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CHEMISTRY

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UNITED STATES ATOMIC ENERGY COMMISSION

THE CHEMICAL ANALYSIS OF ZIRCONIUM
AND ZIRCALOY METALS

By
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January 31, 1957

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AND ZIRCALOY METALS

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January 31, 1957

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INTRODUCTION

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Previous to the time the Atomic Energy Commission became interested in zirconium metal, the analytical chemist's concern with this element had been confined to methods for the quantitative analysis for zirconium in minerals, refractories, and a few alloys. Details concerning a number of reliable methods for the separation and gravimetric determination of zirconium are described in standard analytical texts.^(1,2,3) Other texts^(4,5,6) describe gravimetric, colorimetric, and turbidimetric methods of analysis which may be applied to the determination of impurity elements found in zirconium.

Soon after the start of the AEC Metallurgy Program, the need for chemical and spectrographic methods of analysis for impurities in zirconium metal became evident. For the purpose of developing reliable chemical and spectrographic methods of analysis, a zirconium analytical program was organized. Eleven laboratories participated in this cooperative undertaking.

Argonne National Laboratory (ANL)
Battelle Memorial Institute (BMI)
Foote Mineral Company (Foote)
Institute for Atomic Research, Iowa State College,
Ames, Iowa (Ames)
Los Alamos Scientific Laboratory (LASL)
MIT Metallurgical Project (MIT)
Bureau of Mines, Albany, Oregon (Bu Mines)
Westinghouse Atomic Power Division (WAPD)
Carbide and Carbon Chemicals Company, Y-12 Plant (Y-12)
Oak Ridge National Laboratory (ORNL)
AEC New Brunswick Laboratory (NBL)

Initially, the program was directed by C. J. Rodden of the AEC New Brunswick Laboratory. Subsequently, the responsibility for this program was transferred to the MIT Metallurgical Project, and the coordination of this work was assumed by the author.

Samples of crushed, hydrided zirconium were prepared by the MIT Metallurgical Project and were distributed to the various cooperating laboratories for analysis. The AEC New Brunswick Laboratory supplied a series of oxide samples for spectrographic standards. The Y-12 Production Laboratory prepared extremely pure oxides of hafnium, and zirconium for the preparation of standards by the individual laboratories.

As a result of the cooperative effort of these laboratories, methods are now available for the quantitative determination of most of the impurities found in commercial zirconium. Chemical and spectrographic methods are used in analysis for elements other than hafnium. Spectrographic, x-ray-fluorescence, and pile-activation techniques have been applied to the analysis for hafnium.

Problems Associated with Analysis of Zirconium-Base Metals

Sampling of Zirconium Metal

A prerequisite to any reliable analysis is a sample that is representative of the material to be analyzed. This is especially true in the case of zirconium-sponge metal in which the impurities exhibit considerable segregation.

Gilbert and Morrison⁽⁷⁾ investigated sampling techniques for sponge zirconium. The metal was crushed to pass a 3/8 inch screen and -20-mesh fines were rejected. A number of 3-lb samples were obtained by splitting, and each sample was briquetted in a 4-inch diameter die with a hydraulic press. Chips were obtained by drilling and by turning on a lathe. The most representative sample was found to be made up of chips obtained on a lathe by cutting from the cylindrical surface after discarding the surface cut. This method was found to be satisfactory for sampling an arc-melted ingot. To prevent appreciable pickup of nitrogen and oxygen, the metal was cut at low speed and cooled by directing a jet of air at the point of contact of the cutting tool with the zirconium.

When plates of zirconium are to be sampled, punchings of small diameter may be taken from various sections of the piece. If possible solid pieces of metal should be taken as samples for oxygen and nitrogen analysis.

Preparation of Samples for Analysis

Methods for obtaining samples in the proper form for chemical and spectrographic analysis are discussed by Rodden,⁽⁸⁾ Petretic,⁽⁹⁾ and Read.⁽¹⁰⁾ Samples for spectrographic analysis may be in the form of oxide, fine metal chips, solid metal sections, or acid solutions of the metal. Usually zirconium metal is dissolved in hydrofluoric acid alone or mixed with another mineral acid. For the determination of carbon the metal should be in the form of fine chips; however, solid pieces of metal are best when analyzing for oxygen and nitrogen. Oxides for spectrographic analysis are obtained by ignition of metal chips in an atmosphere of air, oxygen, or a mixture of oxygen with an inert gas.

Proper precautions must be taken to prevent any contamination of the sample during this oxidation treatment. The chips may be ignited without contamination if they are placed in a platinum boat and are heated in a quartz tube or quartz-lined muffle furnace.

After ignition, the oxide is ground to a fine powder in a suitable mortar. The mortar should be carefully selected so as not to contaminate the oxide with one of the elements which is of interest to the analyst. Mortars of relatively pure zirconium metal have been used in some laboratories. These mortars, however, require frequent machining of their grinding surfaces. Other commercial mortars are available such as agate, synthetic sapphire, mullite, tungsten carbide, and boron carbide. All of these mortars, however, will contaminate the zirconium oxide with one or more elements.

Problems Associated with Chemical Analysis of Zirconium-Base Metals

Chemical analysis for small amounts of other elements in zirconium require, as a rule, special techniques to eliminate interferences due to the presence of large quantities of zirconium. Interference of zirconium

is eliminated by the use of complexing agents or by the quantitative separation of the element in question from zirconium. Separation may be obtained with or without the presence of a complexing agent.

Use of Complexing Agents

An example of the use of complexing agents is the addition of tartrates or citrates to a zirconium solution in which iron is to be determined by a colorimetric method. These reagents prevent precipitation of the zirconium at the pH required for this determination.

Separation of Zirconium From Other Elements Which Are Present in Minor or Trace Amounts

Precipitation

Numerous methods for the separation of zirconium by precipitation have been reported in standard texts,^(1,2,3) but in most cases evidence is not available as to whether microgram quantities of other elements are retained in the zirconium precipitate. Eberle⁽¹¹⁾ reported complete separation of aluminum after precipitation of zirconium from an acid solution by the addition of salicylic acid.

Extraction

Freund⁽¹²⁾ obtained complete separation of aluminum by extracting zirconium cupferrate from an acid solution with chloroform but found an appreciable amount of aluminum in the reagent. Bane⁽¹³⁾ used a very pure grade of cupferron and obtained a much lower reagent blank. Most separations, however, involve the extraction of a complex of the element of interest, the dithizonate of copper for example, with an organic solvent leaving the zirconium in the aqueous solution.

