RT-0029	1000	20	no coating	180
2	RT-0029	1000	20	-- 1	22.5
2	RT-0029	1000	20	-- 1.5	17.5
2	RT-0029	1000	20	-- 2.00	10
2	RT-0029	1000	60	3.00	<5

A high degree of protection is afforded only by an adherent uniform coating. Stresses such as those occurring when the grayish to black coating oxidizes will disrupt the coating. An example of this is seen in figure 19. An RT-0029-grade graphite was coated with ZrO_2. During the oxidation test at 1000°C the coating spalled off. Oxidation of the unprotected substrate is clearly seen.

The results of a series of oxidation tests in still air of various grades of graphite (RT-0029, ATJ, and AX) coated with ZrO_2 are shown in figures 20, 21 and 22. Coating thicknesses of 1.0, 1.5, and 2.0 mils were used and compared with uncoated specimens. In figure 23, the results of coating RT-0029-grade graphite with HfO_2 are given. The degree of protection afforded these different grades of graphite at 1000°C are the same. Apparently the optimum coating thickness has not been reached. This will change, however, with the stabilizing and sintering of coatings for use at 1800°C and above. At higher temperatures the matching of thermal expansion of the substrate and coating is needed. This method should have sufficient flexibility by using mixed alkoxides as starting materials.

Single Crystals

The first single crystals of hafnium isopropoxide to be grown were made under this program. These crystals, grown in CS_2, are shown in figure 24.

SUMMARY

The vapor pressures of zirconium and hafnium tetra-tertiary butoxides are the same within experimental error at low temperatures. Above 100°C the zirconium compound is more volatile. At 200°C the difference is 10 mm.

With the obtaining of infrared spectra for hafnium and thorium isopropoxides data on all of the Group IV B isopropoxides spectra are now available. The zirconium and hafnium spectra are identical except for one peak at 6.55 for the hafnium compound. The thorium isopropoxide spectrum is significantly different from the hafnium and zirconium compounds. The zirconium and hafnium derivatives are soluble in CCl_4 and CS_2 for infrared studies while the thorium derivatives are not soluble in CCl_4 and CS_2. Thorium isopropoxide is more soluble in isopropanol which is indicative of its more ionic character.

Decomposition of the isopropoxides were studied using X-ray, emission spectrographic, combustion, and colorimetric analysis. Decomposition of zirconium isopropoxide to zirconia is complete in N_2 atmosphere at 350°C and at 300°C in air. Recrystallized zirconium isopropoxide decomposed in a thermal balance in one step after losing bound isopropanol.

$$Zr(OR)_4 \cdot 1\ i\ PrOH \rightarrow Zr(OR)_4 + i\ PrOH \rightarrow ZrO_2 + R{=}R + 2ROH$$

Some ZrO_2 is always found as a result of side reactions during the distillation of zirconium isopropoxide at reduced pressures. The distillate analyzed for $Zr(OR)_4$, theoretical: C, 44.0%; H, 8.6%; residue, 37.6%; Zr, 27.9%. Found: C, 39.4%; H, 7.5%; residue, 43.3%; Zr, 32.6%. The distillate was substantially purer than the original starting material $ZrCl_4$ and the Hf content was down from 1.5% to about 0.5%. The possible separation of hafnium and zirconium by this method is suggested.

Using the isopropoxides of zirconium and hafnium as starting materials, coatings of the respective oxides were obtained from 1 to 3 mils in thickness on graphite. The oxidation rates were observed at 1000°C for various grades of coated graphite and various coating thicknesses. The rate for 3 mils HfO_2 on RT-0029-grade graphite was <5 mg/cm^2 in one hour. For uncoated RT-0029 the rate was 180 mg/cm^2 in 20 minutes. A high degree of protection is afforded, however, the performance is below that of commercial SiC coatings. Sintering of coatings and stabilization of the oxides using mixed oxide systems should improve the performance.

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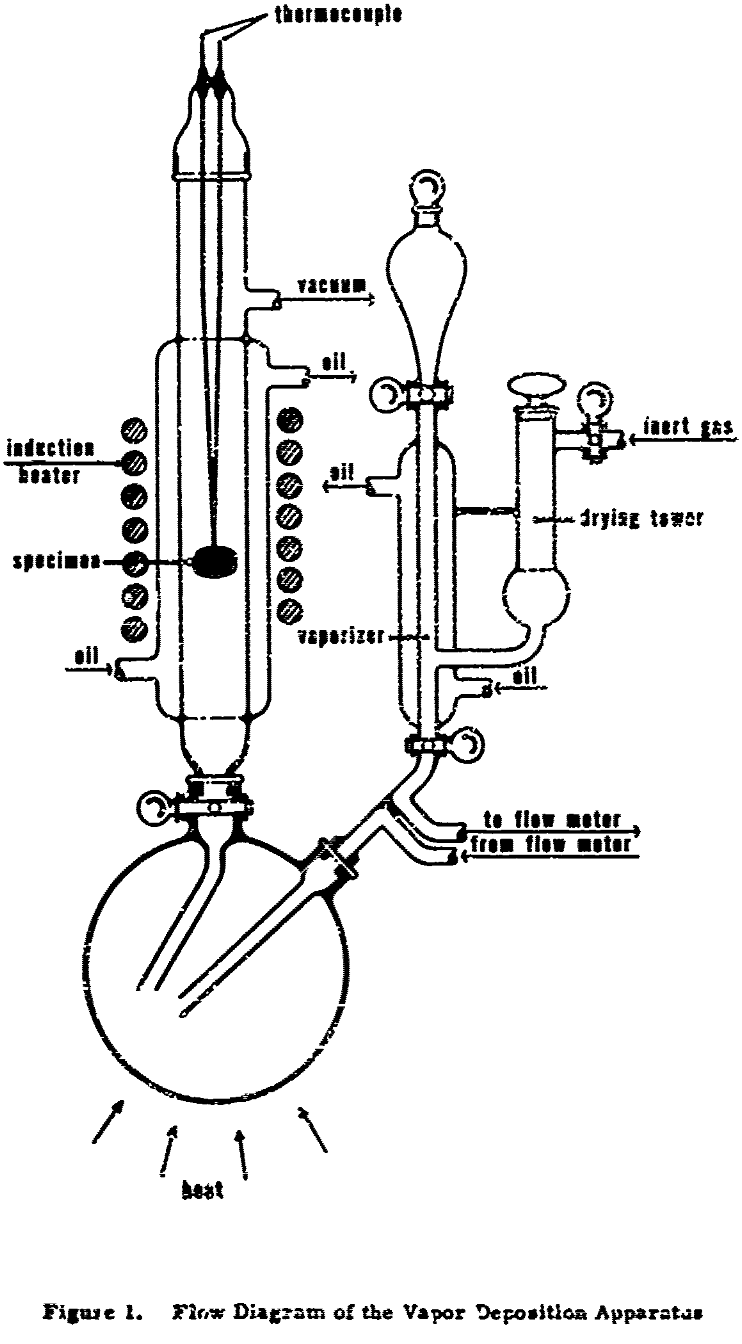

