

ERRATA - May 1962

The following corrections are applicable to ASD-TDR-62-90, entitled "Synthesis and Pyrolysis of Refractory Metal Alkoxides", and dated February 1962:

Page 1

Last line on page, alcohol misspelled.

Page 9

Last sentence of page add equation (10) after in.

Page 10

Equation (8) insert 2 in front of ZrO
Eighth line should read: from equation (10) one may conclude that:

Page 11

Equation (19) add subscript 2 at the end of the equation " CH_2 ".

Page 15

Top photograph is "Uncoated 50X".
Bottom photograph is "Coated 50X".

Page 16

Top left photograph is "Coated 250X".
Top right photograph is "Coated 250X".
Bottom photograph is "Uncoated 250X".

Page 17

Insert beneath photograph "1.5X".
Add to figure caption AX Grade Great Lakes Graphite (A) Coated and
(B) Uncoated

Directorate of Materials and Processes
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

ASD-TDR-62-90 Errata Continued

Page 18

Top photograph is "Uncoated 100X".
Bottom photograph is "Coated 100X".

Page 19

Top photograph is "Uncoated 250X".
Bottom photograph is "Coated 250X".

Page 20

Insert beneath photograph "4X".
Add to figure caption "AWG Grade of National Carbon Co. Graphite, (B)
Coated and (A) Uncoated".

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FOREWORD

The work described in this report was initiated in the Directorate of Materials and Processes under Project No. 7350, "Refractory Inorganic Nonmetallic Materials," Task No. 735002-A, "Graphitic Materials Development."

The work was a joint effort made by K. S. Mazdiasni, C. R. Connors, and C. A. Pratt of the Ceramics and Graphite Branch, Metals and Ceramics Laboratory, Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

The report covers work done between March 1961 and December 1961.

The authors wish to acknowledge the valuable assistance and suggestions given by L. B. Robinson, Geoffrey Bruce, and F. W. Vahldiek of the Ceramics and Graphite Branch. Acknowledgement is also made to William Crawford, William Baun, and John Renton of the Analytical Branch, Physics Laboratory, and to personnel of the Zone Shop Branch, Fabrication and Modification Division, Directorate of Maintenance under the direction of K. D. Holdcraft for their assistance.

ABSTRACT

Procedures and techniques for the synthesis of metal alkoxides of zirconium and hafnium are described. The procedure is a modification of that used by D. C. Bradley and co-workers. Sufficient quantities of principally zirconium isopropoxide and tetra-tert butoxide were produced to use as a starting material for impregnation and coating purposes.

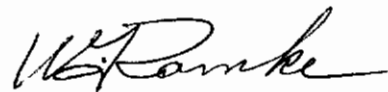
The compounds were prepared by simple chemical reactions but precautions were taken to prepare under and maintain extremely dry atmosphere. The purity, concentration, order of stability, melting temperature, vapor pressure, and decomposition temperature are described. The compound has exhibited excellent properties for coating applications.

While the compound may be applicable to coating various materials, experiments have been limited to coating graphite. The compound was pyrolyzed at 250° - 500°C. Tetragonal-monoclinic thin film ZrO_2 was deposited on graphite of various grades.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



W. G. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Laboratory
Directorate of Materials and Processes

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Contrails

INTRODUCTION

Space age requirements for high temperature materials have created a considerable interest in graphite, because it has good high-temperature physical and mechanical properties. It is one of the most inert materials with respect to chemical reactions with other elements and compounds. Oxidation and reaction with carbide forming metals are the two most important deficiencies. However, its low oxidation resistance and its reactivity with carbide forming metals limit its use in many AF advanced systems. The oxide, formed when graphite is heated to relatively high temperatures in the presence of oxygen, is gaseous and no protective oxide film is formed. Also, the porous nature of graphites allows oxygen penetration and presents a large surface area for oxidation.

This lack of oxidation resistance is considered to be the most serious deficiency of graphites today, as is the case with many other materials being considered for Air Force systems high temperature structural components. The best coating for graphite available today is silicon carbide which offers protection only at temperatures below approximately 1500°C.

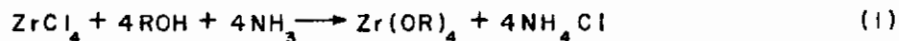
Our work has been directed toward synthesis and development of a coating material with a refractory oxide film that will be sufficiently gas tight to prevent oxidation of the substrate material. The present effort has been directed toward preparing and extending a reliable experimental technique for preparing the compound and applying the material to graphite as a coating.

The selection of the metal alkoxide of zirconium as the compound for investigation is based on the importance of ZrO_2 as a coating material. We are interested in the alkoxides of hafnium and thorium for future investigations.

These alkoxides exhibit excellent properties as vaporizable refractory compounds. The literature review and research was undertaken in the belief that these metal alkoxides, under controlled conditions of pyrolysis, dissociate to zirconium oxide (ZrO_2). Other investigators have considered using halogenated compounds such as $ZrCl_4$, or $ZrOCl_2$ and similar compounds (with bromine, iodine, chlorine of silicon, titanium, and aluminum). The principle disadvantage of such reagents is the chlorine which cannot be completely removed and is detrimental to a subsequently formed coating system.

GENERAL PROCEDURE

The alkoxide of zirconium was prepared according to the procedure reported by D.C. Bradley and W. Wardlow (1), that is, treating a solution of zirconium tetrachloride in alcohol with anhydrous ammonia.



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Where R in this equation is n-propyl, n-butyl, or n-amyl alcohol. This method was particularly successful in preparing the zirconium isopropoxide, which was readily prepared and purified by crystallization. (2) In preparing the metal alkoxide, special precautions were taken to avoid hydrolysis. The isopropyl alcohol, benzene, and zirconium isopropoxide were purified and prepared as follows.

Materials

Isopropyl alcohol, a commercial product of analytical reagent grade, contained 0.25% water. The alcohol, according to a method by Gilson, (3) was dried by shaking the alcohol over sodium hydroxide pellets. The alcohol was allowed to remain over the sodium hydroxide pellets 24 hours and then purified by fractionation over a column (70 cm long) packed with Fenske helices.

Thiophene free benzene, an analytical reagent grade, was dried over magnesium perchlorate crystals for 24 hours before using.

Zirconium tetrachloride reagent grade, a pale yellow powder, was obtained from the Matheson Coleman and Bell Company.

Apparatus

An all glass apparatus was used consisting of a column (70 cm long) packed with Fenske helices and fitted to a total condensation variable take off still head.

