



FINAL REPORT

ON

A STUDY OF SELECTED METALLIC BORIDES, NITRIDES, & PHOSPHIDES

TO

OFFICE OF NAVAL RESEARCH

Final Report
To Office of Naval Research
Contract N8onr-80200
Project NR 032-274



UNIVERSITY OF LOUISVILLE INSTITUTE OF INDUSTRIAL RESEARCH
LOUISVILLE 8, KENTUCKY

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R. C. Ernst, Director

L. S. Churchill, Assistant Director

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BY

R. W. F. Morel
G. C. Williams
F. E. Ryerson

TABLE OF CONTENTS

List of Figures	iv
List of Tables.	iv - v
Summary	vi
Introduction.	1
Special Equipment Used.	2
Procedure	
Preparation of Compounds	3
Purification of Compounds Produced	16
Analytical Methods	16
Discussion of Results and Conclusions	18
Recommendations for Further Work.	21
Literature Cited.	24
Appendix.	27

LIST OF FIGURES

Figure		Page
1	Section View of Tube Furnace	53
2	Section View of Graphite-Resistance furnace	54

LIST OF TABLES

Table		Page
I	Physical Constants of the Elements Used	28
II	Symbols Used	29
III	Molybdenum Nitride Preparation and Comparison X-Ray Diffraction Patterns	31
IV	Vanadium Nitride Preparation and Comparison X-Ray Diffraction Patterns	35
V	Zirconium Nitride Preparation and Comparison X-Ray Diffraction Patterns	38
VI	Tantalum Nitride Preparation and Comparison X-Ray Diffraction Patterns	40
VII	Palladium Nitride Preparation and Comparison X-Ray Diffraction Patterns	41
VIII	Molybdenum Boride Preparation and Comparison X-Ray Diffraction Patterns	43
IX	Tantalum Boride Preparation and Comparison X-Ray Diffraction Patterns	46

Table		Page
X	Thorium Boride Preparation and Comparison X-Ray Diffraction Patterns	48
XI	Vanadium Boride Preparation and Compari- son X-Ray Diffraction Patterns	49
XII	Zirconium Boride Preparation and Compari- son X-Ray Diffraction Patterns	50

SUMMARY

The original project plans, based on a thorough literature search, were to prepare the borides, nitrides, and phosphides of columbium, hafnium, indium, molybdenum, palladium, rhenium, rhodium, scandium, tantalum, thorium, vanadium, yttrium, and zirconium. A procedure was proposed for the preparation of these compounds, and amended procedures were to be added as the project progressed.

The compounds for which preparations were actually attempted are the nitrides of molybdenum, vanadium, zirconium, tantalum, and palladium; the borides of molybdenum, tantalum boride, thorium, vanadium, and zirconium.

The following paragraphs list the reactions that were investigated in the preparation of each compound. In each instance, only those reactions were tried for which there was a good probability of success, on the basis of theoretical considerations. The conditions under which the reactions were investigated were the optimum conditions that were possible with the available equipment.

The preparation of molybdenum nitride was attempted by reacting (1) molybdic anhydride with ammonia gas, (2) molybdic anhydride with ammonia gas and carbon, (3) molybdenum chloride and ammonia gas, and (4) molybdenum metal with ammonia gas. The last of these methods gave a favorable result. Molybdenum was heated in the tube furnace in a stream of ammonia at 900°C. The final analysis gave 88.5% molybdenum and 9.77% nitrogen. This composition closely corresponds to Mo_5N_4 . X-ray diffraction patterns verified that this compound had been prepared.

INTRODUCTION

The probable stability of the phosphides, borides, and nitrides of some of the less common metals such as zirconium, hafnium, etc., warranted an examination of their compounds. Only a few of the compounds have been prepared. In many instances it is questionable that the prepared materials are true compounds rather than a mixture of compounds. Physical and chemical data alike are not available, but analogies based upon the periodic similarity of related materials have been used to provide some plausible information on these materials. Heat resistance, chemical stability, physical toughness and hardness should typify the nature of these materials. The evaluation of physical properties was not the concern of this phase of the work, however. The preparation of the materials by any methods and by several methods provided the scheme of the project. Purification of the materials produced was deemed necessary for quantitative examination of the materials, and desirable from a processing standpoint. The question of a commercial method for any process was beyond the scope of the work, however.

The bulk of the work carried out involved the formation of nitrides, although not all nitrides were examined. Introductory work on borides was started. Phosphides were not attacked mainly because of their insidious chemical nature. It was believed more appropriate to develop methods for nitrides and borides first so that safe procedures could be outlined for phosphides.

SPECIAL EQUIPMENT USED

Controlled atmospheres and high temperatures were required for most of the reactions. Several types of high temperature laboratory furnaces were constructed. The two furnaces that have met the requirements are a wire-wound tube furnace and a graphite-resistance furnace. The former was constructed by winding Chromel "A" wire on a 3-inch i.d. alumina tube ten inches long. The tube was insulated with "Silocel" and the whole was placed in a piece of standard 10-inch pipe and fixed into position by casting collar plates of electroplast in the ends. Steel plates with center gas inlet and exit fixtures were bolted, by means of flanges, to each end. To introduce a sample, one of these plates was removed. Thermocouple leads were introduced and cemented into position in the permanent end-plate. The temperature was controlled by means of a controlling pyrometer with a range of 1600°F. The maximum temperature obtained in this tube furnace was 1810°F. It was operated at 110 volts A.C.

The graphite-resistance furnace was constructed with a 2-inch i.d. graphite helix heating element. This furnace was used with a 30 kw transformer with voltage taps of 20, 40, 60, and 80 volts. Air-convection cooling of the contacts was used, and the furnace was used successfully at temperatures above 2000°C.

PROCEDURE

PREPARATION OF COMPOUNDS

In the following experiments the reactants usually ranged between 0.2 and 5 grams, except where it is stated otherwise. The reactants were proportioned so that there would be the least contamination of the product or so the contaminating reactants could be removed most easily.

The following reactions were investigated.

Molybdenum Nitride

Reduction of molybdic anhydride by ammonia gas

Molybdic anhydride (MoO_3) was heated with ammonia gas at 800°C in the tube furnace for 1 hour. The product was a black substance which analyzed 76.6% molybdenum. Since MoO_2 has 75% Mo (1) and the X-ray pattern showed the presence of this substance, no nitride was presumed formed. Molybdenum oxide was heated in a zirconia crucible at 2000°C in a stream of ammonia gas in the graphite-resistance furnace. The product was red and contained 2% nitrogen. (2) The X-ray powder patterns indicated molybdenum oxide. Additional work on the reaction between molybdic anhydride and ammonia was performed in the presence of carbon. However, ineffective separation of the reaction products showed that it was inadvisable to continue. (3)

Reduction of molybdenum chloride by ammonia gas

Molybdenum was heated in a stream of chlorine and the resulting molybdenum chloride (assumed to be MoCl_2) was heated in a stream of ammonia until no white fumes were evident, and then for an additional half-hour. The product analyzed 86.7% molybdenum and 10.3% nitrogen,

corresponding to a compound of the composition Mo_5N_4 . The X-ray powder pattern did not correspond to Mo , MoO_3 , MoO_2 , or Mo_2O_3 . (4) Attempts to prepare larger quantities of MoCl_2 in a pure form were unsuccessful; therefore, the higher chlorides were heated in a stream of ammonia. The reaction products analyzed 89 to 91% molybdenum and 6 to 10% nitrogen. (2) Close study of the X-ray powder patterns led to the conclusion that Mo_5N_4 was the only molybdenum nitride formed, and on this assumption purification procedures were investigated. After 130 hours of water washing and digestion the sample analyzed 88% molybdenum and 8.5% nitrogen, which further verified the formula to be Mo_5N_4 . This procedure, however, did not seem practical for large scale production and, therefore, other investigations were continued. (5)

Reaction between molybdenum metal and ammonia gas

Molybdenum was heated in the tube furnace in a stream of ammonia gas at 900°C for 12 hours. (3) The black product analyzed 91% molybdenum, and the X-ray pattern checked that of the sample prepared by the reaction of ammonia with molybdenum chloride. The sample was ground and reacted with ammonia at 900°C for 6 more hours and then a complete analysis was made with the following results: Mo 88.5%, N 9.77%. This composition closely corresponds to Mo_5N_4 . Additional similar reactions gave similar results. Samples of molybdenum weighing 25, 35, (3) 50, and 75g (6) were heated, consecutively, in a stream of ammonia gas from 30 to 50 hours at 800°C in the tube furnace. Molybdenum analysis of the 35g

sample after 30 hours was 89.75%. The nitrogen analysis of this sample by the Kjeldahl method was 7.6%. (3) X-ray diffraction patterns of the 75-gram sample were made at regular intervals. After eleven hours the characteristic lines of molybdenum had disappeared. After thirty hours most of the lines believed to be characteristic of Mo_5N_4 appeared on the X-ray pattern. (6)

Vanadium Nitride

Reduction of ammonium vanadate by ammonia gas

In three separate runs, ammonium vanadate (NH_4VO_3) was heated in a stream of ammonia gas for six hours, at 760° , (6), 1400° , and 1600°C (7), respectively. The products in each case were black crystalline powders. The run at 1400°C gave the best results, a product that analyzed 3.65% nitrogen and 66.86% Va., but separation of the small percentage nitride was considered impractical and these reactions were discontinued.