Volatilization

Zirconium can be volatilized as ZrCl_4 by heating the metal in a stream of dry HCl gas at temperatures above 450°C . This reaction has been used to determine oxygen in the metal.^(14,15,16)

Ion-Exchange

Freund and Miner⁽¹⁷⁾ obtained complete separation of aluminum in amounts between 10 micrograms and 38 milligrams from 1 gram of zirconium by passing solutions which were 0.06 M in HCl and 0.8 M in HF through an ion exchange column of Dowex-1 resin.

Chemical Analysis for Impurities and Alloying Elements in Zirconium-Base Metals

Chemical methods have been applied to the quantitative analysis for a great many elements found as impurities in zirconium or as alloying elements in Zircaloy. A list of 23 of these elements is given in Table I with the approximate minimum concentration (ppm) of each element which may be determined by chemical analysis.

TABLE I
Approximate Minimum Concentrations of Various Elements
Which May Be Determined by Chemical Analysis

<u>Metallic Elements</u>			
<u>Element</u>	<u>Minimum conc. ppm</u>	<u>Element</u>	<u>Minimum conc. ppm</u>
Aluminum	10	Molybdenum	5
Cadmium	5	Nickel	5
Chromium	5	Tin	500
Copper	5	Titanium	5
Iron	10	Tungsten	10
Lead	10	Vanadium	5
Magnesium	50	Zinc	10
Manganese	5		
<u>Nonmetallic Elements</u>			
Boron	0.1	Phosphorus	20
Carbon	10	Silicon	10
Chlorine	5		
<u>Gaseous Elements</u>			
Oxygen	50	Hydrogen	1
Nitrogen	5		

NOTE: For each element listed above, one or more procedures are given in detail and other methods are summarized.

ALUMINUM

Eberle⁽¹⁸⁾ applied a fluorimetric method to the determination of aluminum in zirconium. The zirconium was separated from acid solution by precipitation with salicylic acid. Aluminum was determined in an aliquot portion of the filtrate by measurement of its fluorescence under ultraviolet light when a solution of the dye Pontachrome Blue Black R, the sodium salt of 4-sulfo-2-hydroxy- α -naphthalene-azo- β -naphthol, is added. The use of this reagent for qualitative and quantitative determination of aluminum had been reported by White and Lowe⁽¹⁹⁾ and by Weissler and White.⁽²⁰⁾ Eberle⁽¹⁸⁾ developed the fluorescence by adding the dye to a potassium-sodium acetate-acetic acid solution (pH 4.8) at 80°C. He reported that fluoride ions must be absent and only microgram amounts of zirconium should be present. Colored ions such as iron, copper, chromium, nickel, and cobalt, masked the fluorescence. Titanium and vanadium destroyed the fluorescence.

Freund and Miner⁽¹⁷⁾ obtained a solution of zirconium which was 0.06 M in HCl and 0.08 in HF and passed the solution through an ion-exchange column of Dowex-1 resin to obtain almost complete separation of the zirconium, which was retained on the resin while aluminum passed through the column. The iron and small amount of zirconium left in the eluate were removed by a cupferron-chloroform extraction, and the aluminum was determined by the aluminon colorimetric method.

Goward⁽²¹⁾ of Westinghouse Atomic Power Division separates aluminum from zirconium by the ion-exchange technique of Freund and Miner.⁽¹⁷⁾ Interfering impurities and/or alloying elements are separated by mercury cathode electrolysis. Aluminum is determined in the resulting solution by extraction of the aluminum 8-hydroxyquinoline complex with chloroform, and measurement of the fluorescence intensity of the extract.

Details of this method are described below with references to earlier publications of Freund and Miner,⁽¹⁷⁾ Tullo,⁽²²⁾ and Goon.⁽²³⁾

Method of Westinghouse Atomic Power Division

Apparatus

1. Polyethylene or polystyrene exchange column 50 cm long by 2.5 cm diameter fitted to Fisher filtrator.
2. Polyethylene beakers, 400 ml.
3. Platinum beakers with covers, 250 or 400 ml if available.
4. Eberbach "Dynacath" mercury cathode apparatus.
5. Fisher Nefluoro-Photometer or other fluorescence measuring instrument.
6. Separatory funnels--pearshape, 125 ml.
7. Volumetric flasks, 50 and 250 ml.
8. Polyethylene reagent bottles, 0.5 to 2 liters.
9. Polyethylene or polystyrene graduate cylinders 10 and 100 ml.

Reagents

10. Ion exchange water--prepared by passing distilled water through a 40 x 4 cm polystyrene column of Rohm and Haas MB-1 ion exchange resin.
11. Perchloric acid (72% solution).
12. Hydrochloric acid (3 N solution)--prepared from concentrated hydrochloric acid and ion exchange water.
13. Elutriant solution--to 855 ml of ion exchange water in a polyethylene bottle, add 18 ml of 3 N hydrochloric acid and 27 ml of 48% hydrofluoric acid.
14. Dowex-1--strong base anion exchange resin.
15. Ammonium carbonate (20% solution)--dissolve 100 gm of ammonium carbonate in 500 ml of ion exchange water. Extract the amount required for each day's work with 10 ml portions of 8-hydroxyquinoline solution until no color forms in the chloroform layer.
16. 8-hydroxyquinoline (0.5% solution)--dissolve 5 gm of 8-hydroxyquinoline in 1 liter of Baker reagent grade chloroform.
17. Anhydrous sodium sulfate.
18. Stock aluminum solution (10.0 γ /ml)--dissolve 0.1763 gm of $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24 \text{H}_2\text{O}$ in 1 liter of 0.1 N sulfuric acid.

19. Sodium fluorescein solution--dissolve 1.33 mg of fluorescein in 10 ml of water and 0.5 ml of 50% sodium hydroxide; dilute to 1 liter with distilled water.

20. (a) Fluorescence Calibration Curve

Pipette 0, 5, 10, 15 and 20 ml (0, 50, 100, 150, and 200 γ) of the standard aluminum solution into platinum beakers. Add 350 ml of elutriant solution and 10 ml of 72% perchloric acid. Cover the beakers and take to fumes of perchloric acid. Fume strongly for one minute. Cool and wash down the sides and covers of the beakers. Repeat the fuming process twice. Approximately 4 to 5 ml of perchloric acid should remain in each beaker. Transfer the contents of the beakers to 250 ml volumetric flasks and dilute to the mark with distilled water. Transfer 25 ml aliquots (0, 5, 10, 15, and 20 γ) of each solution to small beakers. Add 20 ml of ammonium carbonate solution to each to bring the pH to 8.3 ± 0.2 . Extract each solution twice with two 10 ml portions of 8-hydroxyquinoline solution by shaking for two minutes in 125 ml separatory funnels. Drain the extracts into 50 ml volumetric flasks containing 1.0 gm of anhydrous sodium sulfate. Make the solutions to volume with 8-hydroxyquinoline solution and shake for 30 seconds to allow the sodium sulfate to absorb any water present. Using the Fisher Nefluoro-Photometer with blank center, 430 right and 525 left filters, balance the fluorescein generating solution against the 20 γ standard at 100% T. Read the 0, 5, 10, and 15 γ standards, rebalancing against the 20 γ standard after each reading. Subtract the blank reading and plot γ of aluminum versus percent T.