Figure 1. Flow Diagram of the Vapor Deposition Apparatus

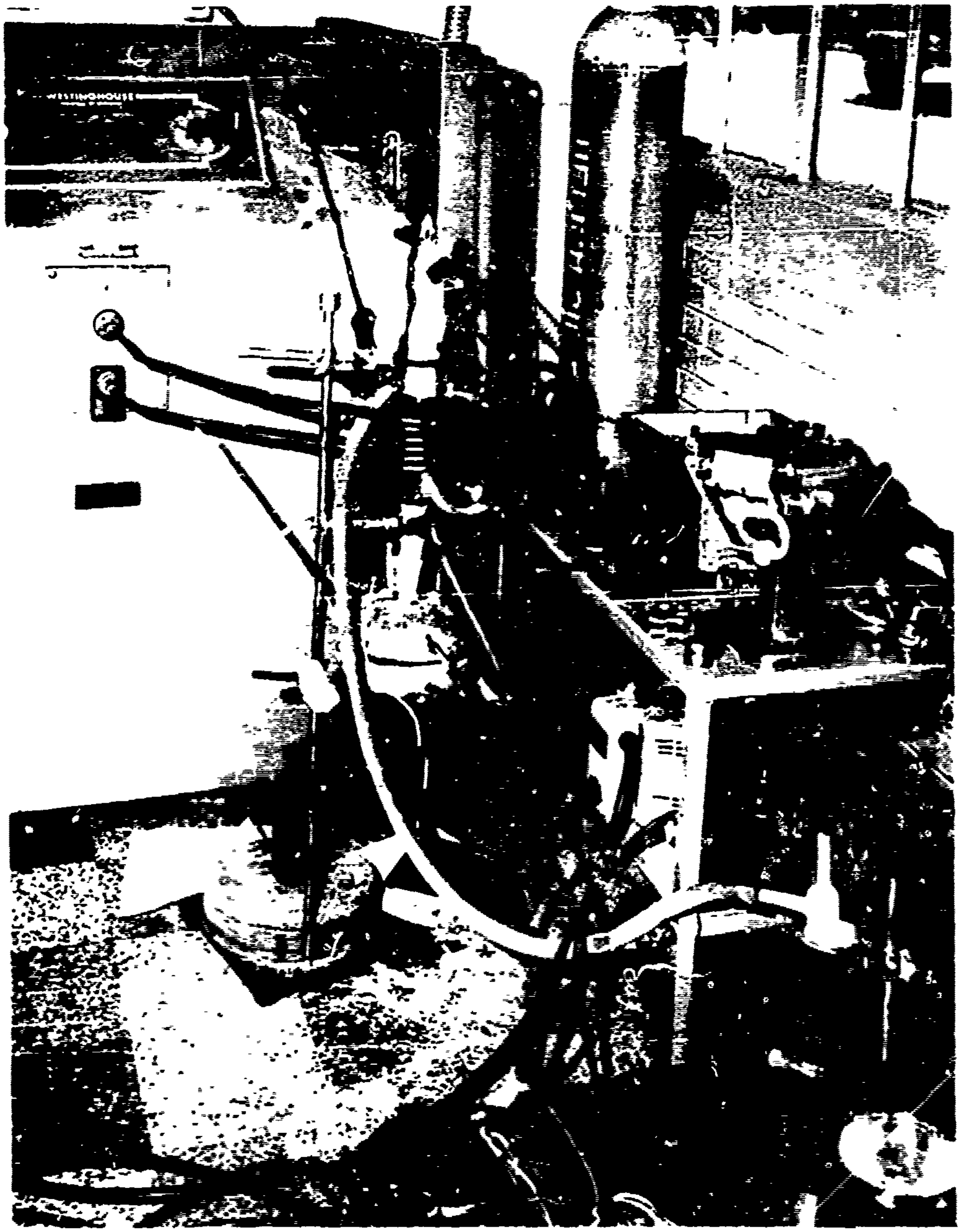

Figure 2. Deposition Apparatus and Supporting Equipment

Figure 3. Graphite Specimens Used for Coating

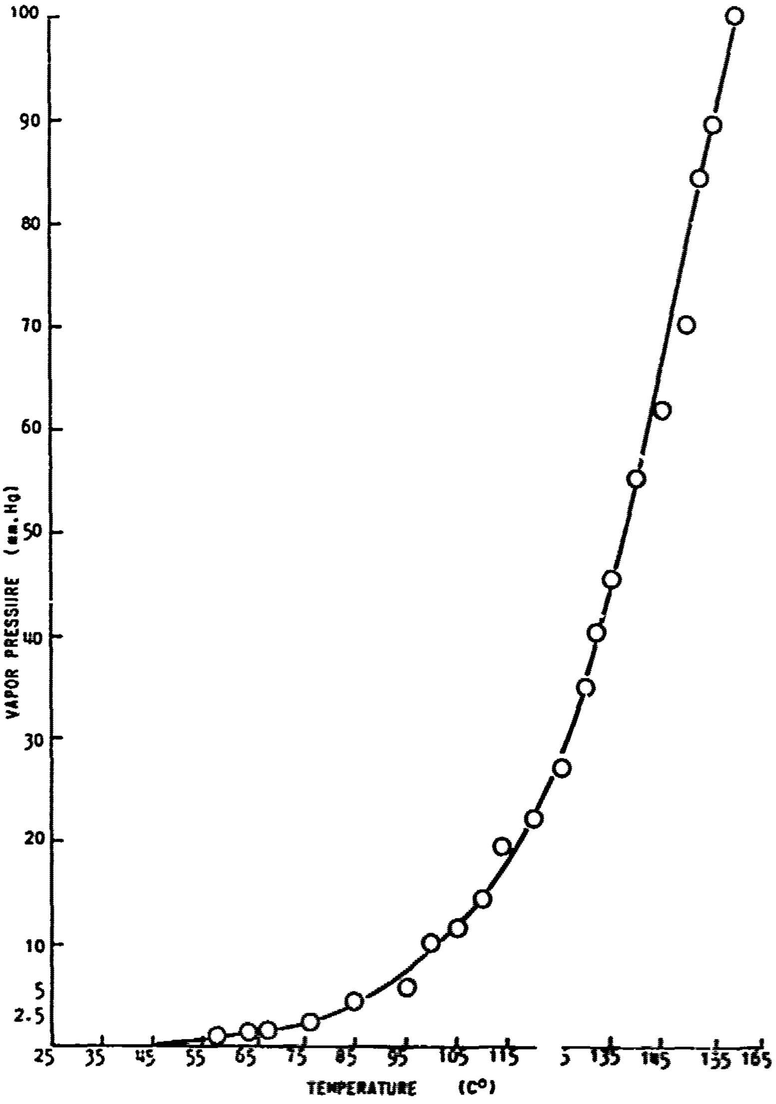

Figure 4. Vapor Pressure vs. Temperature Zirconium Tetra-Tertiary Butoxide

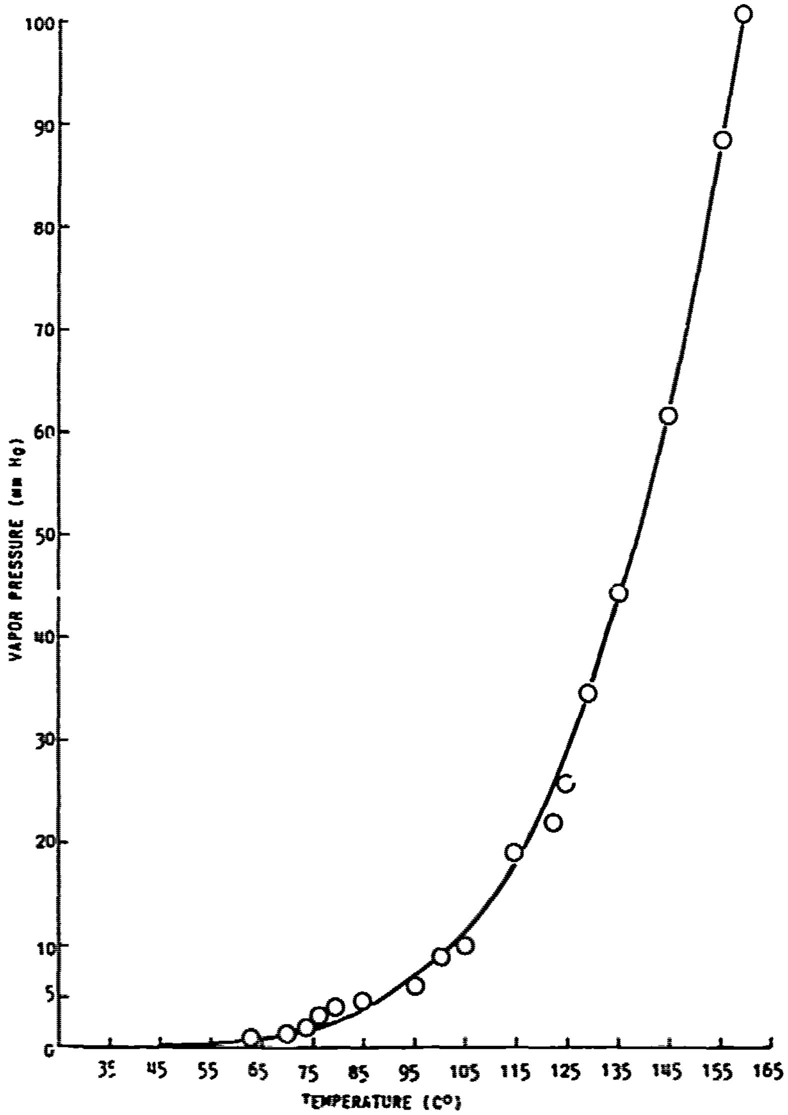