Reduction of vanadium pentoxide by ammonia gas (4)

In a number of different runs, ammonia gas was passed over vanadium pentoxide heated to various temperatures. At first a steel pipe and a Meker burner were used, but later runs were made in the tube furnace and in the graphite resistance furnace. Runs were made at 800° , 1000° , 1400° , and 1600°C , and the heating period was usually one hour. The products of all the runs were gray-black or black. The products analyzed low in nitrogen with the exception of one run (3) which showed 7.78% nitrogen and 62.1% vanadium. X-ray analyses indicated the presence of vanadium

oxides, but no large amounts of nitride.

Direct combination of vanadium metal with nitrogen gas

Vanadium powder was heated in a stream of nitrogen gas for eight hours at 1600°F. (7) The product was black with particles of unreacted metal dispersed throughout. The vanadium analysis was 71.0% and the nitrogen of two separate runs was found to be 1.87% and 3.55%.

Reaction involving ammonium chloride

Several mixtures of ammonium chloride and vanadium pentoxide were placed in covered beakers and heated over a Bunsen burner. The products consisted of blue and black crystals. Because of the large number of by-product impurities, this method of preparation was discontinued. (7)

Reaction between vanadium metal and ammonia gas

Vanadium powder heated in a stream of ammonia gas for four hours at 1600°F yielded a product of black fused material, (7) which was easily rubbed to a powder. This product was then heated for an additional four hours at 1600°F in a stream of ammonia gas. The final product was insoluble in hot hydrochloric acid and contained 66.9% vanadium and 10.8% nitrogen. This indicates an analysis of 50% VN.

Reaction of vanadyl chloride by ammonia gas (8)

In several separate runs vanadyl chloride ($V_2O_2Cl_4$) was heated in a stream of ammonia gas with a Meker burner. The reaction time used was ten minutes. The product was a mixture of black and blue particles. After the product was purified by boiling in 1:1 hydrochloric acid,

analysis indicated 8.14% nitrogen.

Two reactions were conducted in the tube furnace. Vanadyl chloride decomposes on heating, and reacts with ammonia at ordinary temperatures. Therefore, it was necessary to preheat the furnace to the desired temperature, and to introduce the chloride and ammonia simultaneously. Maintaining an atmosphere of ammonia, the furnace was held at the desired temperature for an hour and allowed to cool. The temperatures employed were 800°F. and 1000°F. The products of the reactions, which consisted of blue and black particles, were boiled in (1:1) hydrochloric acid in order to remove oxide impurities.

It was found that the product of the reaction conducted at 800°F. was entirely soluble in hydrochloric acid indicating that no nitride had been formed. The black residue obtained from the acid treatment of the product of the reaction conducted at 1000°F. contained 0.7 percent nitrogen. Apparently, the optimum conditions of operation have not been obtained. The investigation of this reaction is being continued.

Reactions involving calcium nitride

A series of reactions was run to determine the optimum temperature and ratio of reactants for the double-decomposition of calcium nitride and vanadium pentoxide. Neutral atmospheres were employed for the reactions. The products were treated with 1:1 hydrochloric acid solutions to remove excess calcium oxide, leaving a black product. It was (7) found that 1400°F and a ratio of 5:1 parts by weight of calcium nitride

to vanadium pentoxide gave optimum results. (8) (9) A 25-gram sample of vanadium nitride was prepared by the procedure which had proved most successful in the preliminary investigations. (10) A stream of nitrogen was passed through the furnace and the temperature was maintained at 1400°F for 1 hour. The product was treated with water, then with (1:1) hydrochloric acid, and finally was left in contact with cold concentrated sulfuric acid for several days. The final water washed sample analyzed 75.5% vanadium and 19.0% nitrogen. This nitrogen content indicates 88% VN.

Zirconium Nitride

Double decomposition reaction of calcium nitride and zirconium dioxide

In the preparation of zirconium nitride by the double decomposition of calcium nitride and zirconium dioxide, several reaction temperatures were used, namely 800°, 1000°, and 1600°F, with varying weight ratios of reactants. The materials were heated in neutral atmospheres. X-ray analysis indicated the presence of calcium oxide, zirconium dioxide, and zirconium metal. Chemical analysis showed no nitrogen present in the product. (7)

Double decomposition reaction of calcium nitride and zirconium tetrachloride

In the double decomposition reaction of calcium nitride and zirconium tetrachloride, a mixture of zirconium tetrachloride and calcium nitride was heated slowly with a Bunsen flame. A violent exothermic reaction resulted. The product was a mixture of black and white particles.

The white particles were leached out of the product, leaving a black powder which analyzed 3.1% nitrogen and 65% zirconium. (7)

Reduction of zirconium tetrachloride by ammonia gas

A small quantity of zirconium tetrachloride was heated in a deep crucible while a stream of ammonia gas was directed into the crucible. The crucible was maintained at red heat for one-half hour. The product was water washed and the residue analyzed 4.64% nitrogen. The reaction was repeated and the product was treated with acids, but the percentage of nitrogen continued to be about 4%. (8)

Direct combination of zirconium metal with nitrogen and ammonia gas (9)

To obtain rapid high-temperature reactions, a direct electrical heating method was devised. The reaction vessel was a 1000-ml three-necked flask. A metal strip was clamped between electrical leads brought in through two of the three necks. Gas was introduced and exhausted through the third neck. The voltage was controlled by a variable transformer. Nitrogen was passed through the flask for about thirty minutes to purge the vessel of air. Then ammonia gas was introduced instead of nitrogen and the filament was heated by advancing the voltage across the leads from zero to two volts. This caused the strip to be heated to a red glow. The strip maintained a glow for twenty to thirty minutes before breaking because of embrittlement. During this time some increase in voltage was necessary to maintain the glow. Metal strips reacted in this manner were yellow surfaced. Cold concentrated sulfuric acid was used to remove un-

reacted zirconium metal, and the percentage of nitrogen was increased from 6.87 to 8.4 percent. X-ray analysis verified the presence of ZrN . A large sample of the zirconium nitride was prepared and purified.

Tantalum Nitride

Double decomposition reaction of tantalum pentoxide and calcium nitride

Mixtures of tantalum pentoxide and calcium nitride were heated for 15 minutes in an alundum crucible with a Meker burner. The products of gray and white powder mixtures were purified by boiling with (1:1) hydrochloric acid. A gray powder remained which analyzed 0.73 to 1.73% nitrogen. (10) Mixtures of tantalum pentoxide and calcium nitride were heated in the tube furnace at 500° to $1600^{\circ}F$ in a stream of nitrogen. The furnace products were again purified by boiling in (1:1) hydrochloric acid. The purified products consisted of white powders which analyzed from 0.06 to 0.32%, or negligible, nitrogen.

Reduction of tantalum pentoxide by carbon and ammonia gas

Tantalum pentoxide was heated in the tube furnace at $1600^{\circ}F$ for four hours in a stream of ammonia gas. The product was a yellow powder which analyzed 5.34% nitrogen. (11)

Double decomposition of tantalum pentachloride in a stream of ammonia gas

Tantalum pentachloride was heated in a stream of ammonia gas for four hours at $300^{\circ}F$. The product was a pale yellow solid which analyzed 9.60% nitrogen. A second sample heated at $350^{\circ}F$, in the same manner,

yielded a product containing 10.98% nitrogen. (12) The product was washed with water and dried at 100°C. Analysis now gave 2.15% nitrogen. Subsequent runs at these same temperatures (300° - 400°F) gave products having the same characteristics. The lowering of the nitrogen content by washing was attributed to the removal of soluble ammonium chloride, which was confirmed to be present by X-ray analysis. Little tantalum nitride was considered to be present.