Prior to fractionation, the apparatus was carefully dried with anhydrous nitrogen gas which was dried by passing over a sulfuric acid bath through a deoxidizer.

The entire apparatus was dried with a hair dryer as a further precaution against moisture contamination.

Preparations

Method for Preparing Isopropyl Alcohol

Isopropyl alcohol was refluxed in the apparatus mentioned above. The distillate was collected at 82.4°C as anhydrous isopropyl alcohol. Fractionation was carried out at a ratio of (1:6). A constant temperature of 82.4°C was maintained from 12 to 24 hours. A total 1,000 ml of the distillate was collected.

Preparation of Zirconium and Hafnium Isopropoxide by the Ammonium Method

The preparation was carried out in a dry box, with the exception of reacting anhydrous ammonia with the $ZrCl_4$ solution. The ammonia was dried over soda lime, calcium sulfate, and sodium hydroxide pellets. Dishes of phosphorous pentoxide were placed in the box to eliminate moisture. Anhydrous nitrogen gas was dried over a sulfuric acid bath and flushed the box fifteen minutes prior to use.

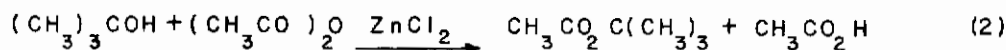
Zirconium tetrachloride (100 grams) was slowly added to a solution of isopropyl alcohol (1,000 ml) and benzene (750 ml) and saturated with anhydrous ammonia at 5°C. After 2 hours refluxing, the product was filtered off at the boiling point (80.1°C). The residue contained 80 grams NH_4Cl . The precipitate was removed and the filtrate was heated under reduced pressure to remove all of the NH_3 . The filtrate was concentrated to remove all the benzene and most of the isopropyl alcohol. It was then evaporated to dryness at 80°C under reduced pressure.

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The impure zirconium isopropoxide was dissolved in boiling isopropyl alcohol and a mass of colorless crystals separated when cooled. The liquid was decanted off and the white crystalline material was evaporated to dryness under reduced pressure. The quantitative yield of the zirconium isopropoxide was: Zr = 23% and C₃H₇O = 77%.

Preparation of Tertiary Butyl Acetate

Tertiary butyl acetate was prepared by the acetic anhydride method (4).



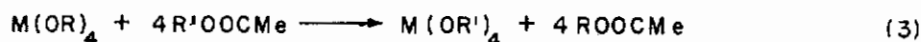
In a one liter flask equipped with a reflux condenser and drying tube were placed 200 ml (2.1 moles) of tertiary butyl alcohol* 200 ml (2.1 moles) of acetic anhydride, and 0.5 grams of anhydrous zinc chloride.

After thorough shaking, the mixture was slowly heated to reflux temperature, maintained at gentle refluxing for two hours, and cooled. The reflux condenser was replaced by a 20 cm Vigreux column through which the mixture was distilled up to a temperature of 110°C. The crude distillate, weighing 200-250 grams, was washed with two 50 ml portions of water and then with several 50 ml portions of 10% potassium carbonate solutions until the ester layer was neutral to litmus. The product was finally dried over anhydrous potassium carbonate (20 gr).

After removing the drying agent, the ester was dried further by shaking with CaSO₄ and stored for ca. 72 hours. The anhydrous ester was then fractionally distilled over 10 grams sodium metal through an efficient fractionation column.** A forerun of 21-37 grams was collected up to a temperature of 95° to 96°C and held. The yield was 129-148 grams (53-60%) (corrected boiling temperature 97.9°C). The ester was stored over calcium hydride prior to use.

Preparation of Tetra-Tertiary Butoxide

The procedure used was reported by R.C. Mehrotra (5) who showed that alkoxide of titanium, zirconium, and hafnium react with organic esters as:



The reaction can be pushed to completion if the organic ester (ROOCMe) formed is more volatile and can be fractionated out of the system.

* The Eastman Kodak Company's best grade of tertiary butyl alcohol and the analytical reagent grade of acetic anhydride were found to be satisfactory. If the alcohol is not of equal grade it should be dried over soda lime and distilled. The acetic anhydride should be redistilled.

** The fractionating column may be a 16-plate Stedman column or a 30-cm Carborundum-packed column.

The method described for the preparation of zirconium tetra-tertiary butoxide required a very long time and the yield in all cases was poor. The fractionation apparatus previously mentioned was used. General Procedure - Crystalline zirconium isopropoxide ($\text{Zr}(\text{Pr}^i\text{O})_4 \cdot \text{Pr}^i\text{OH}$ (12 g.) was refluxed in tertiary butyl acetate (54 g) under the column at a bath temperature of 140-150°C.

A forerun of the distillate was collected and discarded up to a temperature of 94°C. The distillate was collected at a temperature of 94-95°C. Upon cooling, the final product was a pale yellow mobile liquid. This liquid, zirconium tetra-tertiary butoxide, distilled under reduced pressure became a colorless mobile liquid.

The quantitative yield of the zirconium tetra-tertiary butoxide was so small that it could not be utilized for coating purposes. However, thermal stability and vapor pressure of this compound have been studied. Table 1 (6) gives results compiled by Bradley and co-workers.

The tetra-tertiary butoxide is the best starting material for organo-metallic vapor deposition and the most volatile zirconium alkoxide known. All experiments involving this compound were carried out under a pressure of 760 mm Hg.

TABLE I
DECOMPOSITION OF ZIRCONIUM TETRA-TERTIARY BUTOXIDE

EXPT.	PERMANENT GAS	BATH TEMP. °C	TIME MIN.	VOLATILE PRODUCT	SOLID RESIDUE
1	AIR	250	80	BUTYLENE-TERT BUTYL ALCOHOL	Zr, 65.1 %
2	IMPURE NITROGEN	250	960	" "	Zr, 62.1 %
3	SPECIAL NITROGEN	250	1260	NO DEPOSITION	
4	" "	250	1200	" "	
5	" "	250	1800	BUTYLENE-TERT BUTYL ALCOHOL	Zr, 63.5 %
6	" "	250	2530	" "	Zr, 62.5 %
7	" "	250	4320	" "	Zr, 62.5 %

The vapor pressure of zirconium tetra-tertiary butoxide has been measured by Bradley and Swanwich (7). The data show that the zirconium compounds are more volatile over the whole range of pressures studied than are the corresponding titanium compounds.

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X-Ray and Infrared Analysis

X-ray analysis indicated that the zirconium isopropoxide is a complete amorphous compound. However, the X-ray pattern of the compound after it was completely pyrolyzed, shows material was crystalline (figure 1).