Figure 5. Vapor Pressure vs. Temperature Hafnium Tetra-Tertiary Butoxide

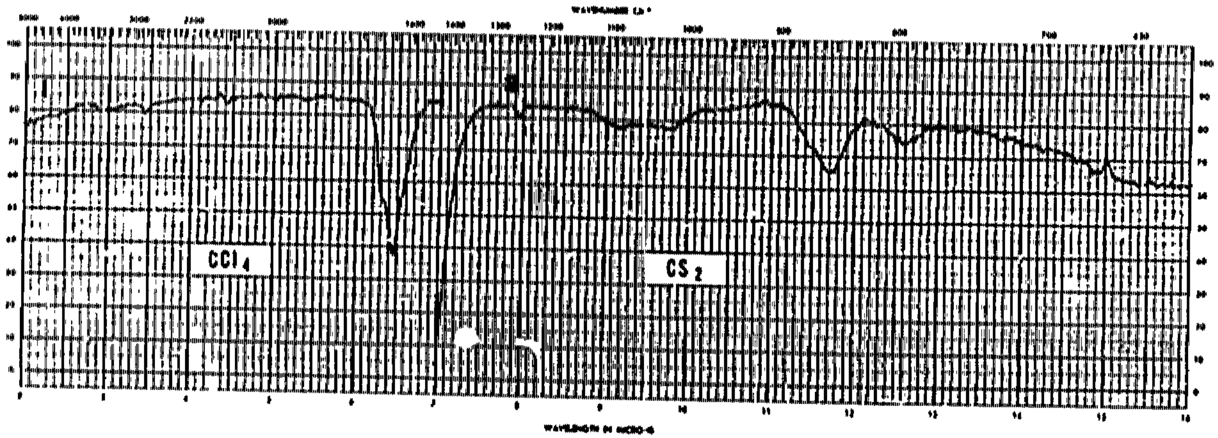

Figure 6. Infrared Spectrum of Reference Solvents CCl_4 and CS_2

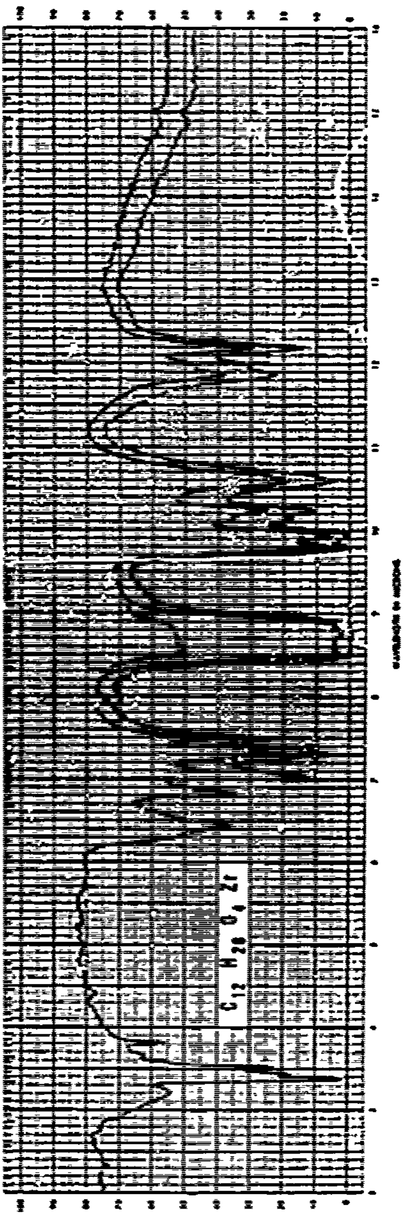

Figure 7. Infrared Spectrum of Zirconium Isopropoxide

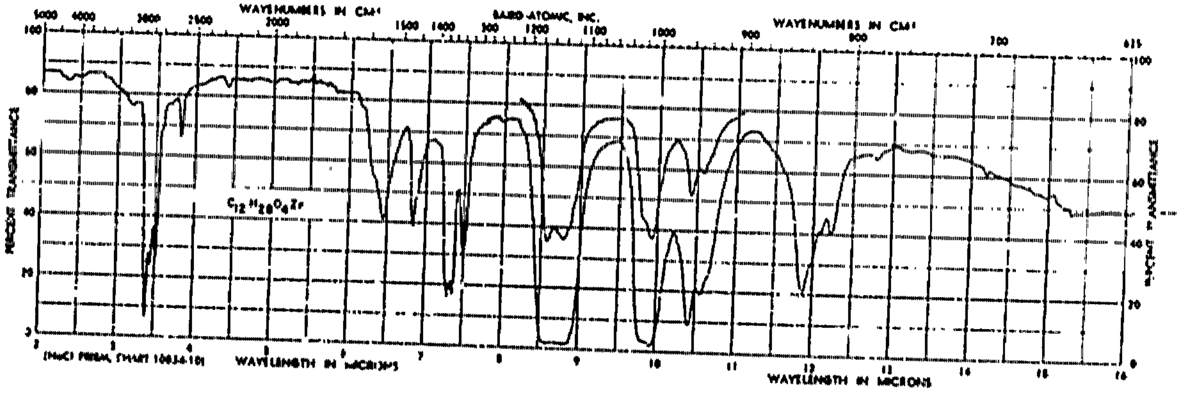

Figure 8. Infrared Spectrum of Distilled Zirconium Isopropoxide