Palladium Nitride

Reduction of palladium black by ammonia gas

A number of runs were made to prepare palladium nitride. Palladium black was heated in a stream of ammonia gas for four hours at 1600°F. The product contained a negligible quantity of nitrogen. (11)

Reduction of palladium black by carbon in a stream of nitrogen gas

Palladium black was mixed with carbon black and heated in a stream of nitrogen at 1600°F for three hours, with negligible nitrogen content in the product. (11)

Reduction of palladium chloride by ammonia gas

Palladium chloride was heated in a stream of ammonia gas for four hours at 500°F. The product was a dark gray powder containing 5.75% nitrogen. The washed sample analyzed 0.91% nitrogen. X-ray analysis showed the presence of ammonium chloride. No palladium nitride is suspected to be present. (12)

Double decomposition reaction of palladium chloride and
calcium nitride

A number of experiments were run with palladium chloride and calcium nitride, by heating the mixtures at 440 to 1500°F in the electric tube furnace in a stream of nitrogen or argon gas. Negligible nitrogen contents were obtained. (11) (13)

Molybdenum Boride

Fusion of elemental powders of molybdenum and boron

In several runs, molybdenum powder or molybdic oxide and boron were ground together and heated in a graphite-helix resistance furnace at several different temperatures, approximately 900° to 2000°C. The X-ray diffraction patterns for these preparations did not disclose any definite findings. (14) (15)

Tantalum Boride

Reduction of tantalum pentoxide by boron

A mixture of tantalum pentoxide and boron was heated in the graphite-helix resistance furnace for 12 minutes at 60 volts and 11-14 kilowatts. The product was a dark gray, almost black, powder which X-ray analysis showed to be predominantly tantalum carbide. (16)

Thorium Boride

Reduction of boric acid by carbon and subsequent reaction
with thorium chloride

Boric acid, activated charcoal, and thorium tetrachloride were ground together and heated in a fused silica combustion boat in the

wire-wound tube furnace in a stream of argon at 1550°F for 3-3/4 hours. The product was a gray-brown solid that easily could be rubbed to a powder. The X-ray diffraction pattern showed a predominance of ThO_2 . (13)

Reduction of thorium tetrachloride by elemental boron

A second mixture of thorium tetrachloride and boron was ground together and heated in the wire-wound tube furnace in a stream of argon at 1550°F for six hours. The product was a white-gray mixture which was deliquescent in air. (13)

Direct fusion of elemental powders of thorium and boron

A mixture of thorium and boron was ground together and heated in the graphite resistance furnace at 60 volts and 13.5 kilowatts for about 8 minutes. The final product was a dark gray, almost black, powder which was water washed and dried. The X-ray diffraction showed a predominance of ThO_2 . (17)

Vanadium Boride

Reduction of vanadium pentoxide and boric acid by carbon and the subsequent reaction between vanadium and boron

Vanadium pentoxide, boric acid, and activated charcoal were ground together thoroughly and heated in the wire-wound tube furnace in a stream of argon at 1505°F for 5-1/2 hours. (18) The product was a very hard, green-black, porous solid which fused into the crucible. The product, insoluble in water, was ground and an X-ray diffraction pattern was obtained. The product could not be identified.

Reduction of vanadium pentoxide by elemental boron

A mixture of vanadium pentoxide and boron was heated in the graphite-helix resistance furnace for 10 minutes at 40 volts and 6 to 7.5 kilowatts. The product was a fluffy black powder. The X-ray diffraction pattern of the water-washed product did not identify the compounds present. (13)

Direct fusion of the elemental powders of vanadium and boron

A mixture of vanadium and boron was ground together and heated in the graphite-helix resistance furnace at 60 volts and 14 kilowatts for 17 minutes. The product was a non-uniform gray powder with hard lumps of fused material present. The X-ray diffraction pattern of the products gave no identification. (13)

Zirconium Boride

Reduction of zirconium dioxide and boric acid by carbon and the subsequent reaction between zirconium and boron

A mixture of zirconium dioxide, boric acid, and activated charcoal was ground together and heated in a stream of argon in the wire-wound tube furnace at 1430°F for 4 hours. The product was a light-gray, very hard solid containing some black material, apparently carbon. The product was not identified. (13)

Fusion of the elemental powders of zirconium and boron

In a series of six reactions, elemental zirconium metal powder and elemental amorphous boron powder were heated in a graphite crucible in the graphite-helix resistance furnace. The temperature was increased for each successive reaction from about 1600° to about 2000°C. The first two runs yielded black products which could not be identified by X-ray diffraction, but the last four yielded dark gray products. The products of runs 3, 4, and 5 gave X-ray patterns which were closely similar to each other and quite distinct. These sharp patterns indicated the presence of a definite compound (or element) which was not identified. The X-ray diffraction pattern of run 6 did not identify the product. (13) (16)

PURIFICATION OF COMPOUNDS PRODUCED

If no products of reaction are removed during the process of reaction (e.g. , gases or water of hydration being driven off), the final product of the reaction should have the same chemical composition as the original mixture of reagents. A chemical or physical separation of the products was considered necessary prior to chemical analyses, and desirable before X-ray diffraction analyses. Most of the products were either completely soluble or insoluble in water or acid solutions, but some of the products allowed partial solution to give a qualitative separation.

The products of each preparation of the investigation were checked qualitatively for possible purification, or separation of the constituents. Solubilities were checked in water and in both concentrated and dilute solutions of the common acids, hydrochloric, sulfuric, and nitric. Several portions of some of the same samples were washed or leached with acids and X-ray diffraction patterns were made of the residues.

ANALYTICAL METHODS

The method of analysis of an unknown compound that will give the most satisfactory crystal composition is X-ray diffraction analysis. After the X-ray patterns have been established, further analyses and verifications can be made chemically, and possibly by other methods.

In the present investigations it was thought most important to establish the presence of any compound that had not been reported in the

literature, by comparison of X-ray diffraction data. If all the X-ray diffraction data are known for the reagents and possible products other than those desired, then X-ray diffraction data can be established for the new compounds. Subsequent purification and further X-ray analyses with intensity comparisons and ultimate chemical analyses should give conclusive information on the nature and composition of the synthesized product.

For X-ray analyses, the product samples were pulverized with an agate mortar and pestle. The thoroughly ground powder sample was then placed in a sample holder and packed to leave a very sharp, clean edge at the top, or apex, of the holder. The X-ray unit was operated at from 4 to 30 milliamperes and 45 kilovolts, and the samples were left in the unit from 3 to 12 hours, with the low amperage being used for the longer time and the high amperage being used for the shorter time (4 hours at 22 milliamperes gave good results). The X-ray film was processed according to the manufacturer's instructions. The film was read on a comparator, and the interplanar spacings were tabulated in angstrom units. The results obtained for the present investigations are given in the appendix.

DISCUSSION OF RESULTS AND CONCLUSIONS

The chemical analyses of the products from the reaction of molybdenic oxide and ammonia showed that the end product always was a lower oxide of molybdenum with some surface formation of a nitride. In none of the runs was the nitrogen in the product in excess of 2%. In the reaction of molybdenum chloride and ammonia a unique X-ray pattern was obtained and chemical analyses indicated the formation of Mo_5N_4 . When carbon was used with the above reagents, the products were the same. When molybdenum was heated in the tube furnace in a stream of ammonia gas at 900°C for 6 to 12 hours, the product was identical to that above. This was considered the best method investigated and was employed for the preparation of bulk samples of Mo_5N_4 .

In the preparation of vanadium nitrides, the double decomposition reaction of calcium nitride and vanadium pentoxide was found to be the most promising for VN preparation. The product, however, required extensive purification by washing with 1:1 hydrochloric acid and finally, with cold concentrated sulfuric acid. The reaction involving metallic vanadium and ammonia at 1600°F produced an appreciable quantity of vanadium nitride, but the hydride was formed also. The separation of the hydride and nitride was impractical. Appreciable vanadium nitride was formed when divandyl tetrachloride was heated in a stream of ammonia gas. The reaction was investigated to only a limited extent,

but the results indicated that this method might be used to produce considerable quantities of vanadium nitride.