20. (b) Preparation of Ion Exchange Column

Shake approximately 50 gm of Dowex-1 resin twice with 200 ml of wash solution prepared from 1710 ml of distilled water, 108 ml of 3 N hydrochloric acid and 54 ml of 48% hydrofluoric acid. Allow the resin to settle and pour off the washings. Place a cotton plug in the bottom of the column and transfer the resin to the column. The height of resin in the column should be about 12 inches. Wash the column with about 1 liter of the above solution. In order to determine if the column

is free of aluminum, pass through 350 ml of elutriant solution. Add 10 ml of 72% perchloric acid and take to fumes in a covered platinum beaker. Fume strongly for 1 minute, cool and wash down the sides and cover of the beaker with ion exchange water. Repeat the fuming process twice, finally leaving 4 to 5 ml of perchloric acid in the beaker. Transfer to a 250 ml volumetric flask and dilute to the mark with ion exchange water. Determine aluminum content in a 25 ml aliquot by extraction with 8-hydroxyquinoline as in paragraph 20(a). If the aluminum content does not exceed that found in 350 ml of the same elutriant solution not passed through the column, then the column has been washed free of aluminum contamination. If this is not the case, washing is continued until no further aluminum contamination is encountered.

20. (c) Treatment of Samples

Weigh a 1.00 gm sample of the metal or alloy into a platinum or plastic beaker and add 15 to 20 ml of ion exchange water. Dissolve the sample by adding 3.0 ml of 48% hydrofluoric acid slowly from a plastic burette or pipette. Add 2.0 ml of 3 N hydrochloric acid and dilute to 100 ml with ion exchange water to make the solution 0.06 N in hydrochloric and 0.8 N in hydrofluoric acids. Pass this solution through the resin column without suction, collecting the effluent in a polyethylene beaker. Elute the aluminum from the column by passing through 250 ml of elutriant solution. Do not attempt to speed up the process by application of suction. Transfer the 350 ml of solution to a platinum beaker and add 100 ml of 72% perchloric acid. Evaporate the solution to fumes of perchloric acid and fume strongly for 1 minute. Wash down the sides and cover of the beaker with ion exchange water and repeat fuming twice. Approximately 4 to 5 ml of perchloric acid should remain. Add ion exchange water and transfer to the mercury cathode apparatus keeping the solution volume below 50 ml. Electrolyze for 1.5 hours at 7 amperes, washing down the electrodes and beaker with a minimum of ion exchange water at least twice during the electrolysis (see Note). Transfer to a 250 ml volumetric flask and dilute to the mark with ion exchange water. Carry a blank through the entire process with the exception of passage through the ion exchange column.

Determine aluminum in 25 ml aliquots of the sample and blank solutions by extraction with 8-hydroxyquinoline as in paragraph 20(a). A 25 ml aliquot covers aluminum contents up to 200 ppm.

Regenerate the column by passing through 3 N hydrochloric acid until no zirconium hydroxide precipitates upon neutralization. Remove the hydrochloric acid by washing with distilled water until silver nitrate solution gives only a faint turbidity. Finally, wash the column twice with ion exchange water.

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NOTE: Amounts of iron greater than 40 γ in the entire sample or 4 γ in the 25 ml aliquot interfere with the final aluminum determination by quenching the fluorescence. In order to be certain that iron is not in excess of this amount, the solutions should be spot tested near the end of the mercury cathode electrolysis as follows. In two spot plate depressions, place, respectively, one drop of the solution from the electrolysis cell and one drop of a standard iron solution containing 0.5 γ per ml. Add to each solution one drop of 10% hydroxylamine hydrochloride, one drop of bathophenanthroline (33 mg in 100 ml of ethanol) and one drop of 20% ammonium acetate. The iron content of the sample solution is acceptable only if it shows considerably less color than the standard iron solution.

CADMIUM

E. J. Center⁽²⁴⁾ and associates developed a colorimetric for the determination of cadmium in zirconium metal. Details of this method have been reported by Read.⁽²⁵⁾ Rodden⁽⁸⁾ describes a polarographic method which was used at the New Brunswick Laboratory. A 1.0 gram sample was dissolved in 2 ml of HF plus 4 ml of H₂O. After solution was complete, 0.5 ml of HCl and a few crystals (0.25 gram) of boric acid were added. The solution was polarographed using high sensitivity. Bismuth, copper, and lead may be determined in the same solution. The method of Center and associates is described below.

Method of Battelle Memorial Institute
E. J. Center

Weigh a 1.0 gram sample and transfer to a platinum dish. Dissolve in a solution containing 25 ml H₂O, 5 ml H₂SO₄, and 5 ml HF (48%). Fume gently to expel traces of fluoride ion. Cool, add 20 ml H₂O and warm to dissolve salts. Add 20 ml of 25% citric acid solution and neutralize with a 50% NaOH solution.

Add 10 ml of 10% NaOH solution and extract with successive 5 ml portions of dithizone solution (20 mg/1000 ml of chloroform) until no trace of the cadmium complex (pink) is indicated in the chloroform layer.

Wash the chloroform extracts with two 25 ml portions of distilled water and discard the water layers.

Extract the chloroform layer with two 25 ml portions of 0.05 N sulfurous acid solution (approximately pH 3).

Wash the combined sulfurous acid solution with 10 ml chloroform, discard the chloroform layer, add 10 ml of 10% NaOH solution and re-extract with dithizone until complete extraction of cadmium is indicated. Dilute the combined extracts to 50 ml, filter through a dry paper, and read in a 1-cm cell at 520-millimicron wavelength against chloroform as a reference. A blank must be carried through all steps of the procedure.

Calculate the cadmium in the sample by referring to a calibration curve prepared by carrying 5 to 40 micrograms of cadmium through the above procedure.