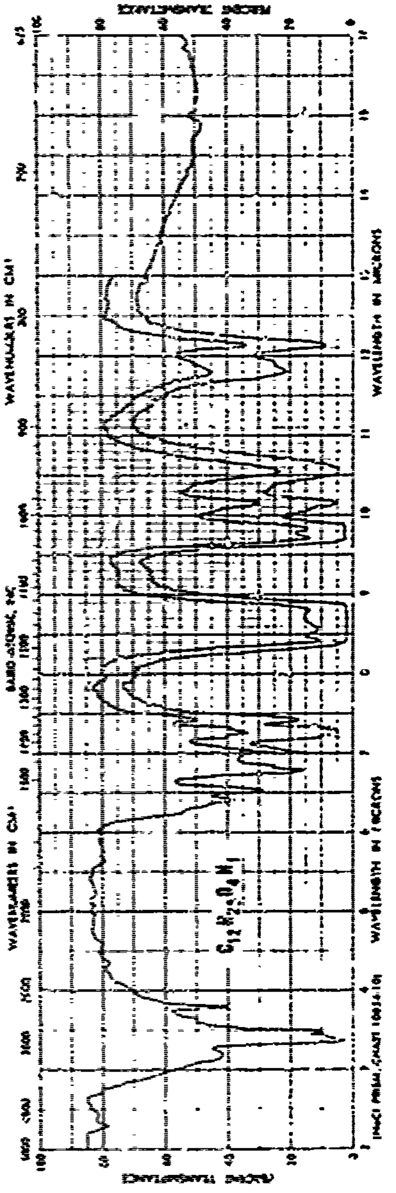

Figure 9. Infrared Spectrum of Hafnium Isopropoxide

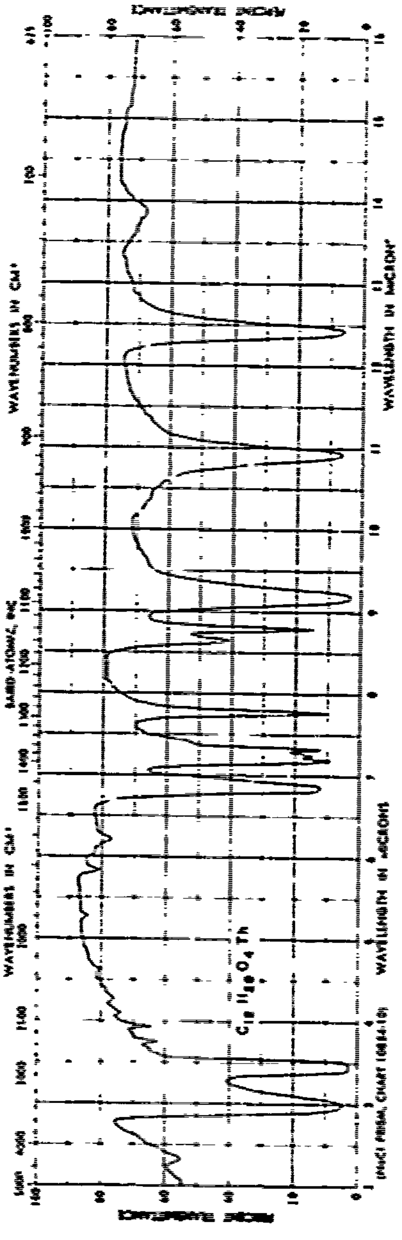

Figure 10. Infrared Spectrum of Thorium Isopropoxide

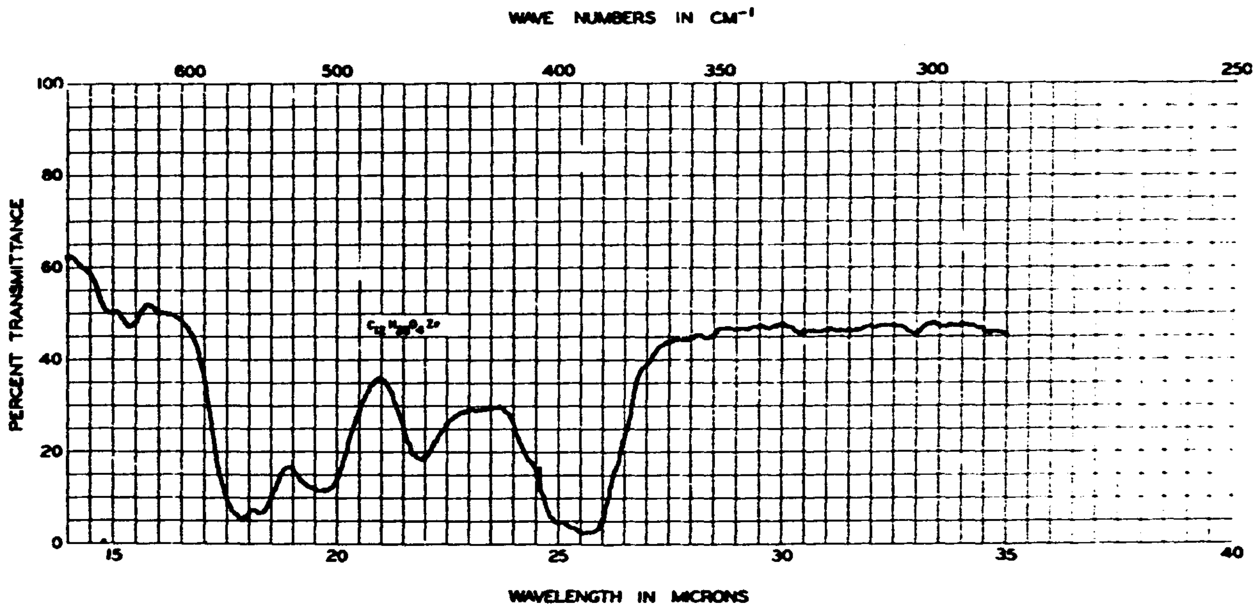

Figure 11. Far Infrared Spectrum of Zirconium Isopropoxide

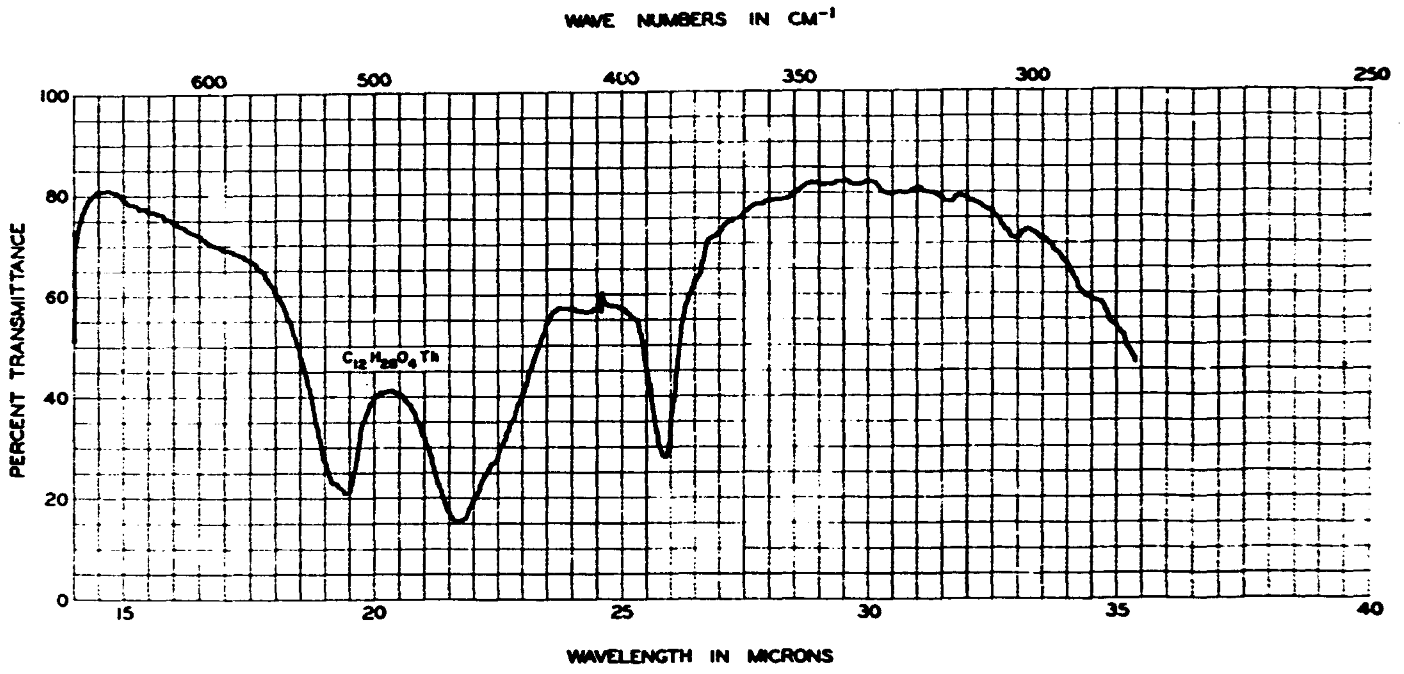

Figure 12. Far Infrared Spectrum of Thorium Isopropoxide

