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THE ANALYSIS OF REFRACTORY BORIDES, CARBIDES, NITRIDES, AND SILICIDES

by

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ABSTRACT

Methods are presented for the analysis of 41 refractory materials. An evaluation of the accuracy and the precision of these techniques is also given. The materials studied are the borides of hafnium, molybdenum, niobium, rhenium, tantalum, thorium, titanium, tungsten, uranium, vanadium, and zirconium; the carbides of hafnium, molybdenum, niobium, silicon, tantalum, thorium, titanium, tungsten, uranium, vanadium, and zirconium; the nitrides of boron, hafnium, niobium, silicon, tantalum, titanium, uranium, and zirconium; the silicides of molybdenum, rhenium, tantalum, titanium, tungsten, vanadium, and zirconium; and mixed carbides of uranium with hafnium, niobium, tantalum, or zirconium.

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1. INTRODUCTION AND GENERAL DISCUSSION

The use of various oxides and silicates as refractory materials has been widespread for many years; however, since World War II there has been a rapid increase of interest in other types of refractory materials among chemists, chemical engineers, metallurgists, and, more recently, nuclear engineers. Because of interest in research involving temperatures as high as 3500° C., refractories of types other than oxides and silicates have become of increasing importance. It seems logical to conclude that demands for better and special refractories will greatly increase in the future.

The property most generally sought is chemical inertness at very high temperatures. This requires that the material have a high melting point, that it not react with its environment at high temperatures, and in many cases that it maintain considerable structural strength at these temperatures.

The types of materials that hold the most promise of generally fulfilling many present day needs are the borides, carbides, nitrides, and silicides of certain transition metals. This paper describes methods that have been satisfactorily applied to the analysis of refractory materials and evaluates the accuracy and precision of these procedures. The following materials were investigated:

HfB_2
MoB
NbB
NbB_2
Re_4B
Re_2B
ReB
Ta_3B_2
TaB
TaB_2
ThB_4
TiB_2
WB
UB_2
UB_4
VB_2
ZrB_2

HfC
Mo_2C
Nb_2C
NbC
SiC
Ta_2C
TaC
ThC
TiC
W_2C
WC
UC
U_2C_3
UC_2
VC
ZrC
Hf-U-C
Nb-U-C
Ta-U-C
Zr-U-C

BN
HfN
NbN
Si_3N_4
TaN
TiN
UN
ZrN

$MoSi_2$
Re_3Si
$TaSi_2$
Ti_5Si_3
WSi_2
VSi_2
$ZrSi_2$

Characteristic Properties of Refractories Which Are Important to the Analyst

Refractory borides, carbides, nitrides, and silicides are relatively inert chemically and resist the action of many aqueous acids and bases. Generally, these materials may be dissolved with a mixture of nitric and hydrofluoric acids. In addition, most are dissolved by an alkaline oxidizing flux such as a mixture of sodium carbonate and nitrate.

Because most transition metal carbides and nitrides dissolve very slowly in acidic mixtures not containing nitric acid, the determination of nitrogen in these materials by the Kjeldahl technique is quite difficult. Many of these materials may be dissolved by heating for hours with acidic mixtures containing selenic acid or other catalyst; however, a long digestion period is inconvenient and introduces potential sources of error in the analysis. It is possible to use nitric acid to dissolve carbide or nitride samples rapidly; however, strong reducing agents in the sample may reduce nitrate ion to ammonia. In addition, some of the nitrogen in refractory nitrides appears to be in a non-nitride form which is not determined by the Kjeldahl method. Fortunately, the Dumas technique, long used in organic analysis, is satisfactory for the determination of total nitrogen in many refractory carbides and nitrides.

The solubility of most carbides and nitrides in mixtures of nitric and hydrofluoric acids makes it possible to determine free graphitic carbon in these materials. Graphite is insoluble in boiling concentrated nitric and hydrofluoric acids for periods of at least 30 minutes, and may be removed on a Monroe crucible after the carbide and nitride portions of the sample have been dissolved.

Reliability

A serious problem encountered in this study was the absence of satisfactory standard materials which could be used to evaluate analytical procedures. With the exception of National Bureau of Standards' silicon carbide, no certified materials are available to the analyst. Samples of niobium and tantalum nitride were prepared in this Laboratory by reacting a known weight of metal powder with spectrographically pure nitrogen gas. The weight gain of the metal was assumed to be equal to the increase in the nitrogen content of the samples. The amount of nitrogen present in the metal powder prior to treatment with nitrogen gas was determined by the Dumas technique.

In the absence of certified materials it was decided to use the summation of the total constituents in the sample, plus the precision of the individual determinations, as an indication of the reliability of the analytical techniques.

Preparation of Samples for Analysis

Refractory borides, carbides, nitrides, and silicides are extremely hard, and attempts to reduce the particle size of these samples in the usual type of mortar results in significant contamination. This difficulty can be eliminated by using a "diamond mortar." All samples are reduced to 100 mesh or finer, following which any iron particles introduced during the crushing process are removed with a magnet. Samples are dried at 105° C. for 1 hour prior to analysis. Refractory carbides containing more than 2% graphite are frequently segregated. A riffle sampler is used to select a homogeneous aliquot from this type of material.

2. THE ANALYSIS OF REFRACTORY BORIDES

The Determination of Boron in the Borides of Hafnium, Molybdenum, Niobium, Rhenium, Tantalum, Thorium, Titanium, Tungsten, Vanadium, and Zirconium

Blumenthal (2) reported a general method for the determination of boron in metal borides. Refractory borides for which this method was suggested include those of niobium, tantalum, thorium, titanium, tungsten, vanadium, and zirconium. A slight modification was recommended by Blumenthal (3) for the determination of boron in molybdenum boride. The reproducibility of these methods was evaluated by duplicate determinations of the boron content.

A slight simplification of the Blumenthal method was found to be satisfactory for the determination of boron in HfB_2, MoB, NbB, NbB_2, Re_4B, Re_2B, ReB, Ta_3B_2, TaB, TaB_2, ThB_4, TiB_2, WB, VB_2, and ZrB_2. Results for the analysis of these materials are presented in Table I (at the end of this section). The recommended procedure follows.

Mix 100 mg. of sample with 1 gram of sodium carbonate in a 20-ml. platinum crucible. Cover and heat slowly until a good fusion melt is obtained. Cool the crucible, add 100 to 200 mg. of sodium nitrate, and continue the fusion until the melt is clear. Note particularly that any material on the crucible cover has fused. (Fuse niobium and tantalum borides in the same manner with potassium carbonate and potassium nitrate.) Transfer the crucible and cover to a covered 400-ml. beaker containing 50 ml. of water and 5 ml. of hydrochloric acid. (Leach the melts of niobium, tantalum, and tungsten borides with water and add 5 ml. of hydrochloric acid only after the melts are in solution.)

When leaching is complete, remove the crucible and cover, dilute the sample to 150 ml. with water, and add 7 grams of powdered barium carbonate, slowly, while stirring with a magnetic stirrer. (To ensure complete precipitation of vanadium in vanadium boride samples, add 50 mg. of ferric iron before treating the sample with barium carbonate.)

(A more basic medium is required for the complete precipitation of molybdenum and rhenium. Adjust the pH to 8.0 to 8.5 with a saturated solution of barium hydroxide for samples of molybdenum or rhenium boride.) Heat the covered beaker on a hot plate until the sample starts to foam. Allow the sample to age on a steam bath for 30 minutes.

Remove the precipitate on a Whatman #42 filter paper, using vacuum, and wash with 200 ml. of hot water. Transfer the filtrate to a 600-ml. beaker, add a small piece of litmus paper, and acidify the solution by adding concentrated hydrochloric acid dropwise. Cover the beaker with a watch glass and boil the sample for 5 to 7 minutes. The litmus paper is held on the floor of the beaker to prevent bumping.

Rapidly cool the covered beaker to 50° to 60° C. in a cold water bath, add 6 drops of indicator, and titrate the sample without delay with a 0.05N sodium hydroxide solution. Note the buret reading at the first tinge of green color, add 8 grams of mannitol, and continue the titration until the first tinge of purple is noticed. The amount of base between the two end points is equivalent to the boric acid in the sample. The mixed indicator contains 100 mg. of methyl red, 100 mg. of bromcresol green, and 1 gram of phenolphthalein per 100 ml. of ethanol. Analyze a blank determination, with the same amount of all reagents, with each group of samples.

The Determination of Boron in Uranium Boride

Uranium is quite soluble in solutions containing carbonate; consequently, the Blumenthal procedure is not applicable to the determination of uranium in uranium borides. The following procedure was developed for the determination of boron in UB_2 and UB_4. Results for the analysis of uranium boride are presented in Table I.

Place a 100-mg. sample in a 250-ml. Erlenmeyer flask. Attach, via a ground-glass joint, a 12-inch air condenser, and add 4 ml. of 1:1 nitric acid. If necessary to effect complete solution of the sample, warm gently on a steam bath. Transfer the sample (rinse both flask and condenser) to a 400-ml. beaker, dilute to 200 ml. with carbonate-free water, and add paper pulp. Adjust the pH to 10 to 11 with a saturated solution of carbonate-free barium hydroxide. Remove the precipitated uranium on a Whatman #42 filter paper, using vacuum. Wash with 100 ml.

of hot water containing a few drops of saturated barium hydroxide solution. Add to the filtrate in a 500-ml. filter flask a piece of litmus paper and enough hydrochloric acid to make the solution barely acidic. Add 6 drops of mixed indicator and titrate with a 0.05N sodium hydroxide solution until the first tinge of green is noted. Record the buret reading, add 8 grams of mannitol, and continue the titration until the first tinge of purple is observed. The amount of base between the two end points is equivalent to the boric acid in the sample. The mixed indicator contains 100 mg. of methyl red, 100 mg. of bromcresol green, and 1 gram of phenolphthalein per 100 ml. of ethanol. Analyze a blank determination, with the same amount of all reagents, with each group of samples.

The Determination of Hafnium and Zirconium in Hafnium and Zirconium Borides

Oesper and Klingenberg (13) have shown that p-bromomandelic acid may be used for the quantitative precipitation of zirconium. This information was used to develop the following procedure for the determination of hafnium and zirconium in hafnium and zirconium borides. Results for the analysis of HfB_2 and ZrB_2 are presented in Table I.

Place a 100-mg. sample in a covered 250-ml. beaker and treat with 5 ml. of sulfuric acid and 2 to 3 ml. of 30% hydrogen peroxide. Warm the beaker on a hot plate and add additional hydrogen peroxide, if necessary to dissolve the sample. After effervescense ceases, remove and rinse the cover glass, replace with a Speedyvap cover, and evaporate the sample to dryness. Add 50 ml. of 3N hydrochloric acid plus 1 drop of 1% Aerosol solution. Heat the sample to boiling and add 60 ml. of 0.1M p-bromomandelic acid. (Thirty milliliters of reagent is sufficient for hafnium boride samples.) Bring the solution to a boil and transfer to a steam bath for 30 minutes. Remove the precipitate on a Whatman #42 filter paper, using vacuum, and wash with 200 ml. of hot water. Ignite the precipitate at 1000° C. in a tared platinum crucible and weigh as ZrO_2 or HfO_2.