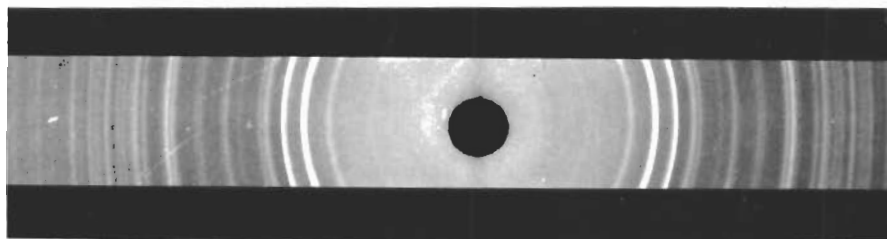


Figure 1. X-ray Pattern of Pyrolyzed Zirconium Isopropoxide

Table 2 shows to some great detail the intensity and identity of the different crystalline forms of ZrO_2 in the specimen.

TABLE 2
DATA FROM
X-RAY FILM OF PYROLYZED Zr-ISOPROPOXIDE TO ZrO_2 AT 500°C

LINE #	2θ	I/I_0	"d"	IDEN
1	23.98	35	3.70	MONOCLINIC
2	28.33	100	3.14	M
3	31.58	85	2.83	M
4	34.18	40	2.62	M
5	35.28	30	2.54	M-T MONOCLINIC-TETRAGONAL
6	38.78	5	2.32	M
7	40.98	25	2.20	M
8	44.83	5	2.02	M
9	45.48	10	1.99	M
10	49.33	55	1.84	M
11	50.28	60	1.81	M-T MONO. TETRA
12	54.13	30	1.69	M
13	55.48	40	1.65	M
14	57.38	10	1.60	M

TABLE 2 (CONT.)

15	58.28	10	1.58	M
16	60.13	40	1.53	TETRAGONAL
17	61.63	5	1.50	M
18	62.93	20	1.47	M-T MONO. TETRA
19	65.53	25	1.42	M
20	69.08	5	1.35	M
21	71.33	10	1.32	M

Infrared Spectrum

The infrared spectrum of the zirconium isopropoxide shown in figure 3 was obtained with a Baird Infra red Spectrophotometer Model B. Reference solvents used were of an analytical reagent grade from Mallinckrodt Chemical Works, Number 1 carbon tetrachloride (CCl_4) in an 0.135 mm cell, and Number 2 carbon disulfide (CS_2) in an 0.135 mm cell. In the range of 8.5-9.00 μ the capillary film was run in a 0.072 mm cell.

Comparison of the absorption frequencies of aluminum isopropoxide spectrum with the absorption frequencies of zirconium isopropoxide shown in table 3 indicates these compounds are similar to some extent.

TABLE 3
INFRARED ABSORPTION FREQUENCIES
ALUMINUM ISOPROPOXIDE ZIRCONIUM ISOPROPOXIDE

3.41 μ	3.40 μ
—	3.45
3.52	3.54
3.81	3.82
6.83	6.85
7.27	7.32
7.35	7.38
—	7.50
8.55	8.58
8.90	8.80
9.65	—
—	9.83
—	9.95
—	10.25
10.55	10.61
11.65	—
—	11.89
12.00	—
—	12.23

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Pyrolysis of Zirconium Isopropoxide

Equipment - The vapor deposition chamber consisted of all Vycor glass with ground joints. The specimen was suspended in the chamber with chromel-alumel thermocouples and the temperature was measured with a Leeds and Northrup potentiometer.

The chamber was brought to a constant temperature by circulating oil at 145°C. The specimen was heated with an induction furnace to 400°C. The inlet end of the chamber was connected to the purified zirconium isopropoxide reservoir and heated to the boiling temperature of the compound ca. 160°C. The exit end was connected to a series of cold traps and a vacuum pump. A McLeod gage was used to measure pressures of 0.1 mm Hg throughout the system. Figure 4 shows the flow diagram of the apparatus used for the vapor deposition experiment.

The specimens used for coating were discs or cylinders of ATJ, AWG graphite grades of National Carbon Company and AX graphite grade of Great Lakes Carbon Co. 3/4 inch in diameter and 1/4 inch to 2 inches thick.

Experimental Results

Exploratory Experiments - The first experiment, carried out mainly to test the equipment and feasibility of the transition metal alkoxide for coating purposes, gave encouraging results. The temperature of the graphite was 400°C and the duration of the decomposition was one hour and thirty minutes, with no attempt to control any of the parameters. The vapor pressure was 0.15 to 0.1 mm Hg. After vapor deposition was completed the specimens were cooled to room temperature under reduced pressure and removed from the chamber. Figures 5, 6, and 7 are photomicrographs of the vapor deposition made as an exploratory experiment. The coating usually was not uniform, ranging from 2500 Å to 1 mil thick. In one instance, Figures 8, 9, and 10, the coating was exceptionally uniform and thicknesses greater than 1.5 mils were obtained. The surface appearance was hard and tightly bonded to the substrate graphite.

It was very difficult to scrape the coated surface of the specimen. The X-ray pattern of the coated graphite is shown in figure 2.

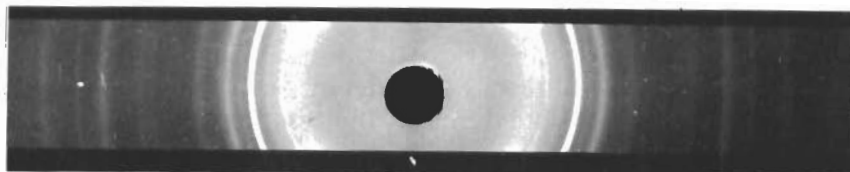


Figure 2. X-ray Pattern of Coated Graphite

TABLE 4

DATA FROM X-RAY FILM OF GRAYISH POWDER SCRAPED FROM GRAPHITE

LINE NO.	$R_1 - C$	$C - R_2$	$\frac{(R_1 - C)(C - R_2)}{2}$	I / I'	(d)	IDEN
1	23.85	23.95	23.90	Ft.(20)	3.72	ZrO ₂
2	26.45	26.45	26.45	V.S(100)	3.36	C
3	28.15	28.15	28.15	40(Diff.)	3.16	ZrO ₂
4	30.25	30.35	30.30	90(Diff.)	2.94	ZrO ₂
5	35.10	35.20	35.15	75(Diff.)	2.55	ZrO ₂
6	42.40	42.60	42.50	30	2.12	C
7	44.35	44.70	44.57	70(Diff.)	2.03	ZrO ₂
8	50.35	50.55	50.45	90(Diff.)	1.77	ZrO ₂
9	54.35	54.55	54.45	70	1.68	C
10	59.80	60.20	60.00	(DBL) 75(Diff.)	1.54	ZrO ₂ -C
11	62.70	62.85	62.77	Ft.(10)	1.47	ZrO ₂
12	74.35	74.65	74.50	V.Ft.(S)	1.27	ZrO ₂
13	77.40	77.55	77.47	80	1.23	C
14	83.50	83.60	83.55	45(Diff.)	1.15	ZrO ₂

DISCUSSION AND RESULTS

Although metal alkoxides of reactive transition metals have been known for many years, it is only during the past ten years that D.C. Bradley and co-workers made systematic physical properties and structural studies of transition metals containing metal-oxygen and metal-nitrogen bonds.