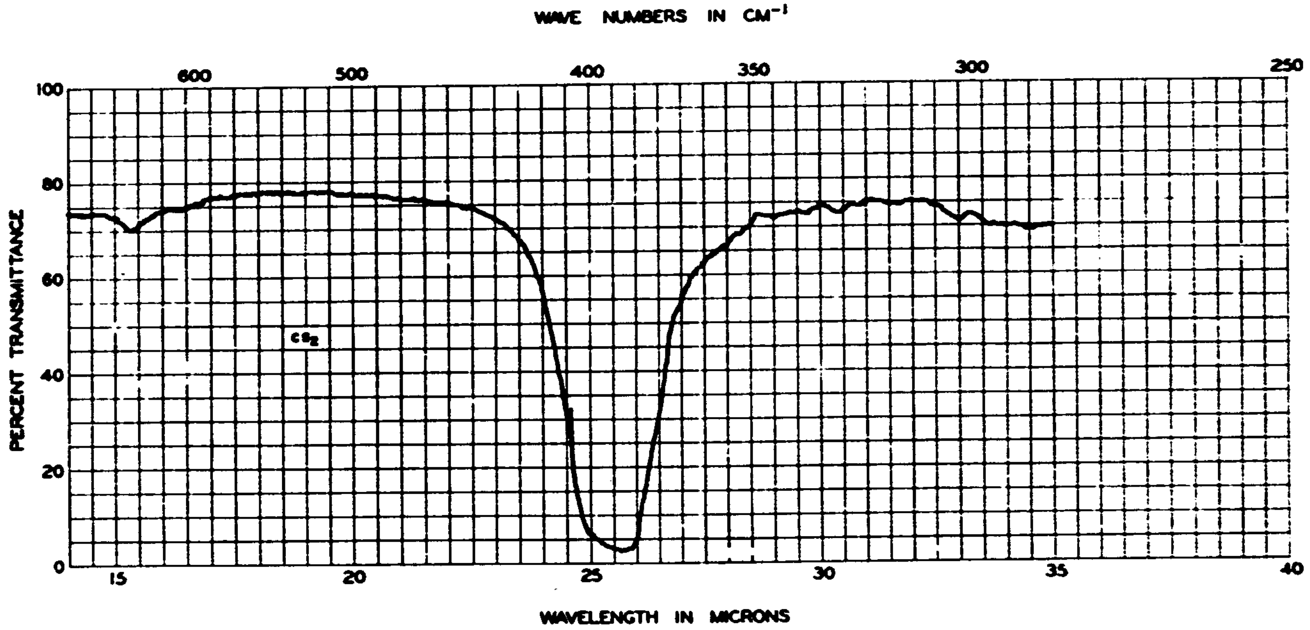

Figure 13. Far Infrared Spectrum of the Reference Solvent CS_2

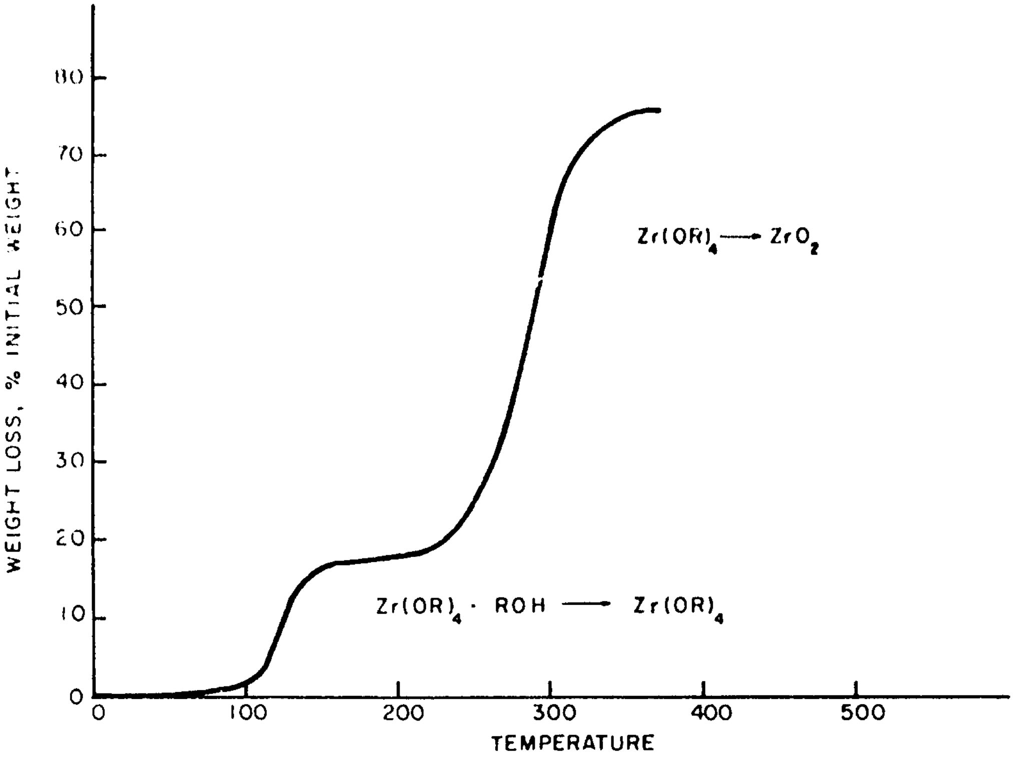

Figure 14. Decomposition of Zirconium Isopropoxide in N_2 Atmosphere

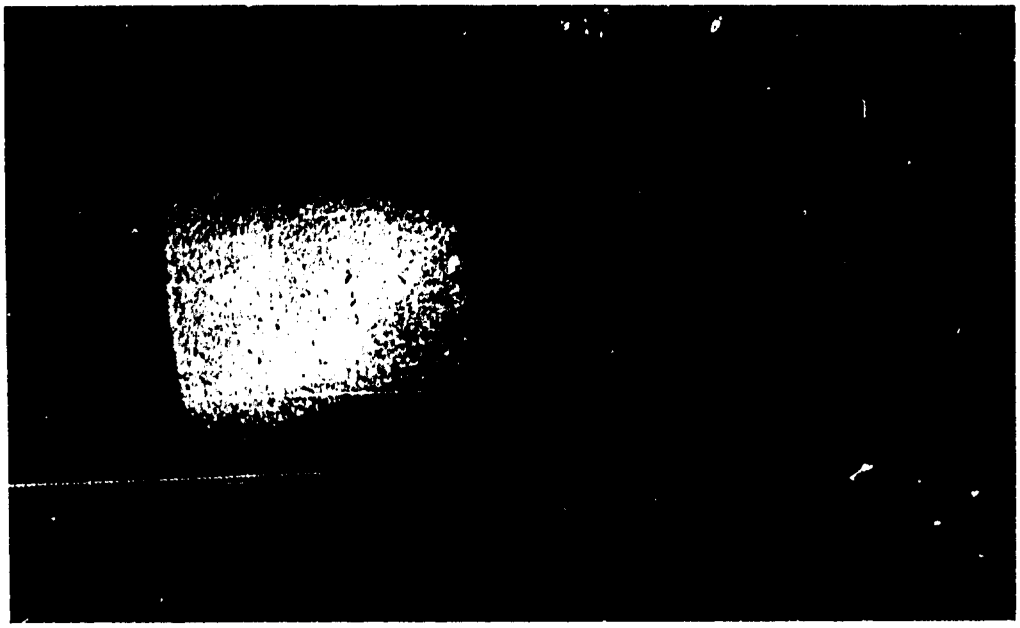

Figure 15. RT-0029 Graphite Coated with ZrO_2, Black and White Regions Clearly Visible 4X

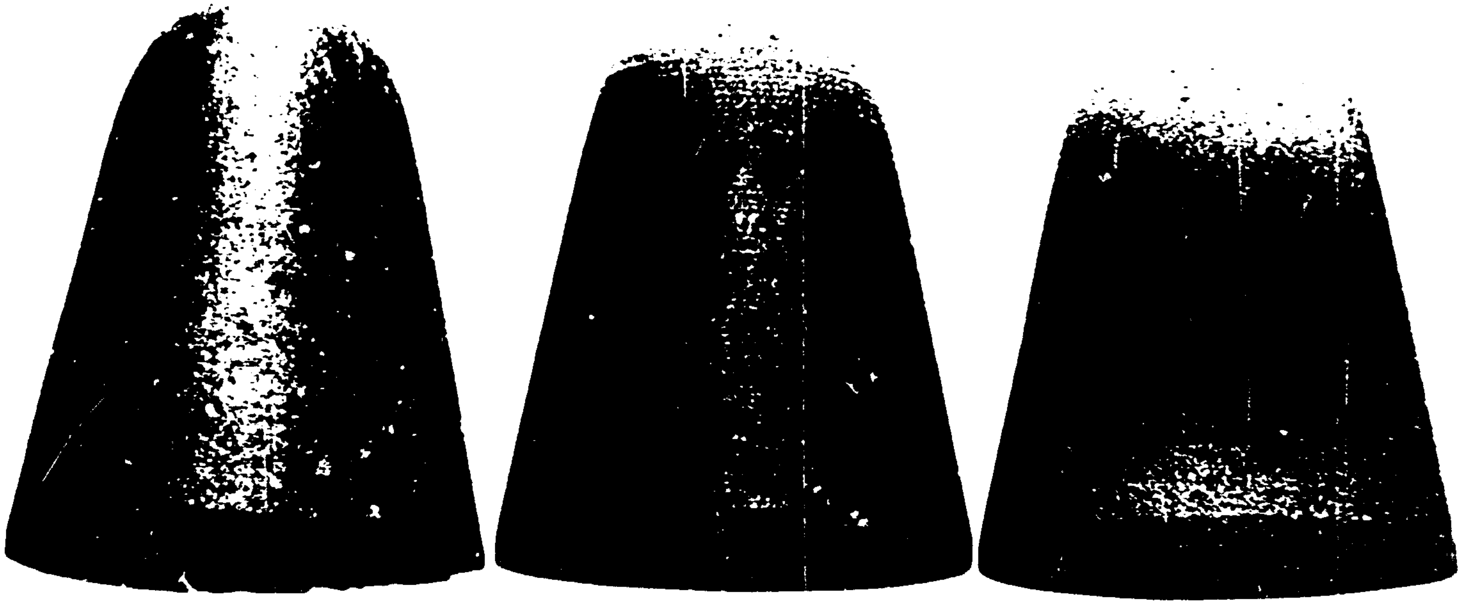