The Determination of Molybdenum in Molybdenum Boride

According to Hillebrand, Lundell, Bright, and Hoffman (7), "the best method for the gravimetric determination of molybdenum is that based on precipitation with α-benzoinoxime." This technique was adapted to the analysis of molybdenum boride. Results for the analysis of MoB are given in Table I.

Place a 50- to 70-mg. sample in a covered 400-ml. beaker and dissolve by warming with 10 ml. of water and 5 ml. of nitric acid. When the sample is in solution, add 100 ml. of water and 5 ml. of sulfuric acid and cool to 5° to 10° C. Dilute the sample to 200 ml. with crushed ice (prepared from distilled water) and stir the sample while adding 10 ml. of 2% (in ethanol) α-benzoinoxime solution. Add paper pulp and enough bromine water to tint the solution a light yellow. Add 2 or 3 ml. of α-benzoinoxime and allow the sample to age for 10 minutes.

Remove the precipitate on a Whatman #41-H filter paper and wash with 200 ml. of a cold, freshly prepared solution containing 25 to 50 ml. of the prepared reagent and 10 ml. of sulfuric acid in 1 liter of distilled water. Use reduced pressure to speed the filtration but take special precautions to prevent loss of precipitate through the paper. Ignite the precipitate in a tared platinum crucible at 500° C. and weigh as MoO_3.

The Determination of Niobium and Tantalum in Niobium and Tantalum Borides

Kriege and Gardner (11, 12) have studied the precipitation of niobium and tantalum by sulfurous acid. The sulfurous acid technique was applied to the determination of niobium and tantalum in NbB, NbB_2, Ta_3B_2, TaB, and TaB_2. Results for the analysis of niobium and tantalum borides are presented in Table I.

Mix a 100-mg. sample with 1 gram of potassium carbonate and heat slowly in a covered 20-ml. gold crucible until a good fusion melt is obtained. Cool the crucible, add 100 to 200 mg. of potassium nitrate, and continue the fusion until the melt is clear. Note particularly that any material on the crucible cover has fused. Transfer the crucible and cover to a covered 400-ml. beaker containing 50 ml. of water. Remove, rinse, and weigh the crucible and cover. If more than 0.5 mg. of gold has dissolved, discard the sample and repeat the fusion with another portion.

Add paper pulp and 5 ml. of hydrochloric acid. Heat the sample to boiling on a hot plate and add 100 ml. of freshly-prepared, concentrated sulfurous acid. Boil the sample for 10 minutes, allow to settle on a steam bath for 10 minutes and remove the precipitate on a Whatman #42 filter paper, using reduced pressure. Wash paper and precipitate with 200 ml. of hot sulfurous acid. Ignite the precipitate at 1000° C. in a tared platinum crucible and weigh as Nb_2O_5 or Ta_2O_5. Correct the oxide weight for the weight of gold crucible dissolved.

The Determination of Rhenium in Rhenium Boride

Willard and Smith (16) studied the gravimetric determination of rhenium with tetraphenylarsonium chloride. Using this method, with the modification suggested by Smith and Long (15), the following procedure was developed for the determination of rhenium in rhenium boride. Results for the analysis of Re_4B, Re_2B, and ReB are presented in Table I.

Place a 1- to 1.5-gram sample in a 250-ml. Erlenmeyer flask. Attach, via a ground-glass joint, a 12-inch air condenser, and add 10 ml. of water followed by 5 ml. of nitric acid. Warm gently on a steam bath to effect complete solution of the sample. If the reaction becomes vigorous, add a few milliliters of water to the sample. Transfer the dissolved sample to a volumetric flask and remove an aliquot containing 50 to 60 mg. of rhenium to a 100-ml. beaker. Add 1.2 ml. of 1:1 sulfuric acid and 2 ml. of hydrochloric acid and warm the uncovered beaker on a steam bath until constant volume is obtained.

Wash the walls of the beaker with 8 ml. of water, add 20 ml. of concentrated ammonium hydroxide, warm on a steam bath until bubbles appear, and add 20 ml. of recently filtered 1% tetraphenylarsonium chloride solution containing 100 grams of sodium chloride per liter. Cover the beaker with a watch glass and allow the sample to age overnight. Remove the precipitate on a tared 30-ml. sintered glass crucible with medium porosity, using reduced pressure. Use only saturated tetraphenylarsonium perrhenate solution to transfer and wash the precipitate. Dry to constant weight at 110° C. The factor for rhenium is 0.2940.

The Determination of Thorium in Thorium Boride

The insolubility of thorium oxalate has long been known, and it was found to be a satisfactory precipitating form for thorium in samples of thorium boride. Addition of the oxalate as ethyl oxalate produces an easy-to-filter crystalline precipitate. Results obtained for the analysis of a sample of ThB_4 by the following procedure are given in Table I.

Dissolve a 200-mg. sample with 10 ml. of 1:1 nitric acid in a covered 250-ml. beaker, warming the sample if necessary. Dilute the sample to 100 ml. with water, heat to boiling, and add 5 ml. of ethyl oxalate. Warm on a steam bath with occasional stirring until the organic phase has decomposed. Age the sample overnight and then remove the precipitate on a Whatman #42 filter paper using reduced pressure. Wash the precipitate with a solution containing 40 ml. of hydrochloric acid and 25 grams of oxalic acid per liter of solution. Ignite the precipitate at 1000° C. and weigh as ThO_2.

The Determination of Titanium in Titanium Boride

Titanium can be precipitated as the oxide from dilute hydrochloric acid (8), and this procedure was used for the determination of titanium in titanium boride. Results for the analysis of a sample of TiB_2 are given in Table I.

Place a 100-mg. sample in a covered 20-ml. platinum crucible and fuse very slowly with 1 gram of potassium pyrosulfate. Care should be taken that material is not lost when the sample is fused. When the vigorous reaction has ceased, add 2 or 3 grams of potassium pyrosulfate and heat the sample until a clear fusion results. Leach the melt in a covered 400-ml. beaker with 50 ml. of water and 2 ml. of sulfuric acid. Warm on a steam bath until solution of the melt is complete.

Remove and rinse the crucible and cover, add 10 grams of ammonium chloride plus some paper pulp, and dilute the sample to 200 ml. Adjust the pH to 2.5 using a pH meter and ammonium hydroxide. Warm the sample on a hot plate to 90° C. and transfer to a steam bath for 30 minutes. Remove the precipitate on a Whatman #42 filter paper, using vacuum filtration. Wash with a solution containing 1% ammonium nitrate and enough hydrochloric acid to have a pH of 2.5. Ignite the precipitate at 1000° C. and weigh as TiO_2.

The Determination of Tungsten in Tungsten Boride

Hillebrand, Lundell, Bright, and Hoffman (9) state that "the most satisfactory method for the determination of tungsten in miscellaneous materials is in weighing it as the oxide, WO_3, after it has been separated as tungstic acid by digesting with hydrochloric or nitric acids, and finally in the presence of cinchonine." This technique was adapted to the analysis of tungsten boride. Results obtained for the analysis of a sample of WB by this procedure are presented in Table I.

Dissolve a 200- to 300-mg. sample by warming with a mixture of 30 ml. of hydrochloric acid and 10 ml. of nitric acid in a covered 250-ml. beaker. When solution is complete remove and rinse the cover glass and replace with a Speedyvap cover. Evaporate to a volume of 15 ml. on a hot plate, dilute to a volume of 150 ml. with water, stir thoroughly, and digest on a steam bath for 30 minutes. Add 5 ml. of a 1:1 hydrochloric acid solution containing 12% cinchonine and continue aging on a steam bath for at least 1 hour. Remove the precipitate on a Whatman #42 filter paper, using vacuum filtration, and wash with a hot solution containing 40 ml. of hydrochloric acid and 3 grams of cinchonine per liter. Ignite the precipitate in a tared platinum crucible at 800°C. and weigh as WO_3.

The Determination of Uranium in Uranium Boride

The volumetric uranium procedure used routinely in this Laboratory proved satisfactory for the determination of uranium in UB_2 and UB_4. Results obtained for the analysis of uranium boride are given in Table I.

Dissolve a 500-mg. sample with 10 ml. of 1:1 nitric acid in a covered 250-ml. beaker. Warm if necessary. Replace the cover glass with a Speedyvap cover and fume the sample to dryness four times with 5-ml. portions of sulfuric acid, taking care to wash the cover glass and beaker walls after each fuming. Dissolve the sample with 50 ml. of 7.5% sulfuric acid and transfer to a Jones reductor. Oxidize the sample with an air bubbler (using a glass frit) for 10 minutes and titrate without delay, using a standard 0.1N ceric sulfate solution with ferroin indicator. Add 3 ml. of 0.1N ferric ammonium sulfate just before the end point of the titration is reached to enhance the color change. Titrate a blank containing all reagents with each group of samples.

The Determination of Vanadium in Vanadium Boride

The fact that ferrous ion quantitatively reduces vanadate has long been known (17). This reaction was used as the basis for a method for the determination of vanadium in vanadium boride. Results obtained for the analysis of a sample of VB_2 by this procedure are presented in Table I.

Dissolve a 100-mg. sample with 20 ml. of perchloric acid in a covered 400-ml. beaker by warming on a hot plate. Fume the sample for 4 hours. Remove from the hot plate, cool, add water, and finally add ammonia to dissolve any vanadium pentoxide which has precipitated. Dilute with water to 150 ml. and add 100 ml. of 1:1 sulfuric acid. Titrate with a standard 0.1N ferrous sulfate solution, using a Beckman pH meter and platinum and calomel electrodes. The platinum electrode should be dipped into a solution of chromic acid for 30 seconds and then rinsed, just prior to the titration.

The Determination of Carbon in the Borides of Hafnium, Molybdenum, Niobium, Rhenium, Tantalum, Thorium, Titanium, Tungsten, Uranium, Vanadium, and Zirconium

The oxidation of some borides is a very exothermic process and ignition of boride samples should be accomplished in porcelain rather than platinum vessels. The following procedure was found to be satisfactory for the determination of carbon in HfB_2, MoB, NbB, NbB_2, Re_4B, Re_2B, ReB, Ta_3B_2, TaB, TaB_2, ThB_4, TiB_2, WB, UB_2, UB_4, VB_2, and ZrB_2. Results for the determination of carbon in borides are presented in Table I.

Place a 300-mg. sample in a porcelain boat and ignite in a combustion furnace (Figure 1) for 1 hour at 1000° to 1200° C. in a stream of oxygen. Absorb the carbon dioxide produced during the combustion in Ascarite. A blank determination should be made before a sample is ignited.