Bradley's work of the quantitative mechanism of the thermal decomposition of metal alkoxides answered the question regarding strength of metal-oxygen bonds in these compounds and investigated the possibility of separating and purifying metals by fractional distillation of the alkoxides.

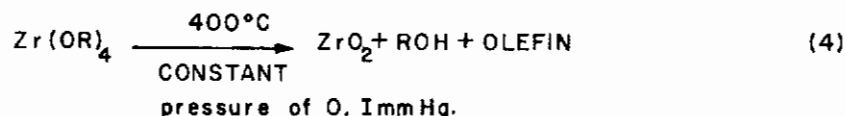
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An intensive review of the literature pointed out interesting features of these compounds (in this case zirconium) as applicable coating material. The compound volatilizes below the decomposition temperature.

Its vapor pressure and decomposition temperature are in practical temperature ranges. However, the development of improved methods and techniques for the preparation of metal alkoxides to provide sufficient quantities of the compound for subsequent pyrolysis studies was necessary.

As an exploratory experiment a very crude and quick vapor pressure measurement of Zirconium isopropoxide was made by the static method in pressure and temperature ranges 0.02-33 mm Hg and 25° - 200°C, respectively. The data will not be presented here; however, we plan to make more detailed studies of the vapor pressure measurements.

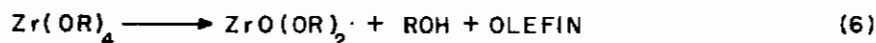
The pyrolysis of the metal alkoxide has yielded the best adhesion to substrate graphite. The deposition of zirconium from this compound is a straightforward decomposition, at temperature of approximately 400°C.



Zirconium isopropoxide is a white amorphous powder with a bulk density of 1.70 grams/ml at 25°C. It boils at 160°C and 0.1 mm of Hg, pyrolyzes and decomposes at 250°C and .1 mm Hg. This amorphous powder absorbs moisture readily and decomposes.

The decomposition rate at constant pressure follows the equation $(\text{Zr alkoxide}) \longrightarrow \text{ZrO}_2 + 2\text{ROH} + 2\text{OLEFIN}$ (5) The addition of ROH or hydrolysis products of the metal alkoxides at 250°C accelerated the reaction rates.

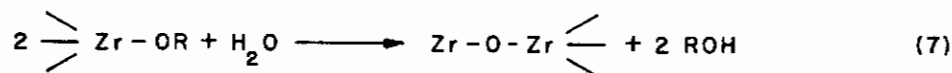
It has been noted by the authors and suggested by Bradley and Faktor that in atmospheric pressure the rate controlling stage might be the dehydration of alcohol. A molecule of H₂O produced from one molecule of alcohol would then regenerate two molecules of alcohol by hydrolysis of the zirconium alkoxide, and hence a chain reaction would be set up. The reaction could be initiated by the thermal decomposition of the zirconium alkoxide.



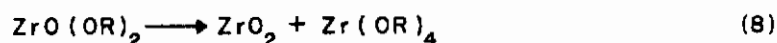
Therefore, one may assume the following to explain the mechanism of the reaction rate:

The rate controlling process is the dehydration of the alcohol.

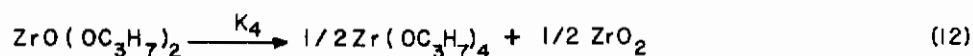
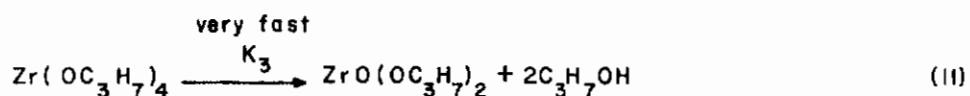
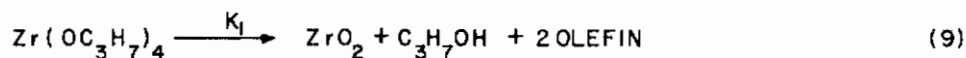
Water produced in, immediately hydrolyses Zr-O-R groups to produce Zr-O-Zr and ROH, e.g.



The intermediate products of hydrolysis (zirconium oxide alkoxides) undergo rapid disproportionation, e.g.



In this case R being isopropyl, the following reaction rate equations are applicable:



from equation (9) one may conclude that:

$$\frac{d(\text{H}_2\text{O})}{dt} = K_2 [\text{ROH}] - K_v \text{H}_2\text{O} \quad (13)$$

and from (11)

$$\frac{d(\text{ROH})}{dt} = 2K [\text{Zr}(\text{OR})_4] - K_v [\text{ROH}] + K_3 [\text{Zr}(\text{OR})_4] [\text{H}_2\text{O}] - K_2 [\text{ROH}] \quad (14)$$

in absence of $\text{ZrO}(\text{OR})_2$

$$\frac{d(\text{ZrO}_2)}{dt} = K_1 [\text{Zr}(\text{OR})_4], \text{ when } \text{ZrO}(\text{OR})_2 \text{ is present } \frac{d(\text{ZrO}_2)}{dt} = K_d [\text{Zr}(\text{OR})_4] \quad (15)$$

where $K_d \ll K_1$

It is suggested that for vapor deposition of ZrO_2 from zirconium isopropoxide on a suitable substrate, the rate controlling step is dehydration of alcohol. Maximum decomposition occurs when $K_v \text{ROH} \geq 2K_1 [\text{Zr}(\text{OR})_4]$. This can be accomplished by reducing pressure, raising temperature, and increasing surface area. Perhaps it is simpler to show the mechanism of the reaction rate by vapor pressure studies as indicated below:

Zirconium isopropoxide when undergoing decomposition as $t_0 \rightarrow t_1$

$$\frac{dp [\text{ROH}]}{dt_1} = \frac{dp [\text{ROH}]}{dt_0} (k_t) \quad (16)$$

where k_t is constant rate.