CHROMIUM

Volumetric methods for the determination of chromium have been described in analytical chemistry texts.^(1,3) These methods may be applied to the analysis for the minor amounts of this element which are present in zirconium alloys. The diphenylcarbazide colorimetric method has been found most satisfactory for the determination of low amounts of chromium in zirconium metal. This method is based on the intense reddish purple complex formed when hexavalent chromium reacts with diphenylcarbazide in slightly acid solutions. Proper conditions for color development, stability, and interference by other ions are discussed by Sandell⁽⁴⁾ and Rodden.⁽⁵⁾

Two slightly different diphenylcarbazide colorimetric procedures for the determination of chromium in zirconium are described by Read.⁽²⁵⁾ In each method, the color is developed in 0.2 N H_2SO_4 solution. Davis⁽²⁶⁾ oxidized the chromium by boiling with a few drops of 0.1 N KMnO_4 solution and developed color in 50-ml volume. Bane⁽¹³⁾ added 5 drops of 1% AgNO_3 solution and 5 ml of 0.002 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution and then heated just under boiling for 20 minutes to oxidize the chromium. The diphenylcarbazide color was developed in 25-ml volume.

Bauman⁽⁴⁶⁾ has determined chromium in zirconium metal and Zircaloy solutions containing hydrofluoric acid. The metal was dissolved in a dilute sulfuric acid solution by the addition of 48% HF solution a few drops at a time. Boric acid was added to complex the fluoride and the diphenylcarbazide color was developed in aliquot solutions containing 50 micrograms or less of chromium.

The methods of Bauman⁽⁴⁶⁾ and Bane⁽¹³⁾ may be applied to the analysis for chromium in zirconium or Zircaloy. Details of these methods are described.

Method of Nuclear Metals, Inc.
F. A. Bauman

Reagents

Silver nitrate solution (AgNO_3) 1%--dissolve 1 gram of AgNO_3 in H_2O and dilute to 100 ml.

Ammonium persulfate solution [$(\text{NH}_4)_2\text{S}_2\text{O}_8$] 10%--dissolve 10 grams of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 100 ml H_2O .

Diphenylcarbazide solution--0.4% in 95% ethyl alcohol, prepared immediately before use.

Boric acid solution (H_3BO_3) 0.85 M.

Sulphuric acid (H_2SO_4)--concentrated.

Hydrofluoric acid--concentrated.

Procedure

Weigh a sample of ca 1.0 gram and place in a platinum dish. Cover the sample with H_2O , add 1 ml H_2SO_4 , and HF a few drops at a time as is required to obtain solution of the zirconium. Heat if necessary to obtain complete solution of the sample and add 25 ml of H_3BO_3 solution. Transfer the solution to a 250 ml volumetric flask, dilute to the mark with H_2O and mix. Pipette aliquots to contain 50 micrograms or less of chromium and not more than 0.1 gram of zirconium into 150 ml beakers. Dilute to 30-35 ml volume, add 9 drops of H_2SO_4 , 3 glass beads, and cautiously heat to boiling. Add 5 drops of the AgNO_3 1% solution, 5 ml of the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 10% solution, and boil cautiously for 10 minutes. Cool the solution to room temperature, transfer to a 50 ml volumetric flask and dilute to ca 45 ml. Treat sample solutions individually from this point on. Add by means of a pipette 1 ml of diphenylcarbazide solution, dilute to the mark with H_2O and mix.

Determine the optical density immediately in 1 cm cells in a Beckman DU Spectrophotometer at a wavelength of 545 millimicrons with H_2O in the reference cell. Correction must be made for a reagent blank treated in the same manner as the sample.

From the corrected optical density, the amount of chromium present is determined by reference to a previously constructed standard curve.

Standard Curve

Acid solutions containing 0, 5, 10, 20, 30, 40, 50, and 60 micrograms of chromium are carried through the entire procedure. From the corrected optical densities obtained construct a standard curve of optical density versus micrograms of chromium.

$$\frac{\text{Corrected OD} \times \text{Standard Curve Factor } (\gamma/\text{OD})}{\text{Weight of Aliquot (grams)}} = \text{ppm Cr}$$

Method of Argonne National Laboratory R. W. Bane

Dissolution Procedure

Dissolve several grams of sample in a platinum beaker in dilute H_2SO_4 and the addition of a few ml HF. After complete solution of the sample, evaporate to fumes of SO_3 , cool, wash down the sides of the beaker with H_2O and repeat the fuming process twice to eliminate the fluoride ion. Add sufficient H_2O to dissolve the salts (heat to obtain complete solution if necessary). Transfer the cooled solution to a 200 ml volumetric flask, dilute to the mark and mix. Record the amount of H_2SO_4 used for dissolution of the sample so that an aliquot for the chromium determination can be taken which, when diluted to 25 ml, will result in a solution of $\sim 0.2\text{--}0.4 \text{ N}$ in H_2SO_4 . Retain the remaining solution for the determinations of iron, nickel, manganese, and vanadium.

Determination

To an aliquot of the sample solution (see above) in a 50 ml beaker add 5 drops 1% AgNO_3 solution and 5 ml 0.002 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution. Dilute to about 25 ml volume and heat near boiling temperature for 20 minutes. Transfer the solution to a 25 ml volumetric flask and cool in an ice bath. Add 1 ml of 0.4% solution of diphenylcarbazide in ethyl

alcohol. Dilute to volume, mix, and determine percent transmission at 540 millimicrons comparing against a reagent blank. Obtain the amount of chromium present from a previously prepared transmittance--concentration curve. It is necessary to read each solution immediately after development of color, in order to prevent an unexplained deepening of the color on standing, thus causing erratic results.

Aliquots taken for analysis should contain no more than 0.1 gram zirconium, and between 1 and 14 micrograms chromium. The lower detection limit of this method is 5 ppm of chromium in sample.

COPPER

Copper has been determined with good success by the dithizone and diethyldithiocarbamate methods described by Sandell.⁽⁴⁾

Recently, two new reagents that are specific for copper have been produced commercially. Breckenridge⁽²⁸⁾ described one of these reagents, 2,2'-diquinoline, which forms no complex with iron but forms an intensely purple colored complex with the cuprous ion. Hoste⁽²⁹⁾ gave the name "cuproine" to this reagent and found it to be specific for copper, ten times as sensitive as diethyldithiocarbamate, and one-fourth as sensitive as dithizone.

Smith and McCurdy⁽³⁰⁾ describe 2,9-dimethyl-1,10-phenanthroline, a new reagent which is specific for the spectrophotometric determination of copper. This reagent was named "neo-cuproine". It is soluble in ethyl alcohol and it was found that its complex with copper will be extracted at pH 3 to 10 in amyl, isoamyl, or n-hexyl alcohol with no metal ion interference. Luke and Campbell⁽³¹⁾ tested the effect of 56 different elements on the extraction of the copper complex and found no interference. Gahler⁽³²⁾ investigated the application of neo-cuproine to the determination of copper in steels, ferroalloys, and ores. He extracted the copper (I) neo-cuproine complex with chloroform in the presence of small amounts of ethyl alcohol at pH 4-6.