The most promising method found for preparing a zirconium nitride was the use of the metal as a heating element in an ammonia gas-filled chamber. The reaction between zirconium metal and ammonia gave a product of about 6% nitrogen. The impurities were unreacted zirconium and zirconium dioxide. Treatment with cold concentrated sulfuric acid for three to four days removed most of the unreacted zirconium. X-ray diffraction analyses of the residue confirmed the presence of zirconium mononitride and zirconium dioxide and the absence of zirconium and zirconium hydride. The purity of the zirconium nitride sample, as calculated from the nitrogen analysis, was about 70%. If more elaborate precautions had been taken, a very pure product might have been obtained.

The work on tantalum nitride preparation and palladium nitride preparation was not advanced sufficiently to develop methods of preparation that might be employed for bulk samples.

In attempting to produce tantalum boride, it was found that tantalum carbide (TaC) had formed in the furnace reaction of Ta_2O_5 and boron in a graphite crucible. It would be necessary to use a crucible of some other refractory material.

When thorium and boron were heated together in the graphite-helix resistance furnace, a considerable quantity of oxide was formed. Thus, additional precautions against oxidizing atmospheres should have been

used. The definite but limited patterns for the products of elemental zirconium and boron heated together in a graphite crucible in the graphite-helix resistance furnace indicate the possible presence of zirconium carbide or zirconium boride. No comparison was found with the three types of zirconium oxides listed in the literature or with the elements of zirconium and boron.

No definite information was gained from the X-ray diffraction patterns of the vanadium boride products, but further investigation possibly would reveal the presence of one or more vanadium borides.

RECOMMENDATIONS FOR FURTHER WORK

A detailed review of the past work indicates that sufficient exploration has been completed to show which of the areas of nitride and boride chemistry require more thorough investigation. It is anticipated also that preliminary exploration can be begun on the phosphides, which have received little attention. The following paragraphs outline the Institute's recommendations for future work.

Nitrides

According to Mittasch (Ber. 59, 15, 1926), foreign materials increase the rate and extent of nitrogen fixation in the formation of nitrides of titanium, aluminum, berium, and silicon. An iron promoted by potassium oxide and alumina is suggested as an initial agent for nitrogen fixation.

A union of nitrogen and the metal is frequently assisted by small amounts of the metal oxide. The gas-solid reaction requires the absence of water vapor.

The formation of high purity nitrides from the elements is presented as a method for circumventing the separation of foreign matter from the products that is required when a nitride is produced from nitrogen and metal compounds. It is generally true that metallic nitrides form at temperatures of not less than 300°C. and not greater than 2000°C. In all cases, the use of pressure is meritorious.

For a successful attack on the problem it is consequently imperative that nitrogenation equipment for high pressure be used. A bomb

such as that used in hydrogenation at pressures as great as 500 atmospheres will be satisfactory.

Borides

Preliminary work with the borides has provided products that require isolation of the boride from by-products in the solid form. The contemplated work should involve formation of borides accompanied by gaseous or sublimable by-products. High temperatures are most certainly necessary. A specially built arc furnace will undoubtedly be required.

Metal-boron reactions provide an elementary method of attack. Water vapor and oxygen cannot be tolerated so that an inert atmosphere is required. Argon probably will be most satisfactory.

Boric acid may be reacted with the metal chloride in a fusion where hydrogen chloride gas is removed. Grinding of the product with carbon will provide a means of reducing the borate to a boride. The use of boric acid may be changed if the by-product water is harmful. In this latter case, boron oxide will be substituted for the acid.

A boron oxide-metal oxide glass may be made and then reduced with carbon to the metal boride.

Summary

In summary, the work that is proposed includes:

1. Formation of nitrides from the metals and gaseous nitrogen with the aid of surface catalysts such as iron promoted by

K₂O and Al₂O₃.

2. Formation of nitrides with the aid of the metal oxide as a carrier.
3. Formation of metallic borides from the elements.
4. Formation of borides from boric acid or oxide and the metal chloride with subsequent reduction by carbon.
5. Formation of borides using a formed glass made from the metal oxide and boron oxide followed by reduction with carbon.
6. Preliminary exploration of phosphide synthesis.

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A P P E N D I X

TABLE I - PHYSICAL CONSTANTS OF THE ELEMENTS USED

Element	Symbol	M.P., °C	B.P., °C	Mol.Wt.	Sp.Gr.	Solubility
Boron	B	2300	2550	10.82	2.32	s.HNO ₃
Molybdenum	Mo	2620	3700	95.95	10.2	s.c.H ₂ SO ₄ i.HCl
Thorium	Th	1845	3000	232.12	11.2	s.HCl, H ₂ SO ₄
Tantalum	Ta	2850	4100	180.88	16.6	s.HF, Fused alk., i.acids
Vanadium	V	1710	3000	50.95	5.96	s.HNO ₃ , H ₂ SO ₄
Zirconium	Zr	1860	2900	91.22	6.4	s.HF, aq.Reg.

TABLE II - SYMBOLS USED

S.-soluble in.	Ni-refers to heavy
c.-cold solution.	lines obtained
i.-insoluble in.	by the incorrect
Aq. Reg.-Aqua Regia.	usage of the nickel
Alk.-alkaline solution	filter.
d-as used in the heading of the X-ray diffraction tables refers to distance in angstrom units of interplanar molecular spacings.	
I-refers to the numerical intensity. The strongest 10 lines are usually numbered in their order of decreasing intensities.	

The method of preparation of each compound is designated by a numbered suffix which specifies the particular run. As an example: Mo_xN_y-2 in Table III refers to the second run for the preparation of molybdenum nitride.

For the X-ray diffraction data obtained from card file of X-ray diffraction data, the following symbols are used as given by the Institute of Physics (Gr. Br.) in listing interplanar spacings and relative intensities:

- b, bb - broad, fuzzy, or diffuse
- d - doublet
- n - not given by all sources
- n c - lines not accounted for by the proposed unit cell
- b - intensity uncertain owing to presence of beta lines, or to overlapping

TABLE II - (Continued)

A qualitative interpretation of numerical intensities is given below:

Numerical Relative Intensity, I/I_1	Interpretation
1.0	Very, very strong (VVS) (strongest line in the dif- fraction pattern)
0.9	Very strong (VS)
0.8	Strong (S)
0.7	
0.6	Medium (M)
0.5	
0.4	Weak (W)
0.3	
0.2	Very weak, faint (VW)
0.1	
0.1/2	Barely visible (VWV)
0.1/4	Barely visible under favorable conditions

TABLE III - MOLYBDENUM NITRIDE PREPARATION AND

COMPARISON X - RAY DIFFRACTION PATTERNS

No.	Mo _x N _y -1		Mo _x N _y -2		Mo _x N _y -3		Mo _x N _y -4		Mo _x N _y -7	
	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁
1					3.322	0.8	3.44	0.4		
2										
3										
4										
5										
6	2.80	0.3								
7										
8	2.48	0.9								
9	2.41	0.9			2.38	0.4	2.44	0.3	2.41	0.4
10									2.355	0.7
11										
12	2.22	1.0	2.21	0.9			2.23	0.5		
13					2.17	1.0			2.175	1.0
14	2.08	0.8					2.055	0.5	2.05	1.0
15										
16	1.86	0.8			1.81	0.4	1.85	0.2	1.89	0.5
17										
18							1.79	1.0	1.81	0.5
19							1.71	0.3		
20					1.667	0.4				
21										
22										
23	1.57	0.1	1.577	0.5	1.54	0.1	1.57	0.3	1.545	0.3
24										
25	1.48	0.2								
26	1.43	0.2							1.455	0.5
27										
28										
29										
30										
31	1.285	0.5	1.28	1.0						
32							1.28	0.5		
33	1.26	0.4			1.27	0.5	1.26	1.0		
34										
35										
36	1.22	0.1								
37	1.20	0.1								
38	1.135	0.3			1.18	0.3	1.07	1.0		
39	1.11	0.3	1.12	0.5			1.025	0.5		
40										
41			0.995	1.0	0.98	0.6	0.995	0.5		

TABLE III - MOLYBDENUM NITRIDE PREPARATION AND
COMPARISON X - RAY DIFFRACTION PATTERNS (Continued)