Table I

RESULTS OF THE ANALYSIS OF REFRACTORY BORIDES BY RECOMMENDED PROCEDURES

Boride	Metal,[a,b,c] %	Boron,[b,c] %	Carbon, %	Oxygen,[d] %	Other Metals,[e] %	Total,[f] %
HfB_2	86.56 (0.16)	9.14 (0.06)	0.13[g]	1.5	1.88[h]	99.2
MoB	87.03 (0.32)	10.17 (0.05)	0.21[g]	2.15	0.15	99.71
NbB_2	80.46 (0.13)	17.76 (0.08)	0.10[i]	0.33	0.58	99.23
ReB	93.19 (0.21)	6.69 (0.05)	0.02[g]	--	0.05	99.95
TaB_2	94.48 (0.17)	5.14 (0.03)	0.02[g]	0.06	< 0.01	99.70
ThB_4	82.83 (0.07)	14.70 (0.08)	2.30[i]	0.29	< 0.01	100.12
TiB_2	68.50 (0.13)	29.40 (0.05)	0.04[i]	1.11	0.55	99.60
WB	93.67 (0.06)	4.63 (0.06)	0.02[g]	0.72	0.62	99.66
UB_4	84.72 (0.06)	14.76 (0.07)	0.09[g]	0.05	0.05	99.67
VB_2	69.22 (0.11)	25.76 (0.06)	2.31[j]	1.4	0.19	98.9
ZrB_2	83.36 (0.18)	16.31 (0.07)	0.20[i]	0.14	0.10	100.11

[a] The major metallic constituent in the sample, corrected for spectrographically determined contaminants.

[b] Each entry is the average of ten determinations.

[c] The values in parentheses refer to the standard deviation of a single determination expressed as per cent constituent.

[d] Determined by M. E. Smith and coworkers, using a vacuum extraction technique.

[e] Determined by O. R. Simi and coworkers, using spectrographic methods.

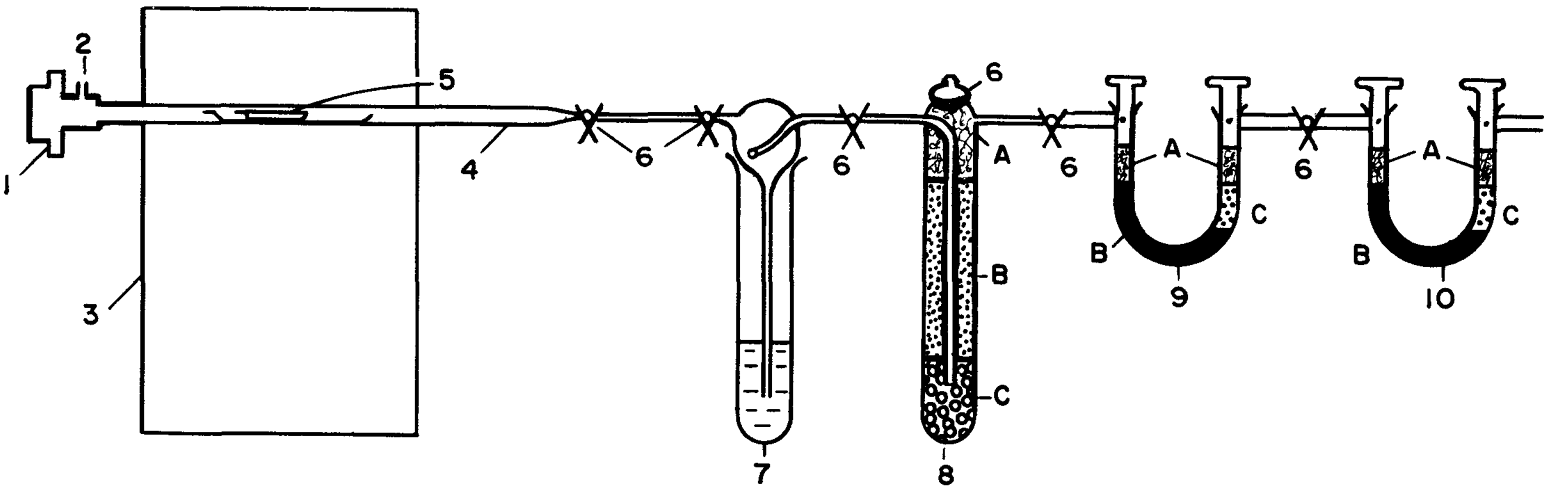
[f] Totals less than 100% can be partially attributed to the presence of undetermined elements, such as hydrogen and nitrogen.

[g] The average of two determinations.

[h] Spectrographic examination found 1.3% zirconium.

[i] The average of four determinations.

[j] The average of three determinations.



1 Screw-type brass cap and breech sealed with lead to the combustion tube

2 Nipple attachment to oxygen source

3 Variable electric furnace with sensitive controls permitting temperatures as high as 1200° C.

4 McDaniel high-temperature combustion tube, 30 × 1 inch (i.d.)

5 Alundum combustion boat, 5 × 3/4 × 7/16 inch, containing platinum boat

6 Dry ground-glass joint secured by a clamp

7 Bubbler containing concentrated sulfuric acid

8 Tower containing glass wool (A), magnesium perchlorate (B), and glass beads (C)

9 Absorption tube with lubricated stopcocks containing glass wool (A), 20-mesh Ascarite (B), and magnesium perchlorate (C)

10 Tare tube containing the same materials as the absorption tube

Figure 1. Detailed drawing of a combustion train for the determination of carbon.

3. THE ANALYSIS OF REFRACTORY CARBIDES

The Determination of Total Carbon in the Carbides of Hafnium, Molybdenum, Niobium, Tantalum, Thorium, Titanium, Tungsten, Uranium, Vanadium, and Zirconium, and the Mixed Carbides of Uranium with Hafnium, Niobium, Tantalum, or Zirconium

Numerous authors have determined total carbon in refractory carbides by igniting the sample in oxygen. The suggestion has been made (14) that the carbon dioxide produced be determined by titration after it is absorbed in a known amount of barium hydroxide solution. It was found more satisfactory in this Laboratory to absorb the carbon dioxide in a conventional Ascarite absorption tube. Bush, Higgs, and Rennles (4) studied the ignition of several carbides in the presence and absence of fluxes such as lead chromate or tin powder and compared the results obtained as a function of temperature. The conclusion was reached in this Laboratory that total carbon may be determined satisfactorily in HfC, Mo_2C, Nb_2C, NbC, Ta_2C, TaC, ThC, TiC, W_2C, WC, UC, U_2C_3, UC_2, VC, ZrC, Hf-U-C, Nb-U-C, Ta-U-C, and Zr-U-C by direct combustion of the sample in oxygen, using no fluxes, provided the sample is finely divided and a sufficiently high ignition temperature is used. A satisfactory temperature for combustion of the individual carbides is indicated in Table II. Figure 1 (at the end of Section 2) details the apparatus used.

The following procedure was used for the determination of total carbon in refractory carbides. Tables III and IV contain the results obtained.

Place the sample in a tared 5-gram platinum boat and ignite for 1 hour in a combustion furnace (Figure 1) in a stream of oxygen. The sample

Table II

RECOMMENDED COMBUSTION TEMPERATURES FOR CARBIDES

Carbide	Sample Size, mg.	Recommended Temperature, °C.
HfC	300 to 400	1000 to 1100
Mo_2C	300 to 400	1000 to 1100
Nb_2C	300 to 400	800 to 1150
NbC	150 to 200	800 to 1150
Ta_2C	300 to 400	1000 to 1100
TaC	300 to 400	1000 to 1100
ThC	300 to 400	1000 to 1100
TiC	75 to 125	1100 to 1200
W_2C	300 to 400	800 to 1200
WC	300 to 400	800 to 1200
UC	300 to 400	800 to 1100
U_2C_3	200 to 300	800 to 1100
UC_2	150 to 200	800 to 1100
VC	75 to 125	1000 to 1200
ZrC	150 to 200	1150 to 1200
Hf-U-C	300 to 400	1000 to 1100
Nb-U-C	200 to 300	800 to 1100
Ta-U-C	300 to 400	1000 to 1100
Zr-U-C	200 to 300	1150 to 1200

is placed in a tared boat so that a simultaneous determination of the metal content may be made.

Thorium carbide hydrolyzes rapidly in moist air and all handling of this material should be done in an inert atmosphere. Uranium carbide may be pyrophoric and extreme care should be used in the ignition of samples of finely divided uranium carbide.

The Determination of Total Carbon in Silicon Carbide

The Certificate of Analysis accompanying National Bureau of Standards' Standard Sample 112 (silicon carbide) details the procedures used at the bureau for the analysis of this material. Since an indication of the reliability of these methods has already been given, no additional study of these procedures was made in this Laboratory. The procedure used at the Bureau is given below.

Transfer an accurately weighed sample of approximately 0.25 gram of dry silicon carbide to a small, glass-stoppered, cylindrical weighing bottle. Add 2 grams of an accelerator, such as red lead (Pb_3O_4) or powdered metallic copper, and thoroughly mix by gentle shaking. Fill a combustion boat (approximately 5 x 3/4 inch) with RR Alundum (90 mesh) or Alfrax 15A (80 to 150 mesh), and by means of a 3/8-inch glass rod or other suitable tool, groove or furrow the bedding. Line the groove thinly with 0.5 gram of the accelerator.

Place the mixed sample thinly and evenly in the boat thus prepared, rinse the weighing bottle with a few small portions of Alundum or Alfrax, and cover the entire charge with a thin layer of the same. Place the boat and contents in a combustion furnace at 1050° to 1100° C., preheat for 1 minute, admit oxygen as in the determination of carbon in steel, and burn for 45 minutes. Absorb the carbon dioxide in Ascarite, cool, and weigh. Correct the result thus found by blank determinations for the furnace, oxygen, boat, bedding material, and accelerator.

The Determination of Graphite in the Carbides of Hafnium, Molybdenum, Niobium, Tantalum, Thorium, Titanium, Tungsten, Uranium, Vanadium, and Zirconium, and the Mixed Carbides of Uranium with Hafnium, Niobium, Tantalum, or Zirconium

The solubility of most carbides in mixtures of nitric and hydrofluoric acids makes it possible to determine free graphitic carbon in these materials. Graphite is insoluble in boiling concentrated nitric and hydrofluoric acids for periods of at least 30 minutes, and may be removed on a Monroe crucible after the carbide portion of the sample has dissolved. Several authors have suggested methods for the determination of graphite in one or more carbides based upon selective solution of the carbide with various acidic mixtures. The acidic mixtures given below for the determination of graphite in uranium carbide (10) and vanadium carbide (6) were suggested by earlier experimenters. The procedure which is given below was found to be satisfactory in this Laboratory for the determination of graphite in HfC, Mo_2C, Nb_2C, NbC, Ta_2C, TaC, ThC, TiC, W_2C, WC, UC, U_2C_3, UC_2, VC, ZrC, Hf-U-C, Nb-U-C, Ta-U-C and Zr-U-C. Results of analyses are given in Tables III and IV.