Figure 16. RT-0029 Graphite. Coated, Slightly Coated and Uncoated 4X

Figure 17. RT-0029 Graphite with a 3-Mil-Thick Coating of HfO_2 Fired in Air at 1000°C 4X

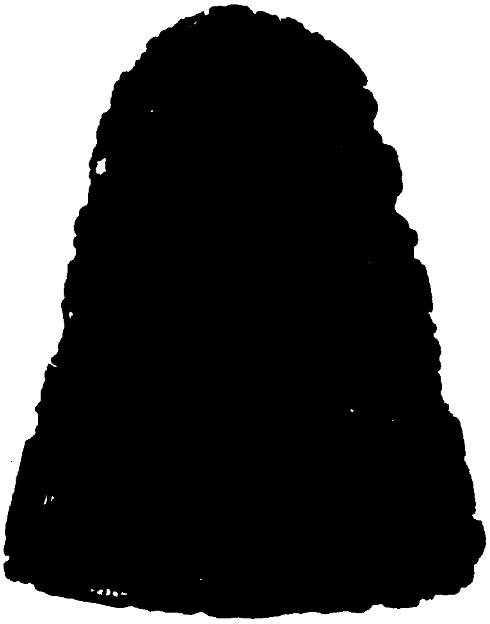

Figure 18. Uncoated RT-0029 Graphite After Oxidation at 1000°C for 20 Minutes 4X

Figure 19. RT-0029 Graphite Coated with ZrO_2, Coating Spalled when Fired in Air at 1000°C 4X