$$dp_{ZrPO} = \frac{dp [Zr(OR)_4]}{dt_i} = \frac{dp [Zr(OR)_4]}{dt_o} - 1/2 \frac{dp [(ROH)]}{dt_i} + 1/2 \frac{dp [(ROH)]}{dt_o} \quad (17)$$

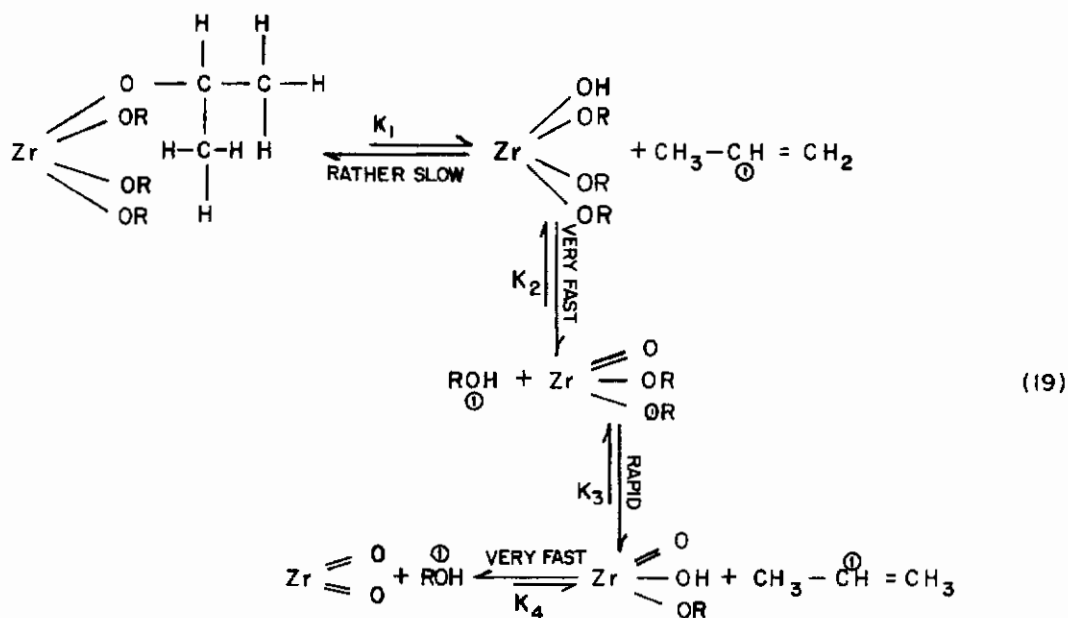
where P is total pressure, P_i is the initial pressure, and P_f is the final pressure

$$P = \frac{dp [(R)]}{dt_i} = \frac{dp [(ROH)]}{dt_i} - \frac{dp [(ROH)]}{dt_o}$$

$$P_i = \frac{dp [Zr(OR)_4]}{dt_o} + 1/2 \frac{dp [(ROH)]}{dt_o} [3K(k_f) - 1] \quad (18)$$

$$P_i = P_f - 2 \frac{dp [Zr(OR)_4]}{dt_o} [-K(t_o - t_i)]$$

Although we have previously shown that the mechanism of the reaction rates is solely dependent on the dehydration of alcohol, we suggest that it is not unreasonable to predict that the following mechanisms will also be applicable for such a system.



By looking at the mechanism in equation (19), one may observe that the reaction is of first order and its rate proportional to the concentration of the starting materials (isopropoxide). If we assume that the rate-controlling step is the decomposition of the alkoxide adduct and that all the other steps are relatively fast, we can derive the kinetic equation:

$$v = kK_1 [Zr(OR)_4] \quad (20)$$

SUMMARY

A refractory metal alkoxide has been synthesized in sufficient quantities to use as a coating material.

The vapor pressure, decomposition temperature, melting temperature, and stability of this organo-metallic compound were determined.

X-ray and infrared analysis of the compound were performed. The X-ray analysis of the compound deposited on the graphite specimen showed the ZrO_2 to be tetragonal at 350°C and tetragonal and monoclinic at 400°C.

A glass chamber for the coating application was designed to carry out the vaporization and the coating simultaneously.

The compound was pyrolyzed on ATJ and AWG grades of National Carbon Company graphite and high density AX grade graphite of Great Lakes Carbon Company.

Thin film coatings were obtained which adhered tightly to the graphite specimen. In some instances, the coating was approximately 2500 Å to 1.5 mils thick. The thin coating was a variety of colors, ranging from a bluish-grey to grey depending on the thickness of the coating. Photo-micrographs of the specimen are shown.

Investigations will be continued to determine the thermal shock and oxidation resistance of this coating. Further efforts will be directed to perfecting an oxidation resistant coating which will sustain a higher temperature than the best coating of today.

Present and future works - Present and planned studies with alkoxides of the above described type may result in graphite coating systems superior to the best present day coating silicon carbide (SiC), which is oxidation resistant to approximately 1500°C (2732°F) and slightly higher for only short periods of time.