Place a sample containing no more than 30 mg. of graphite in a 100-ml. platinum crucible. Add 15 ml. of nitric acid and warm on a hot plate. Add hydrofluoric acid <u>dropwise</u> to maintain dissolution of the sample. When the carbide has dissolved, boil the sample for 30 minutes, adding nitric acid and a trace of hydrofluoric acid as required. Remove the insoluble graphite on a tared Monroe crucible, using vacuum, wash with dilute acid, then water, dry, and weigh. Scrape the major portion of the insoluble material from the crucible, weigh, and transfer to a platinum boat for combustion in oxygen at 1000° C. for 1 hour.

The amount of graphite in the insoluble material, and in the original sample, is calculated from the amount of carbon dioxide formed during combustion of the insoluble material. If the sample contains less than 1 mg. of insoluble material, the combustion may be omitted and the insoluble material is assumed to be totally graphite. Clean the Monroe crucible by heating in a mixture of chromium trioxide and perchloric acid until all graphite has dissolved.

Molybdenum carbide is dissolved with 1:2 nitric acid rather than with a mixture of nitric and hydrofluoric acids. Thorium and uranium carbides are dissolved with concentrated nitric acid rather than with mixed nitric and hydrofluoric acids. Add a trace of hydrofluoric acid to catalyze the decomposition of thorium carbide; however, avoid large amounts of hydrofluoric acid because of the formation of insoluble thorium tetrafluoride. Thorium carbide hydrolyzes rapidly in moist air and the sample should be weighed in an inert atmosphere. Vanadium carbide is dissolved by boiling for only 3 to 4 minutes with a 2:1 mixture of nitric acid to water.

The Determination of Graphite in Silicon Carbide

The Certificate of Analysis accompanying National Bureau of Standards' Standard Sample 112 (silicon carbide) details the procedure used at the Bureau for the determination of free carbon in silicon carbide. This procedure is given below.

Transfer 4 grams of dried silicon carbide to an empty combustion boat, ignite in oxygen at a temperature of 900° to 915° C. for 15 minutes, and absorb the carbon dioxide in Ascarite. Cool and weigh. Correct the result thus found by blank determinations for the furnace, oxygen, and boat.

The Determination of Total Metal in the Carbides of Hafnium, Niobium, Tantalum, Thorium, Titanium, Tungsten, Uranium, Vanadium, and Zirconium

Many experimenters have determined the metal content of simple carbides by igniting these materials to constant weight in oxygen. This technique is rapid, not subject to errors common to determinations involving several manipulations, and accurate unless the sample is contaminated with non-volatile impurities. For materials containing significant amounts of contaminants the methods of analysis recommended for the corresponding metal borides should be used. An alternative procedure is to use the combustion technique, determine the non-volatile impurities in the oxide by spectrographic techniques, and correct for these contaminants. Relatively pure samples of HfC, Nb_2C, NbC, Ta_2C, TaC, ThC, TiC, W_2C, WC, UC, U_2C_3, UC_2, VC, and ZrC can be analyzed for their metal content by the combustion technique presented below. Results for the analysis of carbides by this method are given in Table III.

Place the carbide sample in a tared 5-gram platinum boat and ignite for 1 hour in a combustion furnace in a stream of oxygen. Use the sample size and temperature recommended in Table II for HfC, Nb_2C, NbC, TaC, Ta_2C, ThC, TiC, and ZrC. A simultaneous determination of the carbon content of these materials may be made. Remove the boat and oxide from the furnace, cool, and weigh. The oxides formed are HfO_2, Nb_2O_5, Ta_2O_5, ThO_2, TiO_2, and ZrO_2. Thorium carbide hydrolyzes rapidly in moist air and all handling of this sample should be in an inert atmosphere.

The oxides of tungsten, uranium, and vanadium are slowly volatile at the temperatures recommended for the determination of carbon. Place the carbides of tungsten, uranium, or vanadium in a 20-ml. platinum crucible and ignite to constant weight at 800° C. in a muffle furnace. Some samples of uranium carbide are pyrophoric and care should be taken in igniting these materials. The oxides formed at 800° C. are WO_3, U_3O_8, and V_2O_5, respectively.

The Determination of Molybdenum in Molybdenum Carbide

Molybdic oxide is volatile at temperatures in excess of 550° C. Because ignition of graphite is slow at this temperature, combustion is not recommended for the determination of molybdenum in molybdenum carbide. The α-benzoinoxime technique suggested for the determination of molybdenum in molybdenum boride may also be used for the analysis of molybdenum carbide samples. Results for the analysis of a sample of Mo_2C by the following procedure are presented in Table III.

Place a 50- to 70-mg. sample in a covered 400-ml. beaker and dissolve by warming with 10 ml. of water and 5 ml. of nitric acid. When the sample is in solution, remove any insoluble graphite on a Whatman #42 filter paper, using vacuum filtration, dilute to 100 ml. with water, add 5 ml. of sulfuric acid, and cool to 5° to 10° C. Dilute the sample to 200 ml. with crushed ice (prepared from distilled water) and stir the sample while adding 10 ml. of 2% (in ethanol) α-benzoinoxime solution. Add some paper pulp and enough bromine water to tint the solution a light yellow. Add 2 or 3 ml. of α-benzoinoxime and allow the sample to age for 10 minutes.

Remove the precipitate on a Whatman #41-H filter paper, using vacuum filtration carefully, and wash with 200 ml. of a cold, freshly prepared solution containing 25 to 50 ml. of the prepared reagent and 10 ml. of sulfuric acid in 1 liter of solution. Ignite the precipitate in a tared platinum crucible at 500° C. and weigh as MoO_3.

The Determination of Silicon in Silicon Carbide

The Certificate of Analysis accompanying the National Bureau of Standards' Standard Sample 112 (silicon carbide) details the procedure used at the Bureau for the determination of total silicon in silicon carbide. This procedure is given below.

Mix 0.5 gram of silicon carbide, dried at 105° C., with 3.5 grams of potassium nitrate and 20 grams of sodium carbonate in a large platinum crucible which has been lined with 2 grams of sodium carbonate. Cover the crucible and fuse slowly. Dissolve the melt in water, add an excess of dilute sulfuric acid (1:1), evaporate to fumes of sulfuric acid, and determine silica in the customary manner, including any recovery from the R_2O_3 precipitate. Calculate the percentage of silicon using the factor 0.4672.

The Determination of Hafnium and Zirconium in Mixed Carbides of Uranium with Hafnium or Zirconium

The procedure described for the determination of zirconium in zirconium boride may also be used for the determination of hafnium and zirconium in mixed carbides of uranium with hafnium or zirconium. Results for the analysis of samples of hafnium-uranium carbide and zirconium-uranium carbide are given in Table IV.

Place a 200-mg. sample in a covered 250-ml. beaker and treat with 5 ml. of sulfuric acid and 2 to 3 ml. of 30% hydrogen peroxide. Warm the beaker on a hot plate and add additional hydrogen peroxide if necessary to dissolve the sample. After effervescense ceases, remove and rinse the cover glass, replace with a Speedyvap cover, and evaporate the sample to dryness.

Add 50 ml. of 3N hydrochloric acid plus 1 drop of 1% Aerosol solution. Heat the sample to boiling and add sufficient 0.1M p-bromomandelic acid to provide a 25% excess for the hafnium or zirconium present. Bring the solution to a boil and transfer to a steam bath for 30 minutes. Remove the precipitate on a Whatman #42 filter paper, using vacuum, and wash with 200 ml. of hot water. Ignite the precipitate at 1000° C. in a tared platinum crucible and weigh as ZrO_2 or HfO_2.

The Determination of Uranium in Mixed Carbides of Uranium with Hafnium or Zirconium

The volumetric procedure described previously for the determination of uranium in uranium boride may be used for the determination of uranium in samples of hafnium-uranium carbide and zirconium-uranium carbide. Results for the analysis of samples by this method are given in Table IV.

Dissolve a 500-mg. sample with 5 ml. of sulfuric acid and 5 ml. of nitric acid in a covered 250-ml. beaker. Warm until solution is complete, replace the cover glass with a Speedyvap cover, and evaporate to dryness twice with 5-ml. portions of perchloric acid. Fume the sample to dryness three times with 5-ml. portions of sulfuric acid, taking care to rinse the Speedyvap cover and beaker walls after each fuming.

Dissolve the sample with 50 ml. of 7.5% sulfuric acid and transfer to a Jones reductor. Oxidize the reduced sample for 10 minutes with an air bubbler (using a glass frit) and titrate without delay using a standard 0.1N ceric sulfate solution with ferroin indicator. Add 3 ml. of 0.1N ferric ammonium sulfate just before the end point to enhance the color change. Titrate a blank containing all reagents with each group of samples.

The Determination of Niobium, Tantalum, and Uranium in Mixed Carbides of Uranium with Niobium or Tantalum

The procedures described previously for the determination of niobium, tantalum, and uranium in borides were modified and the method outlined below may be used for the determination of niobium, tantalum, and uranium in niobium-uranium carbide and tantalum-uranium carbide. Results for the analysis of these samples are included in Table IV.

Place a 300-mg. sample in a 2-1/2-inch platinum dish, cover with an oversize platinum Speedyvap cover, and treat with 3 ml. of nitric acid followed by 1 ml. of hydrofluoric acid. Evaporate to dryness on a steam bath. Transfer with water to a 400-ml. beaker containing 2 grams of hydrated aluminum chloride and 5 ml. of hydrochloric acid. Add paper pulp and sufficient saturated sulfurous acid (freshly prepared) to bring the volume to 200 ml. Boil for 10 minutes, allow the precipitate to settle for 10 minutes, and remove the precipitate on a Whatman #42 filter paper, using vacuum filtration. Wash the paper and precipitate with 200 ml. of hot sulfurous acid. Ignite the precipitate in a tared platinum crucible at 1000° C. and weigh as Nb_2O_5 or Ta_2O_5.

Transfer the filtrate from the niobium or tantalum determination to a large beaker and reduce the volume to 100 ml. Transfer to a 250-ml. beaker and evaporate to dryness on a hot plate or steam bath. Fume the sample to dryness with 5 ml. of nitric acid and then four times with 5-ml. portions of sulfuric acid, taking care to wash the Speedyvap cover glass and beaker walls after each fuming. Dissolve the sample with 50 ml. of 7.5% sulfuric acid and transfer to a Jones reductor. Oxidize the sample with an air bubbler (using a glass frit) and titrate without dealy, using a standard 0.1N ceric sulfate solution with ferroin indicator. Add 3 ml. of 0.1N ferric ammonium sulfate just before the end point to enhance the color change. Titrate a blank containing all reagents with each group of samples.