No.	Mo _x N _y -10		Mo _x N _y -14		Mo _x N _y -16		Mo _x N _y -17		Mo _x N _y -A	
	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁
1	3.35	1.0	3.33	0.1					3.32	0.3
2										
3										
4										
5										
6							2.74	0.3	2.72	0.5
7			2.64	0.1	2.68	0.5	2.62	0.4		
8										
9	2.40	0.6			2.44	0.5	2.40	1.0	2.43	1.0
10	2.36	0.6			2.36	0.6	2.33	0.5	2.35	1.0
11										
12										
13			2.17	1.0	2.19	1.0	2.15	0.3	2.17	0.4
14	2.04	0.5	2.07	1.0	2.06	1.0	2.03	0.3	2.045	0.5
15										
16	1.81	0.3			1.83	0.5	1.82	1.0	1.82	0.5
17										
18										
19	1.70	0.7								
20	1.67	0.7			1.63	0.1				
21										
22										
23	1.53	0.4	1.54	0.4						
24	1.505	0.4								
25			1.47	0.4						
26	1.455	0.4			1.455	0.3	1.45	0.3		
27							1.408	0.5		
28										
29	1.39	0.4								
30	1.36	0.4								
31										
32			1.27	0.5						
33							1.258	0.3		
34										
35							1.24	0.3		
36							1.225	0.3		
37	1.205	0.5	1.21	0.5			1.207	0.3		
38	1.195	0.5					1.12	0.5		
39	1.13	0.3								

TABLE III - MOLYBDENUM NITRIDE PREPARATION AND
COMPARISON X - RAY DIFFRACTION PATTERNS (Continued)

No.	Mo _x N _y -20		Mo _x N _y -21		Mo _x N _y -22		Mo _x N _y -24		Mo _x N _y -25	
	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁
1	3.36	1.0	3.35							
2										
3										
4										
5										
6					2.80	0.2	2.80	0.4		
7									2.58	0.2
8					2.48	0.5	2.48	1.0	2.46	0.2
9	2.39	0.9	2.43		2.41	1.0	2.425	1.0	2.39	0.2
10			2.36							
11										
12					2.22	1.0	2.22	0.2		
13										
14			2.12		2.08	1.0	2.095	0.8	2.09	0.2
15										
16			1.81.6		1.86	0.8	1.87	1.0	1.859	0.2
17										
18										
19	1.689	0.8	1.695							
20			1.67							
21										
22										
23										
24	1.51	0.3								
25					1.47	0.2	1.46	0.8	1.48	1.0
26					1.43	0.1	1.44	0.8	1.435	0.5
27					1.40	0.9	1.41	0.3	1.405	0.3
28										
29	1.39	0.3	1.38							
30	1.37	0.3	1.36							
31			1.28				1.285	0.8	1.28	0.8
32			1.27		1.27	0.1	1.27	0.8	1.26	1.0
33					1.26	0.1	1.24	0.6	1.24	0.5
34										
35	1.215	0.3	1.20		1.24	0.1	1.23	0.8	1.22	0.8
36	1.19	0.3	1.18		1.22	0.2	1.22	0.5	1.21	0.8
37			1.13		1.135	0.2			1.135	0.5

TABLE III - MOLYBDENUM NITRIDE PREPARATION AND
COMPARISON X - RAY DIFFRACTION PATTERNS (Continued)

No.	MoO ₂		MoO ₃		Mo ₂ O ₃		Mo Metal		Mo ₂ C	
	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁
1			6.9	0.24						
2	3.415	1.0	3.80	0.6	3.42	1.0				
3			3.46	0.4						
4			3.25	1.0						
5			3.00	0.06						
6	2.811	0.1								
7	2.693	0.1	2.66	0.32					2.60	0.29
8			2.52	0.08						
9	2.424	0.8			2.42	0.8				
10			2.30	0.08					2.36	0.24
11										
12			2.26	0.06	2.22	0.4	2.22	1.0	2.28	1.00
13	2.177	0.2			2.17	0.03				
14			2.13	0.06						
15			1.97	0.24						
16			1.85	0.24	1.84	0.06				
17										
18	1.722	0.6	1.73	0.16					1.75	0.24
19	1.708	0.7	1.70	0.04	1.71	0.80				
20	1.645	0.3	1.67	0.12						
21			1.60	0.12						
22										
23			1.57	0.14	1.57	0.06	1.57	0.36		
24	1.531	0.3	1.50	0.03	1.53	0.16			1.50	0.35
25	1.467	0.1	1.475	0.08	1.47	0.03				
26			1.44	0.20						
27	1.402	0.4	1.395	0.06	1.40	0.20				
28										
29	1.390	0.2			1.35	0.02			1.350	0.35
30	1.301	0.2			1.30	0.02			1.300	0.03
31	1.287	0.1			1.285	0.24	1.281	0.57	1.267	0.35
32					1.211	0.16			1.259	0.35
33					1.18	0.02	1.114	0.17	1.182	0.04
34									1.142	0.06
35							0.995	0.23	1.079	0.04
36							0.909	0.07	1.005	0.07
37							0.871	0.23	0.983	0.03
38							0.787	0.03	0.965	0.19
39							0.704	0.11	0.930	0.09
40							0.672	0.09	0.907	0.05
41							0.643	0.06	0.892	0.05
42							0.617	0.14	0.672	0.04
43									0.837	0.08
44										
45									0.818	0.05

TABLE IV - VANADIUM NITRIDE PREPARATION AND

COMPARISON X - RAY DIFFRACTION PATTERNS

No.	$V_{xN_y}-4$ d I/I ₁	$V_{xN_y}-5$ d I/I ₁	$V_{xN_y}-6$ d I/I ₁	$V_{xN_y}-9$ d I/I ₁	$V_{xN_y}-10$ d I/I ₁	$V_{xN_y}-10$ d I/I ₁
1			9.64 1.0			9.45 1.0
2			4.85 0.4		5.58 0.2	
3			4.24 0.6			
4			3.78 0.2		3.61 0.3	3.64 0.2
5			3.51 0.3			3.49 0.6
6						
7		3.04 1.0	3.16 0.6	3.13 0.4		
8		2.92 0.2	2.91 0.3			2.88 0.2
9	2.75 0.8	2.75 1.0		2.64 0.7	2.69 0.5	2.70 0.3
10			2.60 0.6			2.60 0.2
11				2.42 0.3	2.46 0.4	2.47 0.1
12						
13	2.38 0.8			2.40 0.3		2.37 0.2
14				2.14 0.2	2.18 0.2	
15				2.10 0.2	2.02 0.1	2.05 0.6
16	1.86 0.1	1.80 1.0		1.80 0.1	1.83 0.3	1.82 0.1
17	1.68 0.9	1.69 0.3		1.67 1.0	1.69 1.0	1.69 0.4
18						
19	1.58 0.1			1.63 1.0		
20	1.43 0.9			1.45 0.4	1.47 0.4	1.49 0.3
21				1.41 1.0	1.41 0.8	
22	1.36 1.0			1.32 0.1	1.33 0.3	
23		1.24 0.2				
24						
25				1.20 0.1	1.22 0.1	
26	1.17 1.0				1.17 0.2	
27					1.12 0.1	
28	1.08 0.5				1.09 0.5	
29	1.06 0.5				1.06 0.5	
30						
31	0.953 1.0					
32	0.900 1.0					
33						
34						
35						
36						
37						
38						
39						

TABLE IV - VANADIUM NITRIDE PREPARATION AND COMPARISON

X - RAY DIFFRACTION PATTERNS (Continued)

No.	V_{xN_y-11}		V_{xN_y-12}		V_{xN_y-12}		VN	V		V_2O_5		
	d I/I ₁		d I/I ₁		d I/I ₁		d I/I ₁	d I/I ₁		d I/I ₁		
1												
2										5.7	0.33	
3										4.38	1.00	
4	3.58	0.3	3.63	0.2						4.09	0.13	
5					3.53	0.5				3.39	0.83	
6												
7	3.14	0.2										
8	2.85	0.1								2.87	0.53	
9	2.66	0.5	2.70	1.0						2.76	0.13	
10	2.54	0.1			2.63	0.5				2.68	0.07	
11	2.45	0.4	2.48	0.2			2.47	1.0		2.61	0.13	
12												
13	2.40	0.1			2.40	0.6						
14	2.16	0.1			2.13	0.2	2.14	1.0	2.14	1.00	2.18	0.07
15	2.04	0.2			1.95	0.1					1.99	0.07
16	1.82	0.6			1.78	0.1					1.92	0.13
17	1.68	1.0	1.70	1.0	1.66	1.0					1.86	0.07
18												
19	1.64	0.8			1.59	0.1					1.77	0.10
20	1.46	0.6	1.47	0.3	1.44	0.2	1.513	0.7	1.51	0.07	1.65	0.07
21	1.42	0.8	1.43	0.5	1.40	0.3					1.56	0.07
22	1.32	0.1			1.31	0.2	1.291	0.5			1.51	0.07
23	1.23	0.2					1.235	0.5	1.236	0.20	1.49	0.07
24												
25	1.21	0.1									1.452	0.07
26	1.16	0.1	1.17	0.1							1.305	0.07
27	1.12	0.1										
28	1.09	0.3	1.09	0.1					1.072	0.03		
29	1.05	0.2					0.982	0.7				
30												
31							0.957	1.0	0.958	0.03		
32							0.874	1.0	0.875	0.01		
33							0.824	1.0	0.810	0.03		
34									0.759	0.01		
35									0.711	0.01		
36												
37												
38												
39												