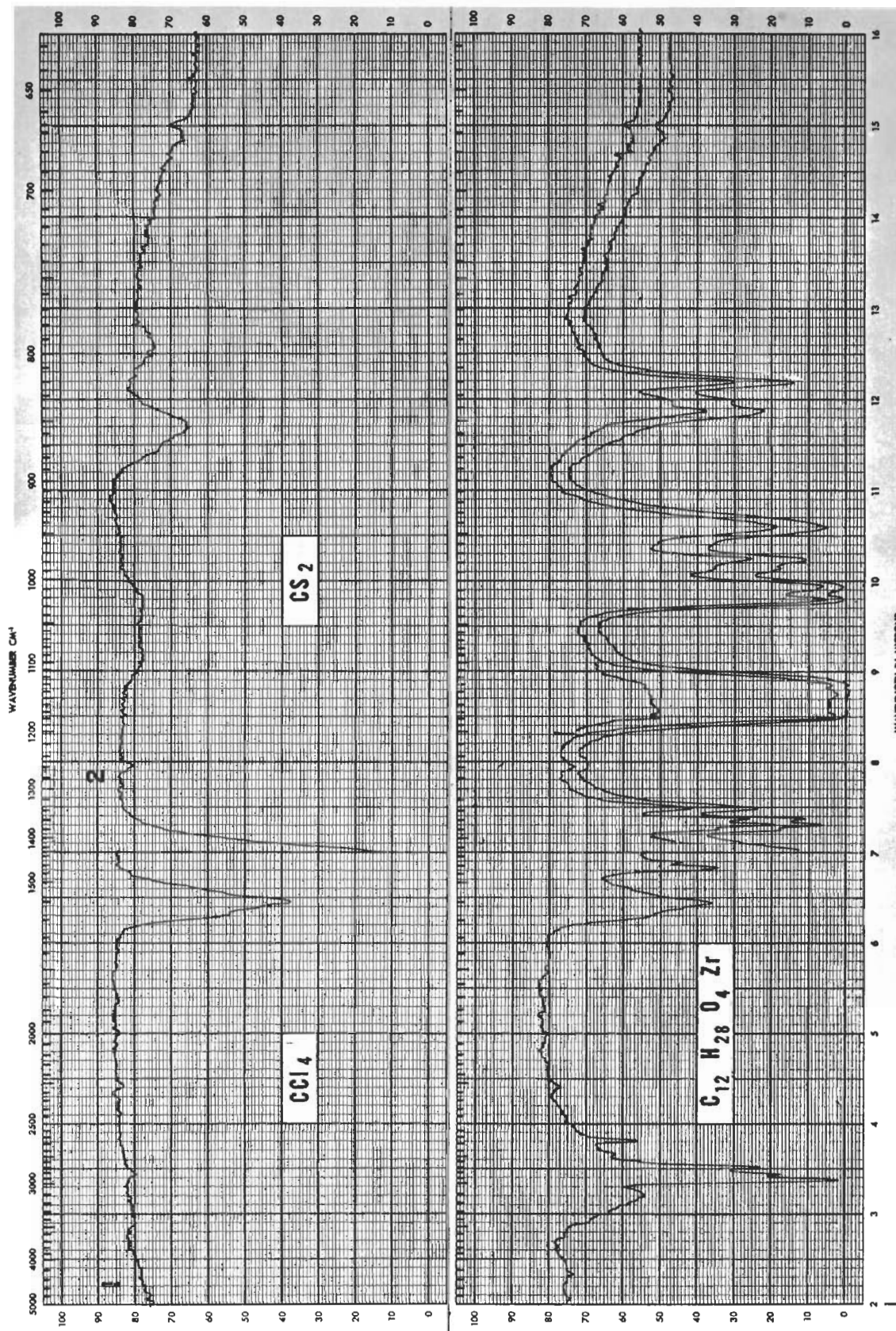


Figure 3. Infrared Spectrum of 100 mg per ml Zirconium Isopropoxide in Reference Solvents #1 CCl_4 and #2 CS_2 in 0.135 mm Cell