The Determination of Nitrogen in the Carbides of Hafnium, Niobium Tantalum, Titanium, Tungsten, Uranium, Vanadium, and Zirconium, and the Mixed Carbides of Uranium with Hafnium, Niobium, Tantalum, or Zirconium

The Dumas technique has long been used for the determination of total nitrogen in organic matter. This method is based upon oxidation of a sample with copper oxide and collection of the nitrogen in the sample, as nitrogen gas, over a potassium hydroxide solution. Two authors (5) reported the determination of nitrogen in uranium carbides by the same method. It was found in this Laboratory that the Dumas technique can be used to determine nitrogen in HfC, Nb_2C, NbC, Ta_2C, TaC, TiC, W_2C, WC, UC, U_2C_3, UC_2, VC, ZrC, Hf-U-C, Nb-U-C, Ta-U-C, and Zr-U-C. The following procedure is satisfactory for the determination of nitrogen in these materials. Results of analyses using this method are presented in Tables III and IV.

Mix a sample containing not more than 5 mg. of nitrogen with 2 to 3 grams of copper oxide (40 to 80 mesh) and quantitatively transfer to a small porcelain boat (88 x 12 x 8 mm.). Cover the sample with a thin layer of copper oxide. Transfer the boat to the combustion tube of the Dumas apparatus (Figure 2). Attach the carbon dioxide supply and then the azotometer, and sweep the system with 400 ml. of carbon dioxide. The leveling bulb of the azotometer should be lowered and Stopcock D opened during the sweeping operation. Raise the leveling bulb of the azotometer, close Stopcock D, and continue passing gas through the system until 100 ml. of gas has a blank of less than 0.01 ml. in the azotometer. Close Stopcock B and open Stopcock C. Level the azotometer at 0.00 milliliter, close Stopcock D, and lower the azotometer bulb to the bench top.

Bring the temperature of the permanent section of the combustion tube to 700° C. with Tube Furnace B. Ignite the sample with Tube Furnace A at 900° to 1000° C. for the carbides of niobium, tantalum, titanium, tungsten, uranium, and vanadium, and the mixed carbides of uranium with niobium or tantalum. A temperature of 1050° C. is required for the complete combustion of hafnium and zirconium carbides and the mixed carbides of uranium with hafnium or zirconium. After 15 minutes sweep the system with 250 ml. of carbon dioxide at a bubble rate which permits the carbon dioxide to be absorbed before the bubbles reach the surface of the solution within the azotometer. Microbubbles should be obtained after 250 ml. of gas have passed through the system. Close Stopcock C, raise the azotometer bulb, disconnect furnaces, and admit a positive pressure of carbon dioxide on the combustion tube while it cools. Allow at least 30 minutes for the azotometer to reach equilibrium and level the bulb.

Measure the volume of gas collected, the temperature of the potassium hydroxide solution in the azotometer, and the atmospheric pressure (barometer). A blank determination should be made every day that a sample analysis is made and should be subtracted from the volume obtained with a sample. Subtract 1.1% from the net volume of gas as a correction for the adhesion of potassium hydroxide solution to the azotometer wall, the vapor pressure of the potassium hydroxide, and the temperature reduction of the barometric reading from room temperature to 0° C. The per cent nitrogen is calculated from the volume, temperature, and pressure of gas collected. One milliliter of nitrogen at 0° C. and 760 mm. pressure weighs 1.2505 mg.

Table III

RESULTS OF THE ANALYSIS OF SIMPLE REFRACTORY CARBIDES BY RECOMMENDED PROCEDURES

Carbide	Metal,[a,b] %	Total Carbon,[b] %	Graphite, %	Nitrogen, %	Oxygen,[c] %	Other Metals,[d] %	Total,[e] %
HfC	92.06[f] (0.08)	5.28[f] (0.02)	0.24[g]	1.05[h]	0.19	1.60[i]	100.18
Mo_2C	94.52[f] (0.27)	5.57[f] (0.02)	< 0.05[h]	--	0.31	0.05	100.45
NbC	88.38[f] (0.04)	11.15[f] (0.03)	0.20[g]	0.20[g]	0.21	< 0.01	99.94
TaC	93.55[f] (0.03)	6.15[f] (0.02)	0.04[g]	0.02[j]	0.05	0.35	100.12
ThC	93.97[k] (0.06)	4.59[k] (0.03)	< 0.10[j]	--	--	1.33	99.89
TiC	77.68[f] (0.05)	19.34[f] (0.04)	2.04[h]	1.88[j]	0.79	0.08	99.77
WC	93.08[f] (0.04)	5.89[f] (0.02)	< 0.05[j]	0.01[j]	0.60	< 0.01	99.58
UC	94.91[f] (0.06)	5.14[f] (0.01)	< 0.05[j]	--	--	0.03	100.08
VC	80.01[f] (0.04)	19.05[f] (0.04)	3.00[g]	0.68[j]	0.18	< 0.01	99.92
ZrC	91.72[f] (0.05)	8.27[f] (0.02)	0.02[j]	0.01[j]	0.06	0.10	100.16

[a] The major metallic constituent in the sample, corrected for spectrographically determined contaminants.

[b] The values in parentheses refer to the standard deviation of a single determination expressed as per cent constituent.

[c] Determined by M. E. Smith and coworkers, using a vacuum extraction technique.

[d] Determined by O. R. Simi and coworkers, using spectrographic methods.

[e] Totals less than 100% can be partially attributed to the presence of undetermined elements, such as hydrogen.

[f] The average of ten determinations.

[g] The average of four determinations.

[h] The average of three determinations.

[i] Primarily zirconium.

[j] The average of two determinations.

[k] The average of six determinations.

Table IV

RESULTS OF THE ANALYSIS OF MIXED REFRACTORY CARBIDES BY RECOMMENDED PROCEDURES

Carbide	Uranium,[a] %	Other Major Metal,[a] %	Total Carbon, %	Graphite, %	Nitrogen, %	Oxygen,[b] %	Other Metals,[c] %	Total,[d] %
Hf-U-C	85.97[e]	7.83 Hf[f]	4.84[e]	--	0.03[e]	0.25	0.98	99.90
Nb-U-C	73.61[g]	19.50 Nb[g]	6.36[f]	0.44[e]	0.02[e]	0.10	< 0.01	99.59
Ta-U-C	44.64[h]	49.45 Ta[h]	5.01[i]	< 0.02[e]	0.01[e]	0.04	0.36	99.81
Zr-U-C	46.50[g]	43.83 Zr[g]	8.01[g]	--	--	--	1.35	99.69

[a] Corrected for spectrographically determined contaminants.

[b] Determined by M. E. Smith and coworkers, using vacuum extraction technique.

[c] Determined by O. R. Simi and coworkers, using spectrographic methods.

[d] Totals less than 100% can be partially attributed to the presence of undetermined elements, such as hydrogen.

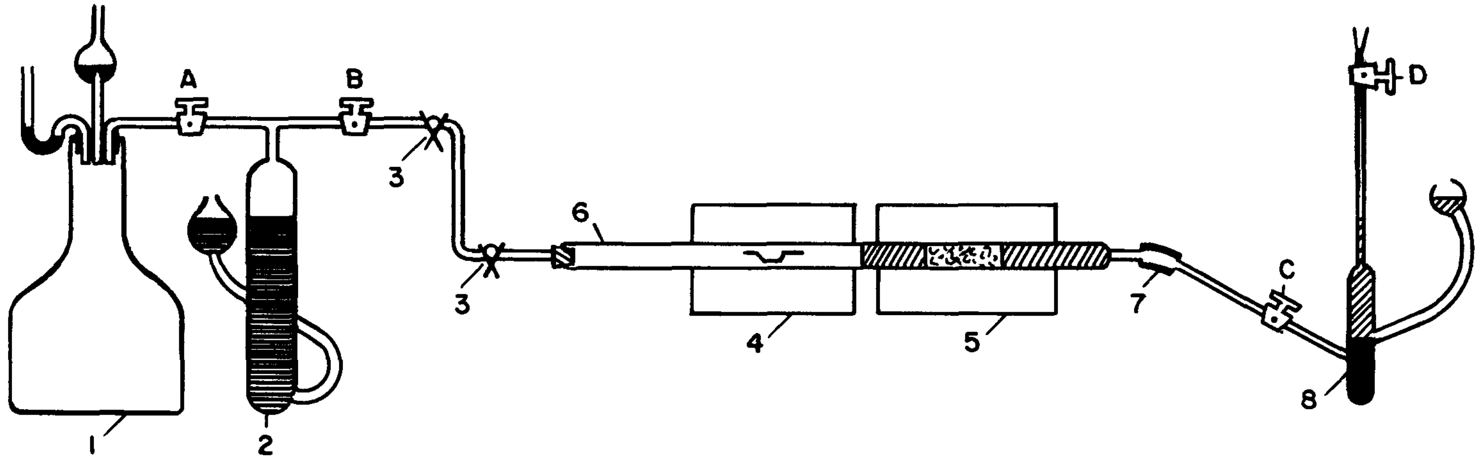
[e] The average of two determinations.

[f] The average of three determinations.

[g] The average of four determinations.

[h] The average of eight determinations. The standard deviation of a single uranium determination is 0.15% uranium and the standard deviation of a single tantalum determination is 0.06% tantalum.

[i] The average of six determinations. The standard deviation of a single carbon determination is 0.02% carbon.



1 Dry ice carbon dioxide generator equipped with bubbler and manometer

2 100-ml. gasometer and leveling bulb filled with mercury

3 Dry ground-glass joint secured by a clamp

4 Tube Furnace A with variable temperature control

5 Tube Furnace B with variable temperature control

6 Quartz combustion tube, 900 × 16 mm. (i.d.) with a 6 mm. (i.d.) tip. The permanent filling consists of 130 mm. of wire-form copper oxide followed by 80 mm. of copper wire and 200 mm. of wire-form copper oxide. Ignited asbestos separates the various sections of the permanent filling. About 100 mm. of the second copper oxide section should extend beyond Tube Furnace B.

7 Heavy rubber tubing

8 5-ml. nitrometer and leveling bulb filled with 50% potassium hydroxide solution

A, B, C, D Lubricated stopcocks

Figure 2. Detailed drawing of the Dumas apparatus for the determination of nitrogen

4. THE ANALYSIS OF REFRACTORY NITRIDES

The Determination of Nitrogen in the Nitrides of Hafnium, Niobium, Tantalum, Titanium, Uranium, and Zirconium

Many methods are reported in the literature for the determination of nitrogen in various refractory nitrides. Most frequent are modifications of the Kjeldahl and Dumas procedures. In general, the Kjeldahl method requires long periods of digestion and determines only nitride nitrogen in the sample. The Dumas method determines total nitrogen and experience in this Laboratory has shown that it is definitely superior to the Kjeldahl procedure for the determination of total nitrogen in refractory carbides and nitrides. Prior to this investigation no exhaustive study had been made of the precision and accuracy of the Dumas technique when used to determine nitrogen in refractory materials.