TABLE IV - Continued

No.	V_2O_3		VC	
	$d I/I_1$		$d I'/I_1$	
1				
2				
3				
4	3.65	0.60		
5				
6				
7				
8				
9	2.70	0.80		
10				
11	2.47	0.60		
12				
13	2.32	0.02	2.40	1.00
14	2.18	0.20		
15	2.03	0.02	2.07	1.00
16				
17	1.83	0.03		
18				
19	1.69	1.00		
20	1.61	0.02		
21	1.57	0.03		
22				
23	1.470	0.25	1.469	0.50
24				
25	1.429	0.30		
26	1.330	0.10		
27	1.235	0.04	1.251	0.25
28	1.218	0.02		
29	1.193	0.02	1.199	0.10
30				
31	1.190	0.06		
32	1.125	0.03		
33	1.093	0.06		
34	1.057	0.06	1.039	0.05
35			0.952	0.05
36				
37			0.929	0.10
38			0.849	0.05
39			0.800	0.03

TABLE V - ZIRCONIUM NITRIDE PREPARATION AND COMPARISON

X - RAY DIFFRACTION PATTERNS

No.	Zr _x N _y	ZrN	Zr	Zr*	ZrH	ZrC
	d I/I ₁	d I/I ₁	d I/I ₁	d I/I ₁	d I/I ₁	d I/I ₁
1	3.20 0.2		2.81 1.0	2.78 0.31	2.75 1.0	2.75 1.0
2	2.95 1.0	2.637 1.0		2.56 0.20		
3	2.62 0.8	2.281 1.0	2.37 0.4	2.44 1.00	2.38 0.4	2.38 1.0
4	2.54 0.5		1.84 1.0	1.88 0.18		
5	2.29 1.0	1.613 0.8	1.60 0.3	1.61 0.18	1.69 0.6	1.683 1.0
6						
7	2.11 0.2		1.52 0.8	1.460 0.18	1.44 0.5	1.435 0.7
8	1.81 0.8	1.375 0.7	1.36 0.4	1.360 0.15	1.38 0.2	1.374 0.5
9	1.61 0.6	1.317 0.4		1.343 0.10		
10	1.50 0.8		1.29 0.4	1.282 0.05		
11	1.49 0.2			1.220 0.03B		
12						
13	1.37 0.8	1.141 0.2		1.180 0.03B	1.19 0.5	1.190 0.2
14	1.31 0.2	1.047 0.4	1.05 0.4	1.082 0.05	1.09 0.3	1.092 0.7
15	1.27 0.2	1.021 0.5		1.038 0.08	1.07 0.3	1.064 1.0
16	1.17 0.2			1.003 0.03		
17	1.14 0.2	0.932 0.5		0.977 0.03	0.97 0.3	0.972 1.0
18						
19	1.05 0.2			0.893 0.03	0.91 0.2	0.916 1.0
20	1.02 0.2		0.81 0.7	0.877 0.03		0.842 0.7
21			0.77 0.8			0.804 1.2
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						

* Considered to be of lower reliability.

TABLE V - ZIRCONIUM NITRIDE PREPARATION AND COMPARISON

X - RAY DIFFRACTION PATTERNS (Continued)

No.	ZrO ₂	ZnO ₂	ZrO ₂
	d I/I ₁	d I/I ₁	d I/I ₁
1	2.93 1.0	3.69 0.5	3.71 0.2
2	2.524 0.4	3.18 1.0	3.34 1.0
3		2.85 1.0	2.95 0.7b
4	1.808 0.6	2.63 0.7	2.69 0.6
5	1.788 1.0	2.55 0.5	2.24 0.6
6			
7	1.551 0.5	2.34 0.2	2.03 0.6
8	1.53 1.0	2.23 0.5	1.845 1.0b
9	1.471 0.6	2.20 0.5	1.712 0.7
10	1.291 0.4	2.01 0.5	1.671 0.5
11	1.269 0.6	1.999 0.5	1.604 0.2
12			
13	1.173 0.4	1.852 1.0	1.561 0.5
14	1.165 0.7	1.814 1.0b	1.504 0.7b
15		1.695 0.7	1.434 0.5
16		1.658 0.7	1.371 0.2
17		1.621 0.6	1.334 0.5
18			
19		1.549 0.7	1.277 0.5
20		1.512 0.5b	1.223 0.5
21		1.466 0.6	1.165 0.5b
22		1.453 0.2	1.113 0.5b
23		1.427 0.6	1.058 0.2
24			
25		1.366 0.5	1.037 0.5
26		1.330 0.6	1.017 0.5
27		1.309 0.5	1.004 0.5
28		1.273 0.6	0.986 0.2
29		1.239 0.2	0.964 0.5b
30			
31		1.220 0.2	0.941 0.5b
32		1.169 0.5b	0.910 0.2
33		1.114 0.5	0.892 0.7
34		1.096 0.5	0.853 0.7
35		1.032 0.9	
36			
37		1.016 0.6	
38		1.001 0.6	
39		0.971 0.5	
40		0.953 0.5	
41		0.915 0.5	
42		0.894 1.0	
43		0.877 0.7	

TABLE VI - TANTALUM NITRIDE PREPARATION AND COMPARISON

X-RAY DIFFRACTION PATTERNS (TaCl_5 & NH_3 Reaction)

Interplanar Spacings A. U.	Relative Intensity
2.73	1.00
2.22	0.5
1.91	0.7
1.56	0.9
1.04	0.5

TABLE VII - PALLADIUM NITRIDE PREPARATION AND COMPARISON

X - RAY DIFFRACTION PATTERN

No.	Pd_xN_y-1	Pd_xN_y-3	Pd_xN_y-8	P8	PdCl_2	CaCl_2
	d I	d I	d I	d I/I ₁	d I/I ₁	d I/I ₁
1	5.36 9		4.95 9		5.3 1.00	4.462 0.6
2	2.645 8	2.78 6	3.11		3.29 0.24	3.428 0.2
3	2.37		2.62 7		3.11 0.28	3.028 1.0
4	2.25 4	2.22	2.49	2.23 1.00	2.39 0.80	2.838 0.6
5	1.95 3	2.00 7	2.38	1.94 0.50	2.25 0.03	2.324 0.8
6	1.775 10		2.24 2		2.02 0.06	2.227 0.6
7	1.64	1.62 4	1.795 8		1.93 0.03	2.071 0.6
8	1.605	1.405 5	1.685 10		1.87 0.10	1.900 0.8
9	1.37 2	1.37 9	1.48	1.371 0.27	1.82 0.13	1.854 0.6
10	1.33	1.26 1	1.37 3	1.170 0.27	1.77 0.24	1.781 0.6
11	1.17 1	1.17 8	1.31	1.120 0.05	1.64 0.40	1.677 0.7
12	1.12 5	1.15 3	1.17 1		1.61 0.13	1.554 0.6
13	1.09	1.12	1.145		1.57 0.20	1.520 0.8
14	0.89 6	1.00 10	1.12 6		1.54 0.03	
15	0.87 7	0.95	1.06	0.970 0.01	1.50 0.03	
16		0.94 2	1.015	0.891 0.05	1.430 0.05	
17			0.99	0.869 0.05	1.370 0.02	
18			0.925	0.793 0.02	1.330 0.06	
19			0.89 4	0.748 0.02	1.308 0.06	
20			0.87 5		1.250 0.03	
21					1.208 0.08	
22					1.124 0.11	
23					1.068 0.02	
24					1.023 0.05	
25					0.960 0.03	
26					0.934 0.05	
27						
28						