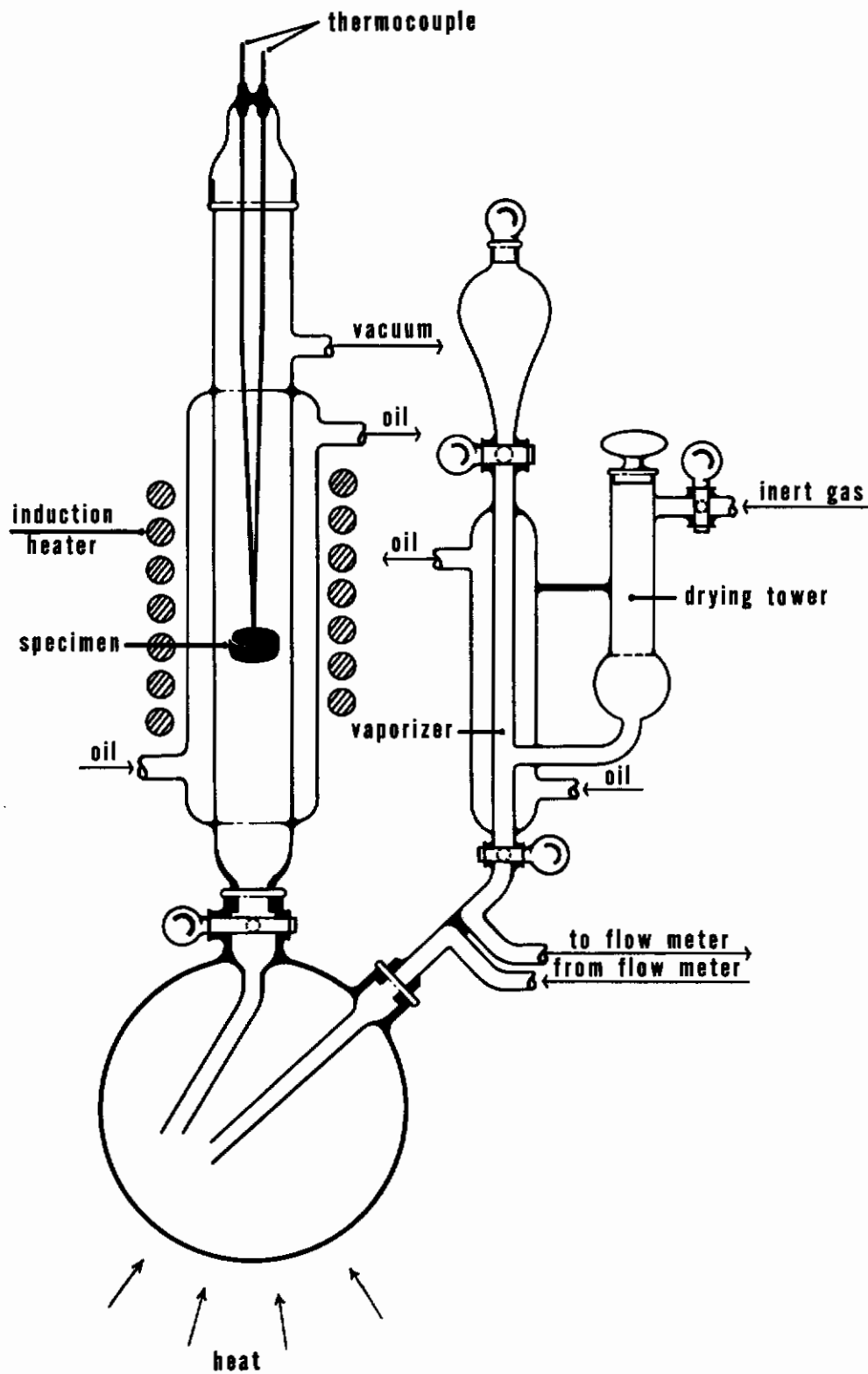


Figure 4. Flow Diagram of the Vapor Deposition Apparatus

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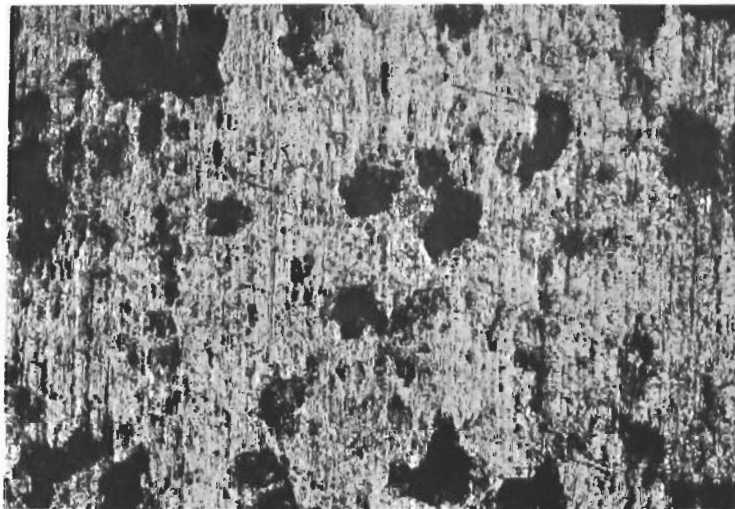
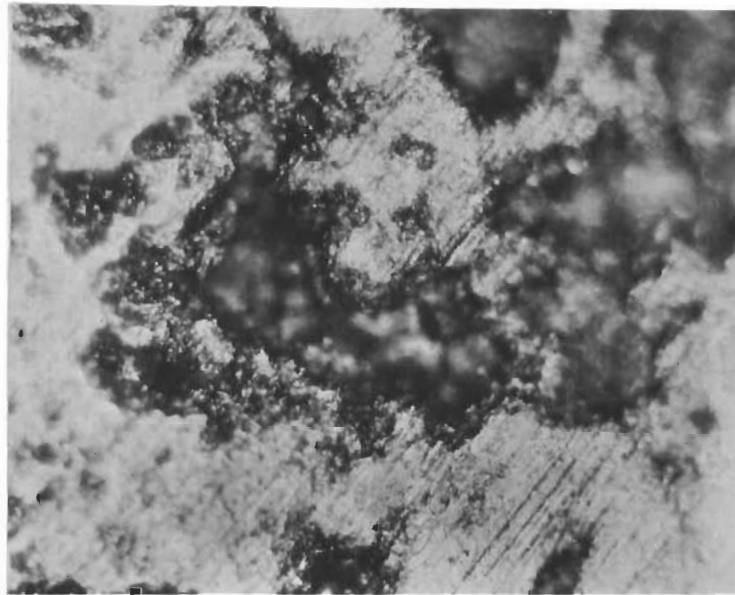


Figure 5. Unknown Grade Graphite, Coated and Uncoated

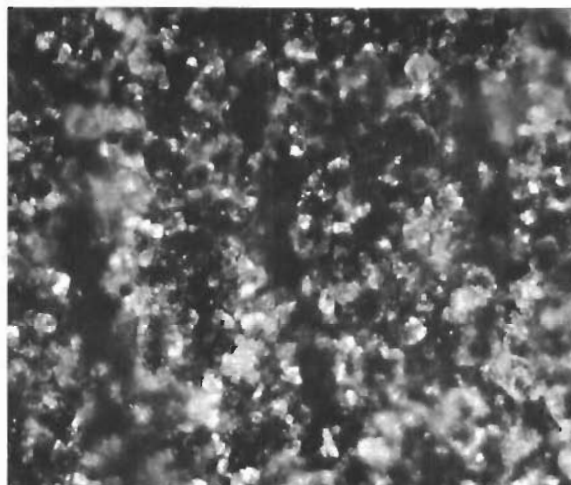


Figure 6. AX Grade Great Lakes Graphite, Coated and Uncoated

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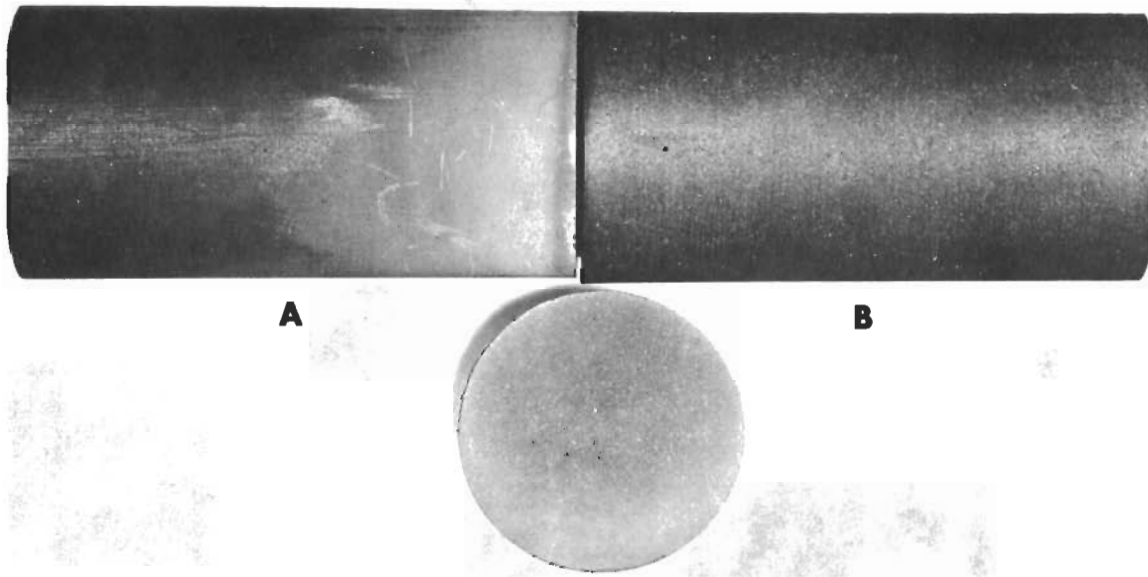