The procedure discussed earlier for the determination of nitrogen in refractory carbides may also be used for the determination of nitrogen in HfN, NbN, TaN, TiN, UN, and ZrN. Ignition temperatures of 900° to 1000° C. are used for the nitrides of niobium, tantalum, titanium, and uranium, while 1050°C. should be used for hafnium and zirconium nitrides. Results of analyses of these materials are presented in Table V.

The Determination of Nitrogen in Boron Nitride and Silicon Nitride

The Dumas method was found to be unsatisfactory for the determination of nitrogen in boron nitride and silicon nitride because of the small sample size permitted and the high ignition temperature required. A caustic fusion technique has recently been reported for the determination of small amounts of nitrogen in metals (1). A modification of this method was found to be satisfactory for the determination of nitrogen in BN and Si_3N_4. Results for the determination of nitrogen in boron nitride and silicon nitride by the following procedure are presented in Table V.

Place a 100-mg. sample in a 4-inch Alundum boat, cover with 5 grams of sodium hydroxide pellets, and place an Alundum cover on the boat. Place the boat in a quartz liner which is inserted in a combustion tube. (Figure 3 gives the dimensions of the tube and liner.) Attach a receiver containing 15 ml. of a saturated solution of boric acid and 6 drops of mixed indicator in 100 ml. of water, and a trap containing 6 drops of indicator and 5 ml. of a saturated solution of boric acid in 100 ml. of water. The mixed indicator contains 100 mg. of bromcresol green and 100 mg. of methyl red in 100 ml. of ethanol.

Bubble a slow stream of nitrogen gas through the system while the furnace is warming to a temperature of 600° to 700° C. (Use 700° C. for the ignition of silicon nitride.) Sweep the tube with nitrogen gas for 1 hour or until all the ammonia in the system has been absorbed in the receiver. If the indicator in the trap changes color, reduce the rate at which the nitrogen sweep gas is being bubbled through the system. Titrate the ammonia in the receiver plus trap with a standard 0.1N hydrochloric acid solution. Subtract a blank determination for all reagents plus sweep gas.

The Determination of Boron in Boron Nitride

A simplification of the Blumenthal (2) method for the determination of boron in metal borides was found to be satisfactory for the determination of boron in boron nitride. Results for the analysis of BN by the following procedure are given in Table V.

Mix 75 mg. of sample with 1 gram of sodium carbonate in a 20-ml. platinum crucible. Cover and heat slowly until a good fusion melt is obtained. Cool the crucible, add 100 to 200 mg. of sodium nitrate, and continue the fusion until the melt is clear. Note particularly that any material on the crucible cover has fused. Transfer the crucible and cover to a covered 600-ml. beaker containing 50 ml. of water and 5 ml. of hydrochloric acid.

When leaching is complete, remove the crucible and cover, dilute the sample to 300 ml. with water, and make the sample slightly basic with a 20% solution of sodium hydroxide. Acidify with hydrochloric acid until 1 drop of acid turns litmus paper pink. Cover the beaker with a watch glass and boil the sample for 7 to 10 minutes. The litmus paper should be held on the bottom of the beaker with a stirring rod to prevent bumping. Note particularly that the solution remains acidic during the boiling. If sufficient carbon dioxide is expelled to make the solution slightly basic, reacidify with 1 drop of hydrochloric acid.

Rapidly cool the covered beaker to 50° to 60°C. in a cold water bath, add 6 drops of indicator, and titrate the sample without delay with a 0.05N sodium hydroxide solution. Note the buret reading at the first tinge of green color, add 8 grams of mannitol, and continue the titration until the first tinge of purple is noted. The amount of base between the two end points is equal to the boric acid in the sample. The mixed indicator contains 100 mg. of methyl red, 100 mg. of bromcresol green, and 1 gram of phenolphthalein per 100 ml. of ethanol. Analyze a blank determination, with the same amount of all reagents, with each group of samples.

The Determination of Total Metal in the Nitrides of Hafnium, Niobium, Tantalum, Titanium, Uranium, and Zirconium

Several workers have determined the metal content of simple nitrides by igniting these materials to constant weight in oxygen. This technique is rapid, not subject to errors common to determinations involving several manipulations, and accurate, unless the sample is contaminated with non-volatile impurities. For materials containing significant amounts of contaminants the methods of analysis recommended for the corresponding metal borides should be used. An alternative procedure is to use the combustion technique and to determine the non-volatile impurities in the oxide by spectrographic techniques and correct for these contaminants. Relatively pure samples of HfN, NbN, TaN, TiN, UN, and ZrN can be analyzed for their metal content by the combustion technique presented below. Results for the analysis of nitrides by this method are given in Table V.

Place a 300-mg. sample in a tared 5-gram platinum boat and ignite for 1 hour in a combustion furnace in a stream of oxygen. A simultaneous determination of the carbon content of these materials may be made. Use an ignition temperature of 1000° to 1200° C. for the nitrides of hafnium, niobium, tantalum, and titanium; 800° C. for uranium nitride; and 1150° to 1200° C. for zirconium nitride. Some samples of uranium nitride are pyrophoric and extreme care should be used in igniting these materials. Remove the boat and oxide from the furnace, cool, and weigh. The oxides formed are HfO_2, Nb_2O_5, Ta_2O_5, TiO_2, U_3O_8, and ZrO_2, respectively.

The Determination of Silicon in Silicon Nitride

The Certificate of Analysis accompanying the National Bureau of Standards' Standard Sample 112 (silicon carbide) details the procedure used at the Bureau for the determination of total silicon in silicon carbide. This procedure was adapted in this Laboratory to the determination of silicon in Si_3N_4. Results for the analysis of a sample of silicon nitride by the method given below are presented in Table V.

Mix 0.5 gram of silicon nitride with 3.5 grams of potassium nitrate and 20 grams of sodium carbonate in a large platinum crucible which has been lined with 2 grams of sodium carbonate. Cover the crucible and fuse slowly. Dissolve the melt in 50 ml. of water in a covered 250-ml. beaker, add an excess of 1:1 sulfuric acid, and evaporate to fumes of sulfur trioxide.

Cool, add 75 ml. of 1:4 hydrochloric acid, and remove the dehydrated silica on a Whatman #42 filter paper, using vacuum filtration. Wash alternately five times with 1:4 hydrochloric acid and cold water, and finally once with cold water. Ignite the precipitate in a clean tared platinum crucible at 1100° C. for 1 hour, weigh, treat with hydrofluoric and sulfuric acids in the usual manner, and reweigh to determine the weight of pure silica in the sample.

The Determination of Total Carbon in the Nitrides of Hafnium, Niobium, Tantalum, Titanium, Uranium, and Zirconium

The combustion apparatus (Figure 1) discussed previously for the determination of total carbon in refractory carbides may also be used to determine total carbon in refractory nitrides. The following procedure was found to be satisfactory for the determination of total carbon in HfN, NbN, TaN, TiN, UN, and ZrN. Results of analyses of these materials are presented in Table V.

Place a 300-mg. sample in a tared 5-gram platinum boat and ignite for 1 hour in the combustion furnace in a stream of oxygen. A simultaneous determination of the metal content of these materials may be made. Use an ignition temperature of 1000° to 1200° C. for the nitrides of hafnium, niobium, tantalum, and titanium; 800° C. for uranium nitride; and, 1150° to 1200° C. for zirconium nitride. Some samples of uranium nitride are pyrophoric and extreme care should be used in igniting these materials. Absorb the carbon dioxide produced during the combustion in Ascarite. A blank determination should be made before a sample is ignited.

The Determination of Total Carbon in Boron Nitride and Silicon Nitride

The Certificate of Analysis accompanying the National Bureau of Standards' Standard Sample 112 (silicon carbide) details the procedure used at the Bureau for the determination of total carbon in silicon carbide. This same procedure was used for the determination of total carbon in boron nitride and silicon nitride. Results for the analysis of samples of BN and Si_3N_4 by the following technique are presented in Table V.

Transfer an accurately weighed sample of approximately 300 mg. to a small, glass-stoppered, cylindrical weighing bottle. Add 2 grams of an accelerator, such as Pb_3O_4 (C and CO_2 free) or powdered metallic copper, and thoroughly mix by gently shaking. Fill a combustion boat (approximately 5 x 3/4 inch) with RR Alundum (90 mesh) or Alfrax 15A (80 to 150 mesh) and by means of a 3/8-inch glass rod or other suitable tool, groove or furrow the bedding. Line the groove thinly with 0.5 gram of the accelerator.

Place the mixed sample thinly and evenly in the boat thus prepared, rinse the weighing bottle with a few small portions of Alundum or Alfrax, and cover the entire charge with a thin layer of the same. Place the boat and contents in a combustion furnace at 1050° to 1100° C. for 45 minutes. Absorb the carbon dioxide in Ascarite, cool, and weigh. Correct the result thus found by blank determinations for the furnace, oxygen, boat, bedding material, and accelerator.

The Determination of Graphite in the Nitrides of Hafnium, Niobium, Tantalum, Titanium, Uranium, and Zirconium

The solubility of most nitrides in mixtures of nitric and hydrofluoric acids makes it possible to determine free graphitic carbon in these materials. Graphite is insoluble in boiling concentrated nitric and hydrofluoric acids for periods of at least 30 minutes, and may be removed on a Monroe crucible after the nitride portion of the sample has dissolved. The procedure which is presented below was found to be satisfactory for the determination of graphite in HfN, NbN, TaN, TiN, UN, and ZrN. Results of analyses are given in Table V.

Place a 1-gram sample in a 100-ml. platinum crucible. Add 15 ml. of nitric acid and warm on a hot plate. Add hydrofluoric acid, dropwise, to maintain dissolution of the sample. When the nitride has dissolved, boil the sample for 30 minutes, adding nitric acid and a trace of hydrofluoric acid as needed. Remove the insoluble graphite on a tared Monroe crucible, using vacuum, wash with dilute acid and then water, dry, and weigh. Scrape the major portion of the insoluble material from the crucible, weigh, and transfer to a platinum boat for combustion in oxygen at 1000° C. for 1 hour.

The amount of graphite in the insoluble material, and in the original sample, is calculated from the amount of carbon dioxide formed during combustion of the insoluble material. If the sample contains less than 1 mg. of insoluble material, it is assumed to be totally graphite and the combustion step is omitted. Uranium nitride is dissolved with concentrated nitric acid rather than a mixture of nitric and hydrofluoric acids.