Goward and Wilson⁽³³⁾ applied the Gahler method to the determination of copper in zirconium and Zircalloys. To an acid solution of the metal 10 ml 20% tartaric acid was added, and the pH adjusted to between 4 and 6 with NH_4OH . After transferring the solution to a separatory funnel, a solution of hydroxylamine hydrochloride is added to reduce the copper, 10 ml of a 0.1% solution of neo-cuproine in ethyl alcohol is added, and the cuprous complex is extracted with chloroform.

Read et al⁽³⁴⁾ add the reagents to an acid solution ($\text{pH} < 1$) and after standing 10 minutes adjust the pH to 5.0 with ammonium hydroxide. The cuprous complex is then extracted with chloroform.

Method of Nuclear Metals, Inc.
H. M. Read, E. Pollock, and E. B. Read

Reagents (a)

HF - 48%.

H₂SO₄ - 98%.

H₂SO₄ - dilute (1-1).

Hydroxylamine hydrochloride - 20 grams per 100 ml H₂O (prepared fresh each day).

Sodium citrate - 300 grams per liter of H₂O.

2,9 dimethyl-1,10 phenanthroline hemihydrate (neo-cuproine) -
0.1 gram per 100 ml 95% ethyl alcohol.

Chloroform.

Ethyl alcohol - 95%.

Ethyl alcohol - absolute.

NH₄OH - 28%.

Procedure

Weigh a sample of ca 2.0000 grams and place in a 100 ml platinum dish. Add 10-15 ml H₂O, 15 drops 98% H₂SO₄ and then add HF a few drops at a time, keeping the dish covered with a platinum lid between additions of the HF, until reaction ceases (approximately 40 drops HF per gram of metal is required). Add 8 ml (1-1) H₂SO₄, place on sand bath and heat to obtain complete solution of the metal. Wash off the lid with distilled water; add washings to the platinum dish. Place the dish on the sand bath and evaporate to fumes of SO₃ under infra-red lamps. Cool, add carefully 25 ml H₂O, heat on sand bath until all salts are in solution. After cooling, transfer the solution to a 100 ml volumetric flask. Dilute to the mark and mix. Transfer a suitable size aliquot^(b) of this solution to a 150 ml beaker and dilute to ca 35 ml volume with H₂O. If the pH of the solution is above 1.0, add H₂SO₄ drop by drop until the acidity is pH 1.0 or less.

Add the following reagents, stirring after each addition, 10 ml hydroxylamine hydrochloride, 10 ml sodium citrate, and 10 ml neo-cuproine. After 10 minutes, adjust the pH of the solution to 5.0 ± 0.1 and transfer to a 125 ml separatory funnel which has been previously rinsed with 95% ethyl alcohol. Add 10 ml chloroform and shake for 45 seconds then allow sufficient time for layers to separate. Place a small wad of dry paper pulp in the cone of a glass funnel and transfer the chloroform layer through this funnel, collecting the extraction in a 25 ml volumetric flask^(c) containing 4 ml absolute ethyl alcohol. Repeat the extraction using 5 ml chloroform and transfer to the volumetric flask as before. Wash the paper pulp by adding about 2 ml chloroform drop by drop, remove paper pulp, and rinse the funnel with 2 ml absolute ethyl alcohol. After adjusting to volume with absolute ethyl alcohol, stopper the flask and mix thoroughly.

Determine the optical density^(d) of this solution in 1 cm cell at a wavelength of 457 millimicrons with H_2O in the reference cell. Correction must be made for a reagent blank treated in the same manner as the sample.

From the corrected optical density, the amount of copper present is determined by reference to a previously constructed standard curve.

Preparation of Standard Curve

Acid solutions containing 0, 5, 10, 25, 50, 75, 100, and 200 γ copper are carried through the entire procedure described above. From the corrected optical densities obtained, construct the standard curve of optical density versus γ of copper.

- - - - -
- (a) All reagents used are prepared from "Analytical Reagent Grade" chemicals.
 - (b) Aliquot should contain between 5 and 150 micrograms of copper.
 - (c) 25 ml volumetric flask must have been rinsed with acetone and dried before use.
 - (d) A Beckman DU Spectrophotometer is used in making optical density measurements.

Method of Westinghouse Atomic Power Division
G. W. Goward and B. B. Wilson

1. Method

(a) Principle

Copper (I) forms a colored complex with neo-cuproine (2,9-dimethyl 1,10-phenanthroline) in a chloroform-ethyl alcohol system with a maximum absorbance at 457 millimicrons.

(b) Scope

The method covers the determination of impurity copper in zirconium and Zircaloy. The concentration range is from 0.01 milligram to 0.15 milligram in 25 ml of solution using a cell depth of 1 cm.

2. Apparatus

(a) Model DU Spectrophotometer or similar instrument.

(b) 150 ml separatory funnels.

(c) 200 ml platinum beakers.

3. Reagents

(a) Use de-ionized or doubly distilled water throughout the method.

(b) Standard copper solution (0.1 mg/ml) - dissolve 0.1000 gram of pure metallic copper in 20 ml of 1:1 HNO_3 . Dilute with water. Boil to remove the oxides of nitrogen. Dilute to mark in a one liter volumetric flask.

(c) Boric acid (0.85 M) - dissolve 55.5 grams of boric acid in warm water. Dilute to 1 liter.

(d) Tartaric acid (20%).

(e) Hydroxylamine hydrochloride (10%).

(f) Ammonium hydroxide (Spec. Gr. 0.90).

(g) Neo-cuproine (0.1%) - dissolve 1 gram of neo-cuproine in 1 liter of ethyl alcohol.

(h) Chloroform (C.P.).

(i) Ethyl alcohol (absolute).