TABLE VII - PALLADIUM NITRIDE PREPARATION AND COMPARISON X - RAY

DIFFRACTION PATTERN (Continued)

No.	CaCl ₂		CaO	
	Ca(OH) ₂ · H ₂ O			
	d	I/I ₁	d	I/I ₁
1	4.92	0.5	2.770	0.7
2	3.32	0.2	2.399	1.0
3	3.15	0.9	1.697	0.9
4	2.75	0.2	1.447	0.8
5	2.46	0.2	1.385	0.8
6	2.34	1.0	1.200	0.6n
7	1.92	0.7	1.101	0.6n
8	1.79	0.3	1.073	0.8
9	1.68	0.1	0.980	0.8
10	1.64	0.2	0.923	0.7n
11	1.52	0.3	0.848	0.3n
12	1.485	0.4	0.811	0.6n
13	1.30	0.3	0.799	0.4n
14	1.267	0.2	0.759	0.4n
15	1.173	0.4	0.723	0.4n
16			0.693	0.1n
17			0.672	0.3n
18			0.666	0.2n
19			0.641	0.3n
20			0.625	0.2n
21			0.582	0.2n
22			0.565	0.2n
23			0.553	0.2n
24			0.549	0.1n
25			0.535	0.1n
26			0.525	0.1n
27			0.522	0.1n
28			0.510	0.1n

TABLE VIII - MOLYBDENUM BORIDE PREPARATION AND COMPARISON X-RAY DIFFRACTION PATTERNS (Continued)

1.55	4	1.55	4	1.54	7	1.54	1.52	1.50	1.50	1.0	1.50	1.0	1.531	0.3
		1.50		1.485		1.45	1.50						1.467	0.1
1.41		1.41		1.42		1.415	1.42	1.43	5				1.402	0.4
1.38				1.37		1.36	8	1.37					1.390	0.2
1.345	1			1.33		1.355	2	1.36	2		1.35	1.0	1.35	1.0
1.34		1.34	1	1.31		1.335	6	1.32	1					
1.28	9	1.28	10	1.28	9	1.285	1.295	1.28	1	1.30	1.30	0.5	1.301	0.2
		1.27		1.27		1.265	1.275				1.26	1.0d	1.287	0.1
1.25	6	1.25	7			1.25	1.24			1.25	1.25	1.0d	1.0d	
1.24				1.24	3	1.21	3	1.23					1.215	0.2
1.20		1.19		1.18	6	1.205	1.19	1.19	4		1.18	0.5d	1.18	0.5d
				1.17		1.17	1.16			1.17				
1.095	7	1.11		1.14		1.13	1.13				1.14	0.7d	1.14	0.7d
1.08		1.10		1.10	5	1.10	1.10	1.095						
1.06		1.08	4	1.08		1.08	1.08	5			1.07	0.7d	1.08	0.7d
1.04		1.06												
		1.045		1.04		1.02	1.03	1.00			1.00	1.0d	1.00	1.0d
1.015				0.995	4	0.995	0.995							
0.99				0.99	1	0.98	0.98	0.99	2				0.98	0.7d
0.975	3	0.975	2	0.98		0.975	0.965							
				0.97		0.97	0.95							
0.95				0.94		0.95	0.945	8						
0.93						0.92	0.92	0.93						
0.91				0.91	10	0.91	10	0.91	9d					
				0.895	2	0.89	0.89	0.91-1.0d						
0.88				0.885		0.88	0.88							
0.865	8	0.87	6	0.86		0.865	0.87							

TABLE VIII - MOLYBDENUM BORIDE PREPARATION AND COMPARISON X-RAY DIFFRACTION PATTERNS (Continued)

0.85	5	0.85	5	0.84	0.845	4	0.85	0.84	3
0.835				0.84-			0.845	0.84-	5
				0.81			0.83		9
				0.81-	0.81-		0.815	0.82	
				0.79	0.78		0.81	0.79	8

* See Table IX for complete boron pattern.

TABLE IX - TANTALUM BORIDE PREPARATION AND COMPARISON
X-RAY DIFFRACTION PATTERNS

Ta _x B _y -1b		Pure B		Pure Ta		TaC	
d	I	d	I	d	I/I ₁	d	I/I ₁
		5.55					
		5.35					
		4.755					
		4.445					
		4.34					
3.91		4.05					
		3.65					
3.35		3.36	1				
3.215		3.225	8				
3.15							
2.68	6	2.735					
2.57	2					2.56	1.0
2.45		2.495	4	2.34	1.0		
		2.32	9				
2.225	4	2.21	10			2.22	0.8
2.06	5	2.05	2				
		1.765	3				
1.655		1.68	7	1.650	0.8		
1.61							
1.58	3					1.570	0.9
1.545		1.55	6				
		1.46					
1.395		1.43	5				
1.38		1.38					
1.34	1	1.35		1.347	1.0	1.341	0.9
1.285		1.30				1.282	0.5
1.24		1.25					
1.195		1.17		1.167	0.8		
1.12	10						
1.10		1.095				1.111	0.5
1.02	9			1.043	1.0	1.020	0.8
1.01							
1.00	7	1.00				0.994	0.8
0.97				0.953			
0.91						0.907	1.05

TABLE IX - TANTALUM BORIDE PREPARATION AND COMPARISON
X-RAY DIFFRACTION PATTERNS
(Continued)

0.89				
0.88		0.881	1.0	
0.86	8			
0.86-				0.856 1.0S
0.84		0.825	0.8	0.786 0.8S

TABLE X - THORIUM BORIDE PREPARATION AND COMPARISON
X-RAY DIFFRACTION PATTERNS

Th _x B _y -1b	Th _x B _y -3b	NaCl	ThO ₂	Boron*
d I	d I	d I/I ₁	d I/I ₁	d I
				4.05
	3.61			3.65
3.41				3.36 1
3.19	3.25 1	3.2492 0.4	3.23 0.7	3.225 8
3.05				
2.77	2.82 12	2.6140	2.80 0.4	2.735
2.61				2.495 4
2.31				2.32 9
2.21	2.21			2.21 10
2.005	1.99 7	1.9898 0.9	1.987 1.0	2.05 2
1.96	1.88			1.765 3
1.675	1.695 6	1.6969 0.1	1.688 1.0	1.68 7
1.60	1.62	1.6246 0.7	1.613 0.5	1.55 6
1.48				1.46
1.445	1.42			1.43 5
1.40	1.40	1.4070 0.5	1.398 0.4	1.38
				1.35
1.28 5	1.285 4	1.2911 0.1	1.281 0.8	1.30
1.25	1.25 8	1.2584 0.8	1.249 0.8	1.25
	1.195			1.17
1.14 3	1.14 3	1.1488 0.6	1.140 1.0	
1.12				1.095
1.08 2	1.08 2	1.0830 0.1/2	1.076 1.0	
	1.05			
0.99	1.02	0.9948 0.2		1.00
	0.95 5	0.9513 0.1/2		
0.945 1	0.95-10			
0.93 4	0.935-	0.9380 0.3		
	0.93			
0.89- 6	0.89-	0.8898 0.2		
0.88 9	0.88			
0.855 7	0.855 9	0.8582 0.1		
0.85 10	0.85	0.8484 0.1		
0.845 8	0.84 11			
0.84	0.84-			
0.81	0.81	0.8123 0.1/2		
0.81-	0.81-	0.7804 0.1/2		
		0.7520 0.1		