Table V

RESULTS OF THE ANALYSIS OF REFRACTORY NITRIDES BY RECOMMENDED PROCEDURES

Nitride	Metal,[a,b] %	Nitrogen,[b] %	Total Carbon, %	Graphite, %	Oxygen,[c] %	Other Metals,[d] %	Total,[e] %
BN	42.34[f] (0.12)	53.41[f] (0.07)	0.16[g]	--	1.91	0.02	97.84
HfN	90.27[f] (0.08)	7.45[f] (0.07)	0.08[h]	< 0.02[g]	0.23	2.12[i]	100.15
NbN[j]	86.81[f] (0.14)	11.53[f] (0.10)	0.12[h]	< 0.02[g]	0.54	0.44	99.44
Si_3N_4	63.08[g]	24.85[k]	4.47[g]	--	3.4	1.82	97.6
TaN[l]	93.10[f] (0.11)	6.28[f] (0.03)	0.04[h]	< 0.02[g]	0.19	< 0.01	99.61
TiN	76.58[f] (0.12)	21.40[f] (0.10)	0.15[h]	--	0.35	0.75	99.23
UN	92.16[h] (0.07)	7.42[m] (0.05)	0.08[g]	< 0.02[g]	0.05	0.08	99.79
ZrN	83.88[n] (0.07)	10.87[h] (0.06)	0.35[h]	< 0.02[g]	0.41	3.79[o]	99.30

[a] The major metallic constituent in the sample, corrected for spectrographically determined contaminants.

[b] The values in parentheses refer to the standard deviation of a single determination expressed as per cent constituent.

[c] Determined by M. E. Smith and coworkers, using vacuum extraction technique.

[d] Determined by O. R. Simi and coworkers, using spectrographic methods.

[e] Totals less than 100% can be partially attributed to the presence of undetermined elements, such as hydrogen.

[f] The average of ten determinations.

[g] The average of two determinations.

[h] The average of four determinations.

[i] Primarily zirconium.

[j] The theoretical nitrogen content of this sample from weight gain on nitridation is 11.52% nitrogen.

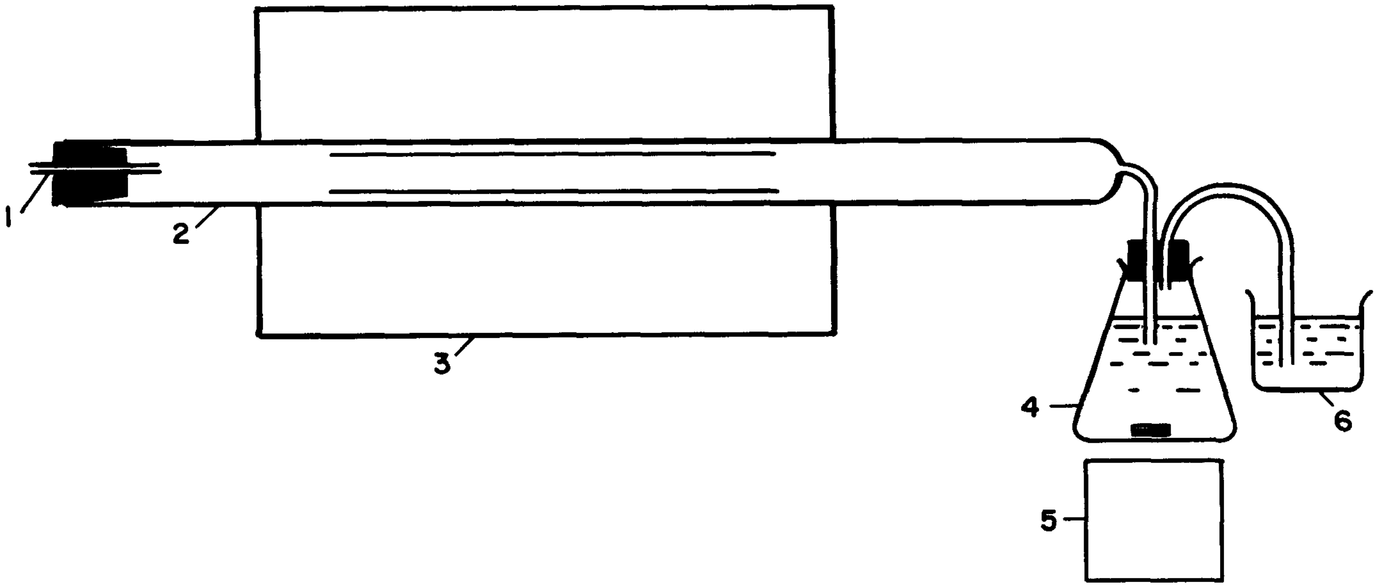
[k] The average of three determinations.

[l] The theoretical nitrogen content of this sample from weight gain on nitridation is 6.24% nitrogen.

[m] The average of eight determinations.

[n] The average of six determinations.

[o] Primarily hafnium.



1 Nitrogen inlet tube

2 Quartz combustion tube, 30 × 1-1/8 inches (i.d.). The quartz liner is 12 × 1 inch (o.d.)

3 Tube furnace with variable temperature control

4 250-ml. Erlenmeyer flask containing a magnetic stirring bar (receiver)

5 Magnetic stirrer

6 250-ml. beaker (trap)

Figure 3. Detailed drawing of the caustic fusion apparatus for the determination of nitrogen.

5. THE ANALYSIS OF REFRACTORY SILICIDES

The Determination of Silicon in the Silicides of Molybdenum, Rhenium, Tantalum, Titanium, Tungsten, Vanadium, and Zirconium

The following general method is recommended for the determination of silicon in the silicides of molybdenum, rhenium, tantalum, titanium, tungsten, vanadium, and zirconium. Table VI contains results of analyses of samples of $MoSi_2$, Re_3Si, $TaSi_2$, Ti_5Si_3, WSi_2, VSi_2, and $ZrSi_2$ by this method.

Mix a 100-mg. sample with 1 gram of sodium carbonate in a 20-ml. platinum crucible. Cover and heat slowly until a good fusion melt is obtained. Cool, add 100 to 200 mg. of sodium nitrate, and continue the fusion until a clear melt is obtained. Note particularly that any material on the crucible cover has fused. Transfer the crucible and cover to a covered 250-ml. beaker containing 50 ml. of water and 5 ml. of sulfuric acid.

When solution of the sample is complete, remove the crucible and cover and add 5 ml. of sulfuric acid. Replace the cover glass with a Speedyvap cover, and heat until the water has been removed and strong fumes of sulfur trioxide have been evolved for 1 hour. Cool, add 75 ml. of 1:4 hydrochloric acid, warm on a hot plate until soluble salts are in solution, and immediately remove the insoluble silica on a Whatman #42 filter paper, using vacuum filtration. Wash alternately five times with 1:4 hydrochloric acid and water, and finally once with water.

Ignite the precipitate in a clean tared platinum crucible for 1 hour at 1100° C. Weigh the crucible and precipitate, treat with 2 ml. of hydrofluoric acid and 2 drops of sulfuric acid, and evaporate to dryness in the usual manner. Ignite at 1100° C. for 1 hour and reweigh the crucible. The weight of pure silica is the difference between the two crucible weights.

Tantalum and tungsten coprecipitate with silica, and a modification of this procedure must be used for tantalum and tungsten silicides. The final ignition of insoluble material should be done in a covered platinum crucible, using care to avoid loss of tantalum or tungsten. The ignition of tungsten oxide should be at 800° C. rather than 1100° C.

The Determination of Molybdenum in Molybdenum Silicide

A method based on the precipitation of molybdenum with α-benzoinoxime (7) was used for the determination of molybdenum in $MoSi_2$. Results of analyses by this procedure are presented in Table VI.

Place a 100-mg. sample in a 2-1/2-inch platinum dish equipped with an oversize platinum Speedyvap cover. Treat the sample with 2 ml. of hydrofluoric acid and add nitric acid dropwise until solution is complete. Rinse the cover with water, add 10 ml. of 1:1 sulfuric acid, and reduce the volume of the sample on a steam bath and hot plate until strong fumes of sulfur trioxide are evolved.

Transfer to a 400-ml. beaker, add 10 ml. of 1:1 sulfuric acid, and dilute to 100-ml. with water. Cool the sample to 5° to 10° C., dilute with crushed ice (prepared from distilled water) to 200 ml., and stir the sample while adding 10 ml. of 2% (in ethanol) α-benzoinoxime solution. Add some paper pulp and enough bromine water to tint the solution a light yellow. Add 2 or 3 ml. of α-benzoinoxime solution and allow the sample to age for 10 minutes.

Remove the precipitate on a Whatman #41-H filter paper and wash with 200 ml. of a cold, freshly prepared solution containing 25 to 50 ml. of the prepared reagent and 10 ml. of sulfuric acid per liter of solution. Vacuum filtration may be used with care. Ignite the precipitate in a tared platinum crucible at 500° C. and weigh as MoO_3.

The Determination of Rhenium in Rhenium Silicide

Tetraphenylarsonium chloride (15,16) was used as a precipitating agent for rhenium in a sample of silicon-deficient rhenium silicide. This material had a composition corresponding to Re_3Si and was analyzed by the following procedure. Results for the analysis of rhenium silicide are presented in Table VI.

Place a 1- to 1.5-gram sample in a 250-ml. Erlenmeyer flask. Add 5 ml. of water followed by 2 ml. of hydrofluoric acid. Attach, via a ground-glass joint, a 12-inch air condenser and add 5 ml. of nitric acid. Warm gently on a steam bath, adding more nitric acid if required to effect complete solution of the sample. Transfer the dissolved sample to a volumetric flask and remove an aliquot containing 50 to 60 mg. of rhenium to a 100-ml. beaker. Add 1.2 ml. of 1:1 sulfuric acid and 2 ml. of hydrochloric acid and warm the uncovered beaker on a steam bath until constant volume is obtained.

Wash the walls of the beaker with 8 ml. of water, add 20 ml. of concentrated ammonium hydroxide, warm on a steam bath until bubbles appear, and add 20 ml. of recently filtered 1% tetraphenylarsonium chloride solution containing 100 grams of sodium chloride per liter. Cover the beaker with a watch glass and allow the sample to age overnight. Remove the precipitate on a tared 30-ml. sintered glass crucible with medium porosity, using vacuum filtration. Wash with a saturated solution of tetraphenylarsonium perrhenate. Dry to constant weight at 110° C. The factor for rhenium is 0.2940.

The Determination of Tantalum in Tantalum Silicide

The following procedure was developed for the determination of tantalum in tantalum silicide. Results obtained for the analysis of a sample of $TaSi_2$ by this technique are presented in Table VI.

Place a 100-mg. sample in a tared 20-ml. platinum crucible, treat with 2 ml. of nitric acid and 2 drops of hydrofluoric acid. Immediately cover the crucible with a platinum cover and swirl the crucible to mix the acids. An exothermic reaction will begin within a few seconds. When the reaction rate has subsided, warm on a steam bath for 5 minutes, followed by 2 or 3 minutes digestion on a hot plate. If undissolved material remains, treat with 1 or 2 drops of hydrofluoric acid. When solution is complete, rinse the cover, add 8 drops of sulfuric acid, and evaporate to dryness on a steam bath.