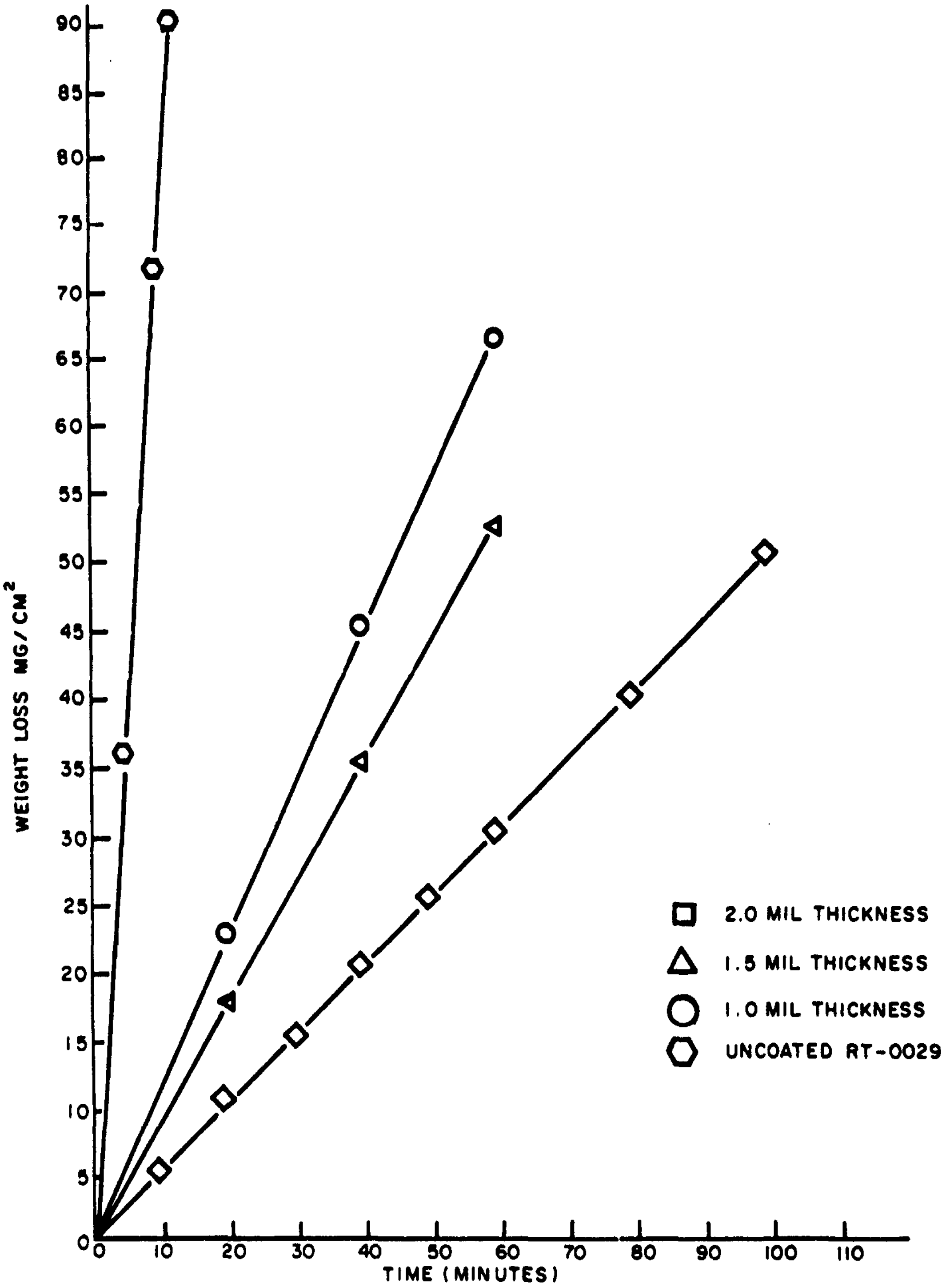

Figure 20. Oxidation Weight Loss vs. Test Time RT-0029 Graphite Coated with ZrO_2 and Tested at 1000°C

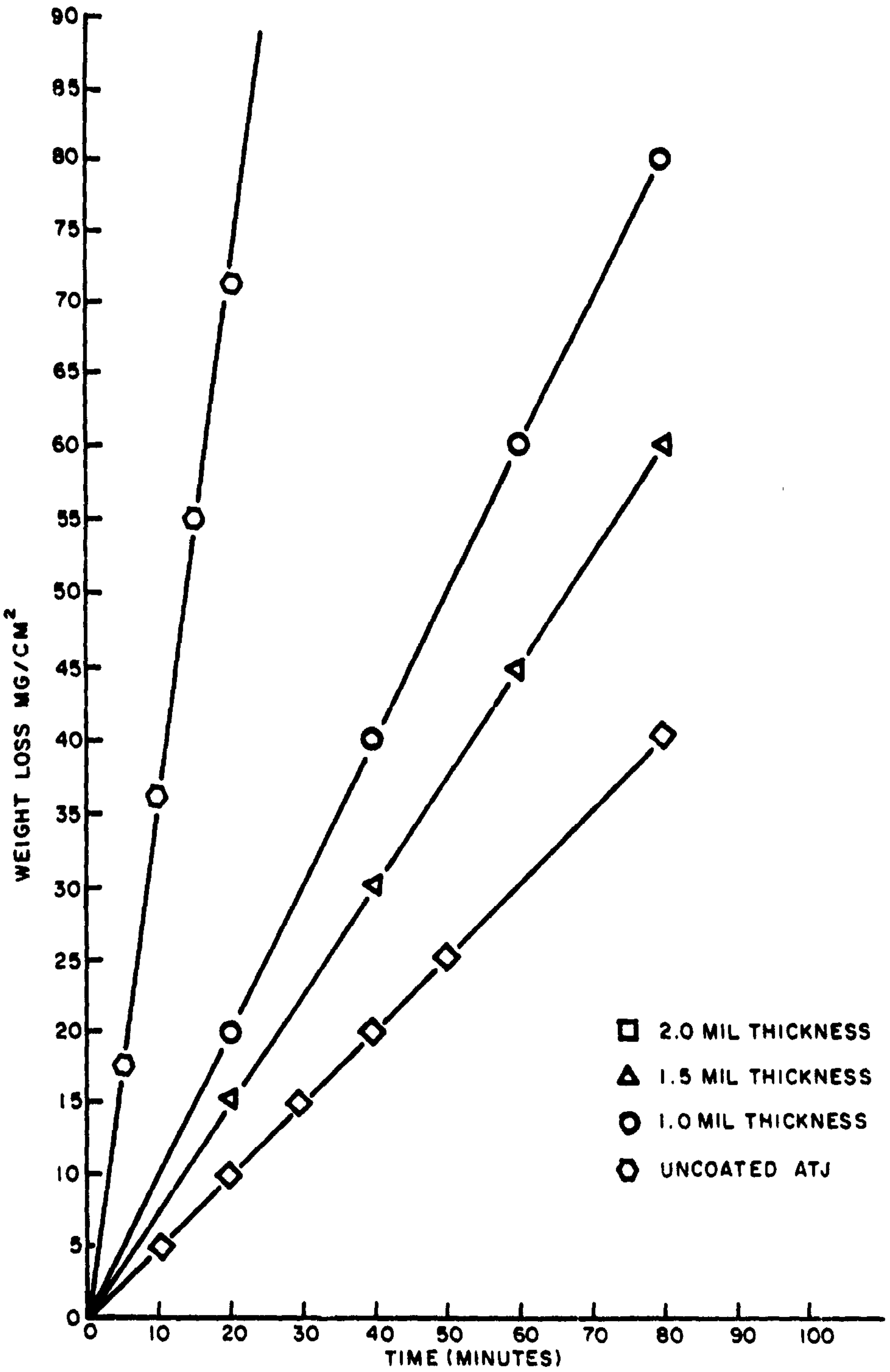

Figure 21. Oxidation Weight Loss vs. Test Time ATJ Graphite Coated with ZrO_2 and Tested at 1000°C