4. Procedure

(a) Calibration Curve

Aliquot 0 (blank), 1, 3, 5, 8, 10, 15 ml of standard copper solution into platinum dishes. Add 1 ml of HF, 25 ml 0.85 M boric acid and 10 ml 20% tartaric acid. Adjust with NH_4OH to give a pH greater than 4 but less than 6. Transfer to 100 ml volumetric flasks. Dilute to volume and mix. Transfer 10 ml aliquots from each flask to 150 ml separatory funnels. Add 5 ml of 10% hydroxylamine hydrochloride to reduce the copper. Add 10 ml of neo-cuproine solution and 10 ml of chloroform. Shake about 30 seconds. Allow the layers to separate and draw off the chloroform layer into 25 ml volumetric flasks containing 3 to 4 ml of absolute ethyl alcohol. Repeat the extraction of the aqueous phase in the separatory funnel with 5 ml of chloroform. Allow the layers to separate and draw off the chloroform solution in the 25 ml flask. Dilute to volume with ethyl alcohol and mix. Measure the absorbancy of the solutions in 1 cm cells on the Beckman Spectrophotometer Model DU at 457 millimicrons using the reagent blank in the reference cell. Plot the absorbancy of the standard solutions against the milligrams of copper in the solution.

(b) Analysis of Samples

Weigh 1.000 gram samples into platinum dishes. Add approximately 15 ml H_2O , 1 ml of HF, and 5 to 6 drops of HNO_3 . After samples are in solution, add 25 ml 0.85 M boric acid and 10 ml 20% tartaric acid. Adjust with NH_4OH to give a pH greater than 4 but less than 6. Transfer to 100 ml volumetric flasks. Dilute to volume and mix. Transfer suitable aliquots from each flask to 150 ml separatory funnels. Extract the copper after reduction with hydroxylamine hydrochloride as in 4(a) above. Measure the absorbancy against a reagent blank carried through the procedure.

5. Calculations

Convert the photometric readings of the sample solutions to milligrams of copper by means of the calibration curve. Calculate ppm of copper present as follows:

$$\text{ppm Cu} = \frac{A \times 10^5}{B \times C}$$

A = milligrams of copper found
in the aliquot used.

B = milliliters in aliquot used.

C = weight of sample.

IRON

The amounts of iron found in zirconium metal are best determined by colorimetric methods of analysis. A number of reagents which form colored complexes with iron are discussed in analytical chemistry texts.^(4,5)

A comprehensive review of colorimetric methods is given by Ayers and Banks⁽³⁴⁾ in addition to data obtained in their study of 1,10-phenanthroline and sulfosalicylic acid as reagents for the determination of iron in zirconium. The reagent most frequently used for the determination of iron in zirconium is 1,10-phenanthroline. Three methods in which this reagent has been applied under differing conditions have been found suitable for the precise determination of iron in zirconium.⁽²⁵⁾ The Iowa State College Institute for Atomic Research at Ames used the Ayers and Banks⁽³⁴⁾ procedure. The color was developed with 1,10-phenanthroline in a sulfuric acid solution containing ammonium tartrate by adjusting the pH to 5-7 after reducing the iron with hydroxylamine hydrochloride. Jensen⁽³⁶⁾ developed the orthophenanthroline color, after reduction of the iron with hydroxylamine hydrochloride, by adding NH_4OH dropwise to the first permanent precipitate of $\text{Zr}(\text{OH})_4$ and then adding acetic acid to clear. Lawler,⁽³⁷⁾ using hydroquinone to reduce the iron, developed the color at pH 3.5 with ammonium citrate present.

Center⁽²⁴⁾ at Battelle Memorial Institute obtained satisfactory results using NH_4SCN as the colorimetric agent⁽²⁵⁾ in a solution obtained by dissolving zirconium in a mixture of HF and HNO_3 .

Details of four methods found to be satisfactory for the determination of iron in zirconium and Zircaloy are given.

Method of Ames Laboratory
A. S. Ayers and C. V. Banks

Dissolution of Sample

Transfer a 10 gram sample of zirconium to a large platinum dish and cover with redistilled H_2O . Add 100 ml of 9 M H_2SO_4 and dissolve the

sample by adding HF a few drops at a time until the rate of reaction subsides. When no more metal particles remain, heat the solution to copious fumes of SO_3 to remove the fluoride ion. After cooling, add carefully 100 ml redistilled H_2O and stir to dissolve the salts, warming if necessary. Transfer the solution to a 200 ml volumetric flask, cool, dilute to the mark and mix well.

Reagents

Hydroxylamine hydrochloride, $\text{NH}_2\text{OH}\cdot\text{HCl}$ - 10% aqueous solution.

1,10-phenanthroline monohydrate - 0.1% aqueous solution.

Ammonium tartrate - 25% aqueous solution.

Procedure

Transfer to a 100 ml volumetric flask an aliquot of the above sample solution which will contain no more than 250 micrograms of iron or more than 1 gram of zirconium. To this zirconium solution, add in the following order 0.5 ml 10% $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution, 5 ml 0.1% 1,10-phenanthroline solution, 15 ml 25% ammonium tartrate solution, and mix well. Add dilute (1:1) NH_4OH a drop at a time, with mixing until the precipitate which forms has dissolved; then add a few more drops and adjust the pH to 5-7 as shown with Hydrion paper. Dilute the sample to the mark, mix, and allow to stand for half an hour; longer standing does no harm. Determine the percent transmission of this solution at 515 millimicrons using 1 cm cuvettes, with H_2O as a reference. Obtain the iron content of the solution by comparison with a previously prepared standard transmittancy-iron concentration curve.

Preparation of Standard Curve

Dissolve 0.100 gram pure iron wire in dilute H_2SO_4 , dilute the solution to 1 liter, and mix. When the standard curve is to be prepared, pipet 10 ml of this solution into a 100 ml volumetric flask, dilute to the mark, and mix. This produces a solution containing 10 γ iron/ml.

Pipet 5, 10, 15, 20, and 25 ml aliquots of this solution into 100 ml volumetric flasks. Treat these solutions in the same manner as for the zirconium sample adjusting the final pH to 5-7 with Hydrion paper. From

the transmittancy values obtained on these solutions construct a standard transmittancy-iron concentration curve on semi-log paper. The points will lie on a straight line that may not go through the origin (this may be due to iron in the ammonium tartrate solution).

Method of Argonne National Laboratory
K. J. Jensen

For dissolution of sample, refer to Argonne National Laboratory procedure for chromium determination.

To aliquots of the sample in 25 ml volumetric flasks add 2 ml 10% $\text{NH}_2\text{OH}\cdot\text{HCl}$ and heat the solutions to near boiling in a water bath. To slightly cooled solutions, add 1 ml 10% $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 1 ml 0.1% ortho-phenanthroline. Add NH_4OH dropwise until the first permanent precipitate of $\text{Zr}(\text{OH})_4$. After standing a few minutes, add acetic acid until a clear solution is obtained. Dilute solutions to volume and read at 505 millimicrons against a blank on the reagents. The amount of iron present is obtained by reference to a previously prepared transmittance-concentration curve.