Transfer the covered crucible to a hot plate and finally to a burner, increasing the temperature *very* slowly to avoid loss of tantalum. Final ignition of the tared crucible and cover is to constant weight at 1000° C. in a muffle. The tantalum is weighed as Ta_2O_5. Correct for spectrographically determined impurities in the oxide.

The Determination of Titanium in Titanium Silicide

Precipitation with cupferron was found to be satisfactory for the determination of titanium in titanium silicide. Results obtained for a sample of Ti_5Si_3 by the following procedure are given in Table VI.

Place a 100-mg. sample in a 2-1/2-inch platinum dish and add 10 ml. of water. Cover the dish with a platinum Speedyvap cover (oversize) and slowly add 1 ml. of hydrofluoric acid. Treat with nitric acid, dropwise, warming if necessary to dissolve the sample. When the sample is in solution, rinse the cover, add 10 ml. of 1:1 sulfuric acid, and evaporate to constant volume on a steam bath. Transfer to a hot plate and evaporate to fumes of sulfur trioxide for 15 minutes.

Cool, add water, and transfer to a 400-ml. beaker containing 40 ml. of 1:1 sulfuric acid. Dilute to 200 ml. with crushed ice (prepared from distilled water) and add 25 ml. of 6% cupferron. Stir in some paper pulp, age for 5 minutes, and remove the precipitate on a Whatman #42 filter paper, using vacuum filtration. Wash the precipitate with a cold solution containing 100 ml. of sulfuric acid and 1.5 grams of cupferron per liter. Ignite the precipitate at 1000° C. and weigh as TiO_2.

The Determination of Tungsten in Tungsten Silicide

The following procedure was used for the determination of tungsten in tungsten silicide. Results obtained for the analysis of a sample of WSi_2 by this technique are presented in Table VI.

Place a 100-mg. sample in a covered, tared 20-ml. platinum crucible and treat the sample with 2 ml. of nitric acid. Add hydrofluoric acid dropwise, gently warming if necessary, until solution of the sample is complete. Rinse and remove the platinum cover and evaporate the sample to dryness on a steam bath. Ignite the sample for 10 minutes on a hot plate, followed by 1 hour at 800° C. Weigh the tungsten as WO_3. Correct for spectrographically determined impurities in the oxide.

The Determination of Vanadium in Vanadium Silicide

The following procedure was developed for the determination of vanadium in vanadium silicide. Results obtained for the analysis of a sample of VSi_2 by this technique are shown in Table VI.

Mix 100 mg. of sample with 1 gram of sodium carbonate in a 20-ml. platinum crucible. Cover and heat slowly until a good fusion melt is obtained. Cool the crucible, add 100 to 200 mg. of sodium nitrate, and continue the fusion until the melt is clear. Note particularly that any material on the crucible cover has fused. Transfer the crucible and cover to a covered 250-ml. beaker containing 50 ml. of water.

When leaching is complete, remove the crucible and cover, add 20 ml. of perchloric acid, and fume almost to dryness on a hot plate. Treat the cooled sample with 25 ml. of water and enough ammonium hydroxide to dissolve any vanadium pentoxide which has precipitated. Carefully add 100 ml. of 1:1 sulfuric acid while cooling in a water bath. Titrate with a standard 0.1N ferrous sulfate solution, using a Beckman pH meter and platinum and calomel electrodes. The platinum electrode should be dipped into a solution of chromic acid for 30 seconds and then rinsed just prior to the titration.

The Determination of Zirconium in Zirconium Silicide

The following procedure was developed for the determination of zirconium in zirconium silicide by precipitation with p-bromomandelic acid (13). Results for the analysis of $ZrSi_2$ are presented in Table VI.

Place a 100-mg. sample in a 2-1/2-inch platinum dish and cover with an oversize platinum Speedyvap cover. Add 1 ml. of nitric acid and sufficient hydrofluoric acid, dropwise, to dissolve the sample completely. Rinse the cover and add 10 ml. of 1:1 sulfuric acid. Expel water and nitric and hydrofluoric acids on a steam bath and evaporate to dryness on a hot plate.

Dissolve the sample with 20 ml. of 1:1 hydrochloric acid and transfer to a 250-ml. beaker. Adjust the volume to 50 ml. containing 12 ml. of hydrochloric acid. Add 1 drop of 1% Aerosol solution, heat the sample to boiling, and add 50 ml. of 0.1 M p-bromomandelic acid. Bring the solution to a boil and transfer to a steam bath for 30 minutes. Remove the precipitate on a Whatman #42 filter paper, using vacuum filtration, and wash with 200 ml. of hot water. Ignite the precipitate at 1000° C. in a tared platinum crucible and weigh as ZrO_2.

Table VI

RESULTS OF THE ANALYSIS OF REFRACTORY SILICIDES BY RECOMMENDED PROCEDURES

Silicide	Metal,[a,b] %	Silicon,[b] %	Oxygen,[c] %	Other Metals,[d] %	Total,[e] %
$MoSi_2$	62.35[f] (0.13)	35.52[f] (0.12)	0.7	0.7	99.3
Re_3Si	97.05[f] (0.22)	2.96[f] (0.05)	--	< 0.01	100.01
$TaSi_2$	73.41[f] (0.12)	24.59[g] (0.15)	0.38	1.01	99.39
Ti_5Si_3	68.23[g] (0.06)	25.14[f] (0.09)	0.72	2.50	96.59
WSi_2	77.28[f] (0.15)	21.84[f] (0.09)	0.03	0.37	99.52
VSi_2	44.75[f] (0.07)	45.14[f] (0.11)	0.06	10.0	100.0
$ZrSi_2$	59.76[f] (0.15)	38.90[f] (0.17)	--	0.46	99.12

[a] The major metallic constituent in the sample corrected for spectrographically determined contaminants.

[b] The values in parentheses refer to the standard deviation of a single determination expressed as per cent constituent.

[c] Determined by M. E. Smith and coworkers, using vacuum extraction technique.

[d] Determined by O. R. Simi and coworkers, using spectrographic methods.

[e] Totals less than 100% can be partially attributed to the presence of undetermined elements, such as carbon, nitrogen, and hydrogen.

[f] The average of ten determinations.

[g] The average of eight determinations.

6. SUMMARY

Methods have been presented for the analysis of 41 refractory borides, carbides, nitrides, and silicides. An evaluation of the accuracy and the precision of these techniques was also made. In most cases the summation of the determined constituents in the sample is very close to 100%. For several samples this summation is significantly lower; however, this is attributed to the presence of undetermined contaminants such as hydrogen, nitrogen, or carbon.

Boron was determined in the borides of hafnium, molybdenum, niobium, rhenium, tantalum, thorium, titanium, tungsten, uranium, vanadium, and zirconium by removal of the metal ion through precipitation with barium carbonate or barium hydroxide, followed by titration of boric acid in the carbonate-free filtrate with a standard sodium hydroxide solution. Hafnium and zirconium were determined in their respective borides by precipitation with p-bromomandelic acid. α-Benzoinoxime was used to precipitate molybdenum in molybdenum boride. The hydrolytic precipitation of niobium and tantalum with sulfurous acid was used to determine these metals in their borides. Rhenium was determined in rhenium boride by precipitation with tetraphenylarsonium chloride. Ethyl oxalate was used to precipitate thorium in thorium boride. Titanium in titanium boride was determined by precipitation from mildly acidic solution as the hydrated oxide. The determination of tungsten in tungsten boride was accomplished by precipitation of tungstic acid in the presence of cinchonine. Uranium was determined in uranium boride by titration with ceric sulfate. A standard ferrous sulfate solution was used to titrate vanadium in vanadium boride. The carbon content of boride samples was determined by ignition of the samples in oxygen and absorption of the carbon dioxide formed.

The total carbon content of the carbides of hafnium, molybdenum, niobium, silicon, tantalum, thorium, titanium, tungsten, uranium, vanadium, and zirconium, and mixed carbides of uranium with hafnium, niobium, tantalum, or zirconium was determined by ignition of the samples in oxygen and absorption of the carbon dioxide formed. A simultaneous determination of the metal content was made for the carbides of hafnium, niobium, tantalum, thorium, titanium, and zirconium, by ignition to a stable weighing form. Vanadium, tungsten, and uranium were determined in carbide samples by ignition at a lower temperature than that used for the determination of carbon. Molybdenum was determined in molybdenum carbide by precipitation with α-benzoinoxime. Silicon was determined in silicon carbide by dehydration of silica. p-Bromomandelic acid was used to determine hafnium and zirconium in hafnium-uranium carbide or zirconium-uranium carbide, following which the uranium was titrated with ceric sulfate. Sulfurous acid precipitation was found to be satisfactory for the determination of niobium and tantalum in niobium-uranium carbide and tantalum-uranium carbide, following which the uranium content was determined by titration with ceric sulfate. The graphite content of the carbide samples (with the exception of silicon carbide) was determined by solution of the carbide with various acidic mixtures and removal of the insoluble graphite on a Monroe curcible, following which it was dried, weighed, and ignited in oxygen. Graphite in silicon carbide was determined by combustion in oxygen at 900° C. The Dumas technique was found to be applicable to the determination of nitrogen in the carbides of hafnium, niobium, tantalum, titanium, tungsten, uranium, and zirconium.

The Dumas technique was used for the determination of nitrogen in the nitrides of hafnium, niobium, tantalum, titanium, uranium, and zirconium. A caustic fusion procedure was used to determine nitrogen in boron nitride and silicon nitride. Total carbon was determined in nitrides by ignition in oxygen and absorption of the carbon dioxide formed. The graphite content of the nitrides of hafnium, niobium, tantalum, titanium, uranium, and zirconium was determined by solution of the nitride with various acidic mixtures and removal of the insoluble graphite on a Monroe crucible. The metal content of nitrides other than boron nitride and silicon nitride was determined by ignition to a stable weighing form in oxygen. Boron was determined in boron nitride by titration with a sodium hydroxide solution after the sample had been fused with sodium carbonate and nitrate. Silicon was determined in silicon nitride by dehydration of silica.

Silica was determined in the silicides of molybdenum, rhenium, tantalum, titanium, tungsten, vanadium, and zirconium by dehydration in a sulfuric acid media. α-Benzoinoxime was used to precipitate molybdenum in molybdenum silicide. Rhenium was determined in rhenium silicide by precipitation with tetraphenylarsonium chloride. Tantalum and tungsten were determined in their silicides by ignition to the oxide following volatilization of silica as the fluoride. Titanium was determined in titanium silicide by precipitation with cupferron. A standard solution of ferrous sulfate was used to titrate vanadium in vanadium silicide. p-Bromomandelic acid was used as a precipitant for zirconium in samples of zirconium silicide.

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