Figure 7. AX Grade Great Lakes Graphite, Coated and Uncoated

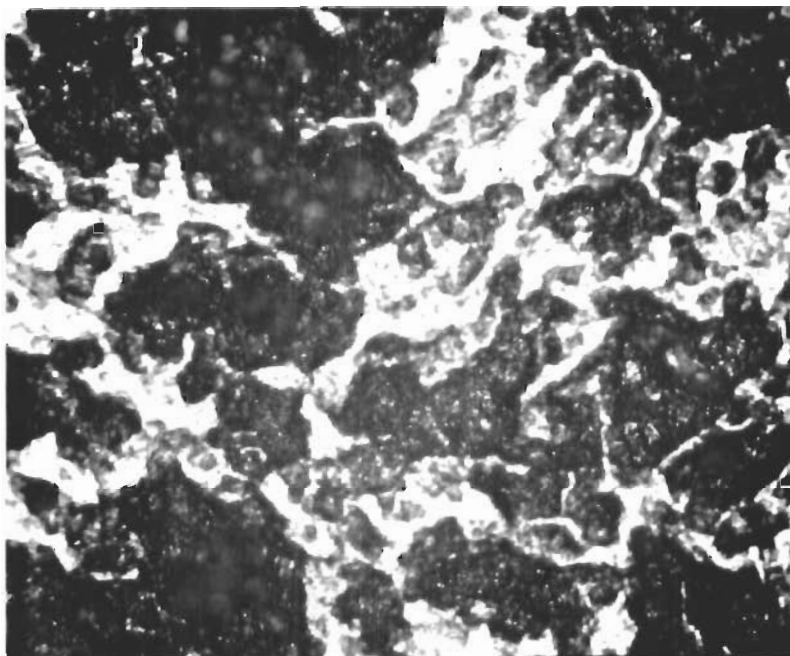


Figure 8. AWG Grade of National Carbon Co. Graphite, Coated and Uncoated

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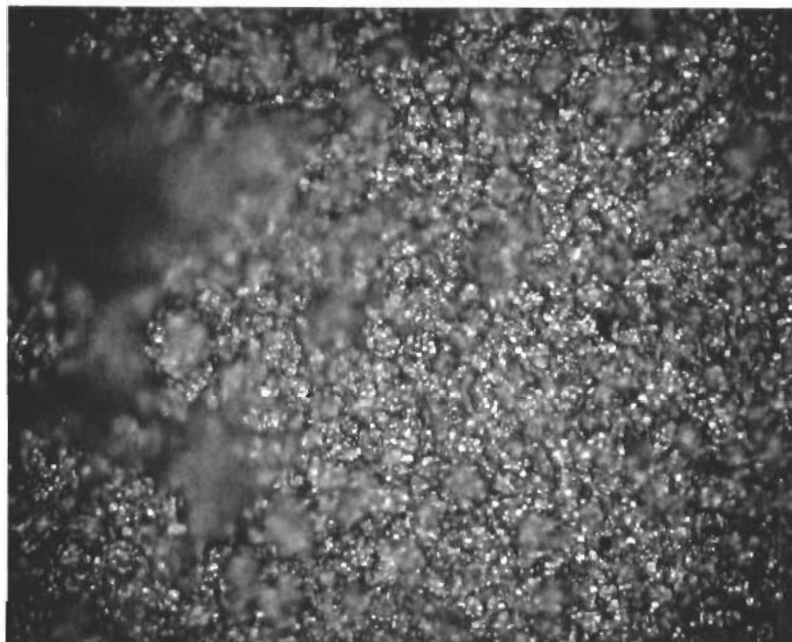
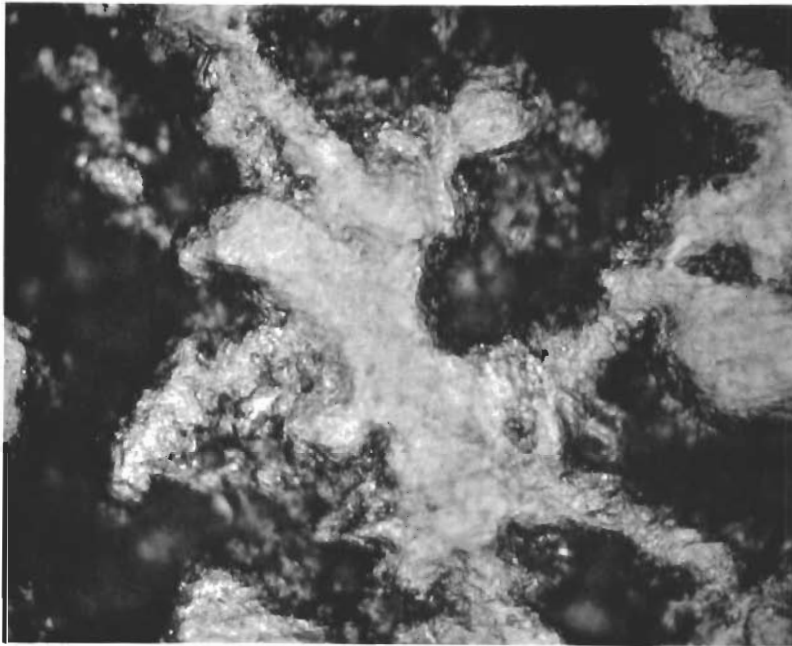


Figure 9. AWG Grade of National Carbon Co. Graphite, Coated and Uncoated

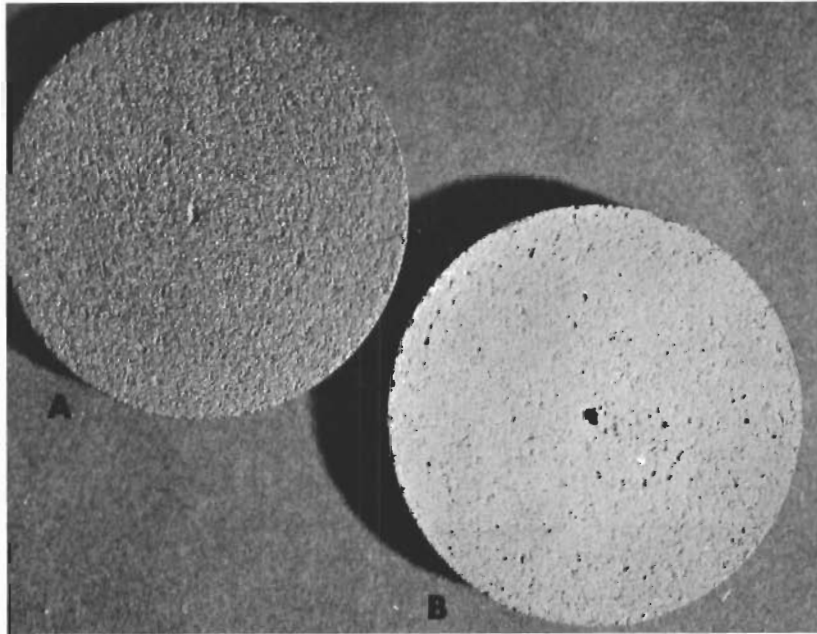


Figure 10. AWG Grade of National Carbon Co. Graphite, Coated and Uncoated

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