* See Table IX for complete boron pattern

TABLE XI - VANADIUM BORIDE PREPARATION AND COMPARISON X-RAY
DIFFRACTION PATTERNS

V _x B _y -1		V _x B _y -2b		V _x B _y -3b		V _x B _y -4b		Boron*		VC	
d	I	d	I	d	I	d	I	d	I	d	I/I ₁
3.65								3.65			
3.49	2							3.36	1		
						3.12		3.225	8		
		2.87				2.88					
2.68	1					2.80		2.735			
		2.60				2.62	4				
				2.56	6	2.53					
2.48						2.505		2.495	4	2.48	1.0
2.40		2.38	8	2.40	8	2.43	1				
						2.32	10	2.32	9		
2.30		2.22		2.24	4	2.24		2.21	10		
2.07	4	2.08	5	2.075	10	2.075	7			2.15	1.0
						2.05		2.05	2		
		2.02	10	2.02		2.01					
				1.98		1.99					
1.92	6			1.95	7						
1.84											
1.745								1.765	3		
1.69		1.67		1.67		1.68(Ni)		1.68	7		
1.665	3										
1.645		1.60		1.605	9						
1.49	5	1.53		1.53	5	1.565	2	1.55	6	1.521	1.0
		1.47	1	1.48	3						
1.44				1.46	2	1.465(Ni)		1.46			
1.39	8							1.43	5		
1.36						1.37	6	1.38			
1.34				1.34		1.325	9	1.35			
1.33	7										
1.32		1.32		1.32							
1.295		1.29	4	1.29		1.29	8	1.30		1.297	0.7
1.26		1.26	2					1.25		1.242	0.7
1.095		1.22		1.19	1	1.22		1.17			
1.06	9	1.20	3	1.12		1.20	3	1.095		1.075	0.5
1.04		0.955	7			1.08(Ni)		1.00		0.986	0.7
0.96		0.93	6			0.94	5			0.962	1.0
0.945		0.91								0.878	1.0
0.895	10	0.88	9							0.828	1.0
0.87											
0.82											

TABLE XII - ZIRCONIUM BORIDE PREPARATION AND COMPARISON X - RAY DIFFRACTION PATTERNS

[illegible]

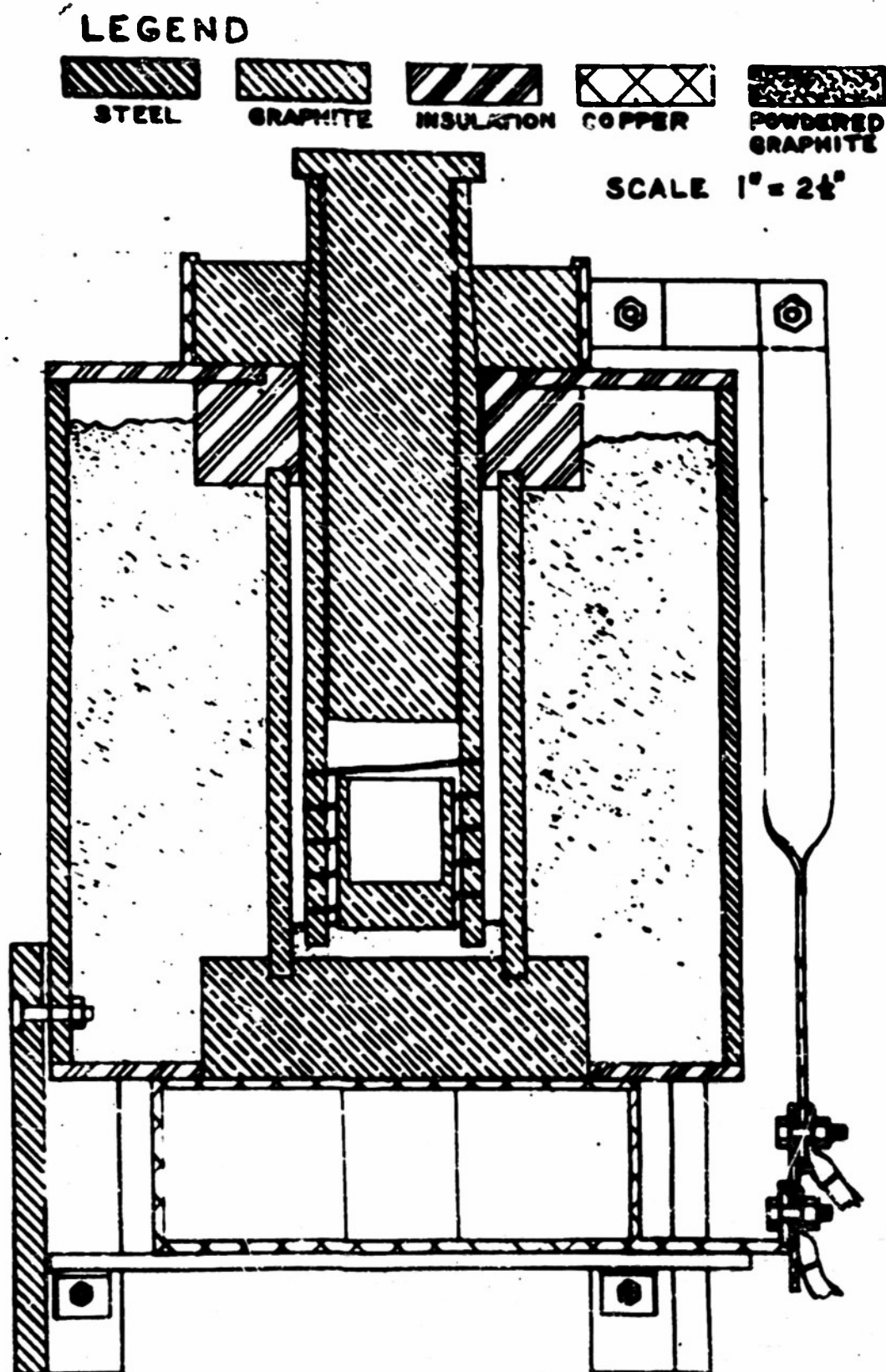
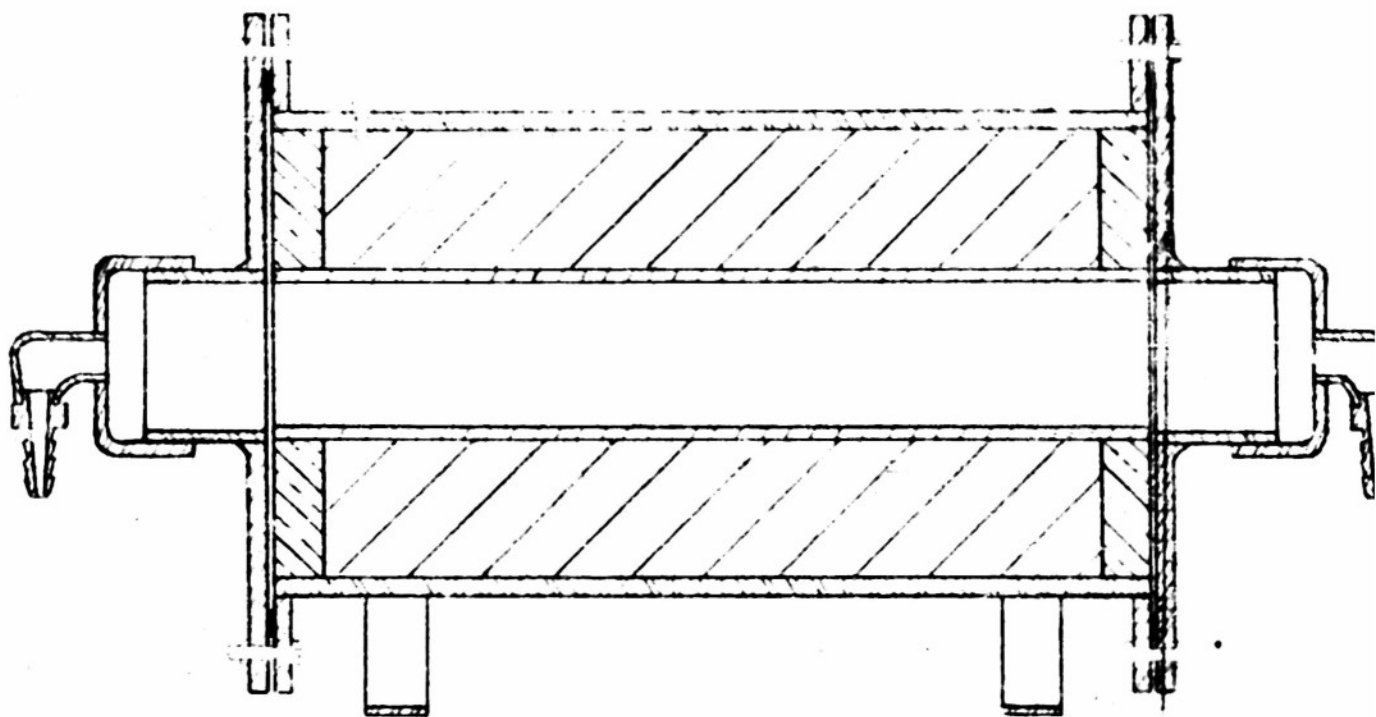


FIG. 1. GRAPHITE-HELIX RESISTANCE FURNACE.



28 1/2