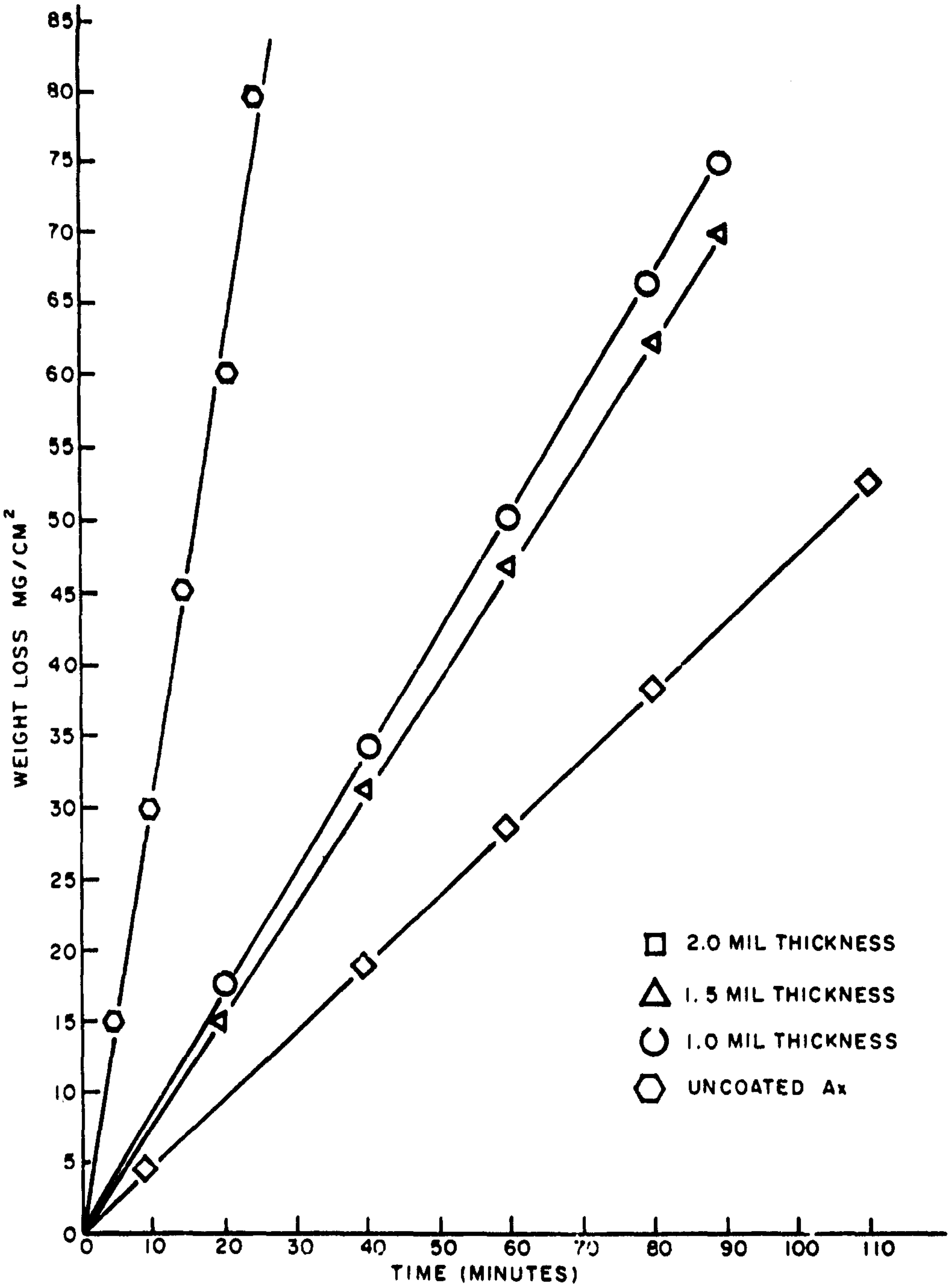

Figure 22. Oxidation Weight Loss vs. Test Time AX Graphite Coated with ZrO_2 and Tested at 1000°C

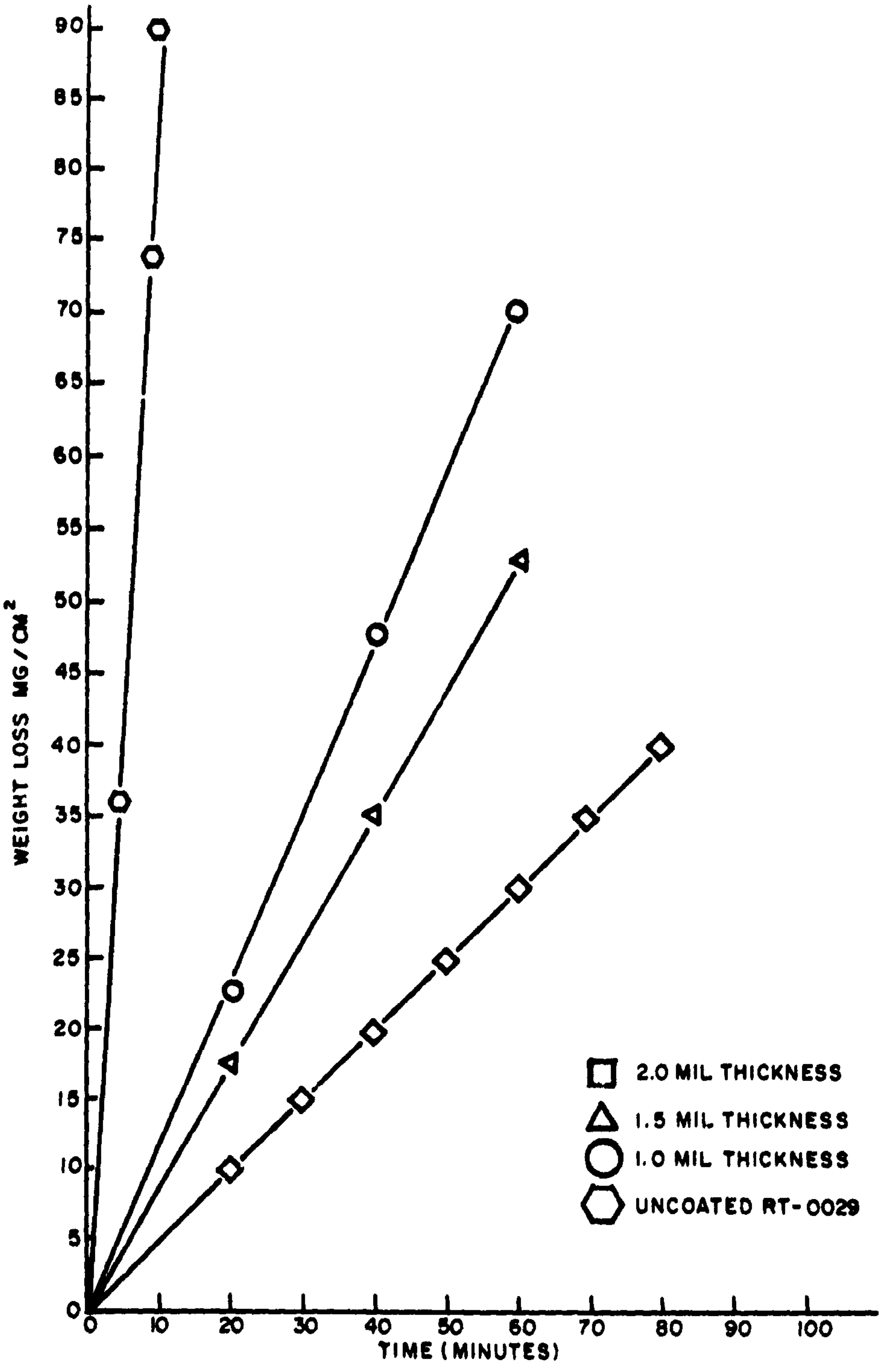

Figure 23. Oxidation Weight Loss vs. Test Time RT-0029 Graphite Coated with HfO_2 and Tested at 1000°C

Figure 24. Single Crystals of Hafnium Isopropoxide Grown in CS_2 Solution 5X

Aeronautical Systems Division, Dir/Materials and Processes, Metals & Ceramics Laboratory, Wright-Patterson Air Force Base, Ohio.
Rpt No. ASD-TDR-63-322. SYNTHESIS AND PYROLYSIS OF METAL ALKOXIDES AS POTENTIAL REFRACTORY OXIDE COATINGS FOR GRAPHITE. Final report, May 63, 40pp. incl illus., tables, 12 refs.

Unclassified Report

The vapor phase deposition of hafnia and zirconia on graphite substrates by decomposition of the isopropyl and tertiary butyl alkoxides has been investigated.
The infrared spectra of the isopropoxides of

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I. AFSC Project 7350, Task 735002
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IV. In ASTIA collection

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Thorium isopropoxide infrared data have also been obtained and the spectra compared with titanium and aluminum isopropoxides.
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Preliminary data on the oxidation resistance to 1000°C of various grades of graphite coated by this method are reported. The results indicate a potential route to more protective refractory coatings than currently available.

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