Aliquots taken for analysis should contain no more than 0.1 gram zirconium and between 5 and 50 micrograms of iron.

Method of M.I.T. Metallurgical Project
H. M. Lawler

Reagents

Hydrofluoric acid - 48%.

Boric acid - 0.85 Molar solution.

Sulfuric acid - concentrated.

Hydrochloric acid - (1:1) equal volumes of HCl and H_2O .

Ammonium hydroxide - (1:1) equal volumes of NH_4OH and H_2O .

Hydroquinone - 1% aqueous solution, prepared immediately before use.

1,10 (ortho)-phenanthroline monohydrate - 0.25% aqueous solution.

Ammonium citrate - 1 Molar solution.

Procedure

The procedure for determining iron in zirconium and Zircaloy is the same in all instances with the exception of the dissolution of the sample.

Dissolution of Sample

Zirconium - Weigh a sample of approximately 1.0 gram and place in a platinum dish provided with a platinum lid. Add 25 ml H_2O , then add HF a few drops at a time (ca 40 drops HF per gram sample) and heat gently to hasten solution of sample. After dissolution of sample, add 25 ml (0.85 M) boric acid solution and transfer to a 250 ml volumetric flask containing 25 ml (0.85 M) boric acid solution, dilute to the mark with H_2O and mix.

Zircaloy - Treat in the same manner as zirconium samples except add 5 ml H_2SO_4 before additions of HF (ca 20 drops of HF required).

Color Development and Determination of Iron

Transfer a 25 ml aliquot of the sample solution to a 150 ml beaker, dilute with H_2O to about a 40 ml volume, and, in the order given add the following reagents, stirring between additions: 3 ml (1%) hydroquinone, 6 ml (0.25%) o-phenanthroline and 6 ml (1 M) ammonium citrate. By means of a pH meter adjust the $pH^{(a)}$ of the solution to 3.5 with 1:1 NH_4OH and 1:1 HCl solutions. Transfer to a 100 ml volumetric flask. After 2 hours dilute to the mark and mix. Measure the optical density^(b) at 513 millimicrons in a Beckman DU Spectrophotometer with H_2O in the reference cell. Determine the iron present by comparison with a previously prepared standard optical density-iron concentration curve. Correction is made for a reagent blank treated in the same manner as the sample.

Preparation of Standard Curve

Acid solutions containing 0, 10, 25, 50, 100, 150, 200, 300, 400, and 500 micrograms of iron are carried through the entire procedure

described above. Construct curves for 1 cm cell and 5 cm cell from optical density values obtained.

- - - - -
- (a) Care should be taken that the pH of the test solution remains below 7 at all times.
 - (b) When a Beckman DU Spectrophotometer is used, as much as 500 micrograms of iron may be determined in 1 cm cells. If less than 100 micrograms of iron is present the optical density measurement may be made in 5 cm cells.

Method of Battelle Memorial Institute
E. J. Center

Weigh a sample of zirconium to contain from 0.05 to 0.40 milligram of iron. Dissolve it in a platinum dish in a mixture containing 8 ml HNO_3 , 2 to 3 ml HF , and 25 to 30 ml H_2O . When solution is complete, add 25 ml saturated H_3BO_3 and warm 10 to 15 minutes. Cool to room temperature, transfer to a 100 ml volumetric flask and add 10 ml of a 30% solution of NH_4SCN in H_2O . Dilute to the mark, mix thoroughly, and read immediately in a 1 cm cell at 480 millimicrons. For a reference solution, use a sample with all reagents added except the NH_4SCN solution. Determine the iron present by comparison with a previously prepared optical density-iron concentration curve.

LEAD

A polarographic method for the determination of lead in zirconium has been described by Rodden.⁽⁸⁾ A dithizone colorimetric method has been applied to the determination of lead in zirconium metals by Center⁽²⁴⁾ and associates at Battelle Memorial Institute. This method is described by Read⁽²⁵⁾ and has been applied to the determination of lead in zirconium and Zircalloys by the laboratories at Nuclear Metals, Inc. and Westinghouse Atomic Power Division. The following is the procedure used by Goward⁽³⁸⁾ of Westinghouse Atomic Power Division, adapted from the method of Center,⁽²⁴⁾ for the determination of lead in zirconium and Zircaloy.

Method of Westinghouse Atomic Power Division

1. Apparatus^(a)

- (a) 250 ml separatory funnels.
- (b) 125 ml separatory funnels.
- (c) Beckman Spectrophotometer Model B or other suitable spectrophotometer.

2. Reagents^(b)

- (a) Nitric acid solution (1:1).
- (b) Ion exchange water - pass distilled water through a column of Rohm and Haas MB-1 ion exchange resin. Use in all solutions.
- (c) Standard lead solution (100 γ /ml) - dissolve 0.1 gram lead metal (C.P.) in dilute nitric acid. Take to dryness. Add 10 ml of concentrated nitric acid and dilute to the mark in a 1 liter volumetric flask.
- (d) Standard lead solution (10 γ /ml) - dilute 10 ml of the 100 γ /ml solution to 100 ml with ion exchange water. Prepare fresh daily.
- (e) Ammonium citrate solution (40%)^(c)
- (f) Potassium cyanide solution (10%) - (sulfide free).

(g) Ammonium hydroxide solution (Spec. Gr. 0.92) - prepare by passing tank ammonia through ice-cooled ion exchange water until the desired specific gravity is obtained.

(h) Hydroxylamine hydrochloride solution (20%).

(i) Dithizone solution (15 mg/l) - dissolve 15 milligrams of dithizone in chloroform and dilute to 1 liter in a volumetric flask with chloroform.

(j) Buffer solution (pH 3.4) - dilute 9.1 ml concentrated nitric acid to approximately 500 ml. Adjust to pH of 3.4 with dilute ammonium hydroxide. Add 2.042 grams potassium acid phthalate and 19.9 ml of 0.1 N hydrochloric acid.

(k) Ammonia cyanide solution - dissolve 20 grams of sulfide-free potassium cyanide in 150 ml of concentrated ammonium hydroxide and dilute to 1 liter.^(c)

(l) Sodium hydroxide solution (10%).

(m) Stopcock grease - (lead free) vaseline is recommended.

3. Procedure

(a) Calibration Curve

Transfer aliquots of the standard lead solution (10 γ /ml) containing 0 (blank), 10, 20, 30, 40, and 50 micrograms of lead to 250 ml platinum beakers. Dilute to approximately 40 ml and follow the procedure for lead determination as outlined in 3(b). Plot the net photometric readings against micrograms of lead.

(b) Analysis of Samples

Dissolve a 1 gram sample in approximately 10 ml of H_2O and HF dropwise. Add 10 ml of sulfuric acid, 5 ml of dilute nitric acid and take to fumes. Cool and dilute to 100 ml in a volumetric flask. Take a suitable aliquot and dilute with water to 40 ml in a platinum dish. Make alkaline with concentrated ammonium hydroxide. Add 10 ml of 40% ammonium citrate, 5 ml of 10% potassium cyanide and 1 ml of 20% hydroxylamine hydrochloride. Adjust the solution to a pH of 9 to 9.5 with 10% sodium hydroxide.

Transfer the solution to a 250 ml pear-shaped separatory funnel and extract with 5 ml portions of dithizone. During the first extraction, shake 2 minutes after the red-colored emulsion is formed. When a last portion of dithizone remains unchanged (green) wash the combined extracts in a clean separatory funnel with 50 ml of pH 3.4 buffer solution. After vigorous shaking so that all lead is transferred to the aqueous phase, discard the chloroform layer.

Add to the aqueous layer 7 ml of ammonia cyanide and again extract the lead with dithizone until the color is unchanged green. The concentration of lead in the sample should be known since a constant amount of dithizone must be added to both the standards and the sample solutions. 15 ml of dithizone is adequate for a range of 5 to 50 γ lead. Make the dithizone extracts up to 50 ml with chloroform in a volumetric flask. If a water layer is visible, filter through a dry filter paper.^(d) Read immediately on the spectrophotometer at a wavelength of 510 millimicrons in 1 cm cells using chloroform as the reference solution. Cover all cells while taking photometric readings. Carry a reagent blank through the entire procedure with each set of samples.

4. Calculations

Convert the photometric readings of the sample and blank solutions to micrograms of lead by means of the calibration curve. Calculate ppm of lead present as follows:

$$\text{ppm of lead} = \frac{A - B}{C}$$

A = micrograms of lead found in aliquot used from sample.

B = micrograms of lead found in aliquot used from blank.

C = grams of sample in aliquot used.

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- (a) Rinse all glass apparatus with dilute nitric acid and ion exchange water.
- (b) Store all reagents in polyethylene bottles.
- (c) Extract these reagents with successive portions of dithizone chloroform solution until no pink color appears in the chloroform layer.
- (d) Render the paper lead free by washing with dilute nitric acid and water. Dry in a drying oven at low setting.

MAGNESIUM

Chemical methods of analysis for the determination of magnesium are reported in analytical chemistry texts^(4,5) and elsewhere in the literature.⁽²⁵⁾ These methods, however, are not suitable for the determination of microgram quantities of magnesium when present in reactor grade zirconium metal. It is possible that ion exchange techniques such as are described by Hettel and Fassell⁽³⁹⁾ might be applied to obtain a suitable quantity of magnesium for chemical analysis.

A method for the separation of magnesium by hot HCl volatilization of zirconium has been described.⁽²⁵⁾ This method is suitable for analysis of metal with magnesium content greater than 50 ppm and for that purpose, details of this procedure are given.

Method of M.I.T. Metallurgical Project

Transfer a 5 to 10 gram sample to a quartz boat and place the boat in the hot zone of the combustion tube used for the determination of oxygen (see Figure 8). Flush the HCl generator and combustion tube with argon, heat the combustion tube to 550°C, then shut off the argon and pass HCl over the sample until volatilization of zirconium is complete.

Remove the boat from the combustion tube and transfer the residue to a platinum dish. Dissolve by the addition of HF and H₂SO₄, finally heating to heavy fumes twice to remove fluoride ion. Add 10 ml H₂O, warm to obtain solution of salts, transfer to a 250 ml beaker and dilute to 100 ml volume. Add 5 grams NH₄Cl, heat to boiling, add a slight excess of NH₄OH and boil 2 minutes. Filter through an 11 cm S and S (black) filter paper, catching the filtrate in a 400 ml beaker. Wash the precipitate on the paper five times with hot 2% NH₄Cl solution and reserve the filtrate. Transfer the filter paper containing the precipitate to the original beaker, add 10 ml HCl and stir to dissolve the

precipitate and macerate the paper. Add 100 ml of boiling H_2O , reprecipitate by the addition of a slight excess of NH_4OH , heat to boiling and filter into the beaker containing the filtrate reserved from the first precipitation. Wash with hot 2% NH_4Cl solution as before. Add 100 ml HNO_3 to the beaker containing the combined filtrates, cover with a Speedy-Vap watch glass and evaporate to dryness to expel ammonia salts. To the residue in the beaker add 5 ml HCl and 50 ml H_2O . Heat to boiling, add excess NH_4OH and filter through an S and S (black) filter paper catching the filtrate in a 250 ml beaker. Wash the paper 5 times with hot 2% NH_4Cl solution and reserve the filtrate for the determination of magnesium.

Determination of Magnesium

Heat the reserved filtrate to $60^{\circ}C$ to $70^{\circ}C$, add 5 ml 8-hydroxyquinoline solution (5 grams of reagent dissolved in 100 ml 2 N acetic acid) and 5 ml NH_4OH . Stir vigorously and allow the precipitate to settle for at least 30 minutes. Filter through a weighed sintered porcelain or glass crucible and wash the precipitate with hot dilute (1:40) NH_4OH . Dry at $130^{\circ}C$ to $140^{\circ}C$ for 1 hour, cool, and weigh as $Mg(C_9H_6ON)_2$.

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COMMENT: This method is not recommended for the analysis of zirconium containing less than 50 ppm magnesium.

MANGANESE

Colorimetric methods for the determination of manganese in microgram amounts depend upon oxidation of the manganese to the permanganate ion and measurement of the color developed in the sample solution. Periodate oxidation in solutions of nitric or sulfuric acids and persulfate oxidation with silver nitrate present as a catalyst are described in analytical texts.^(4,5) Three procedures have been found sensitive enough to determine 5 ppm of manganese in zirconium.⁽²⁵⁾ One method, employed by the Ames Laboratory oxidizes the manganese with ammonium persulfate and the methods of M.I.T. and Argonne National Laboratory use KIO_4 as the oxidizing agent.

The procedures of these three laboratories are described.

Method of M.I.T. Metallurgical Project

Transfer 2.0 grams zirconium to a platinum dish. Add 50 ml (1:1) H_2SO_4 ^(a) and then HF dropwise to obtain solution of the metal. Add 2 ml HClO_4 , evaporate to fumes, and cool. Wash down the sides of the dish with water and fume a second time.^(b) Cool, add H_2O , and transfer to a 150 ml beaker. Adjust the volume to about 100 ml, add 0.5 gram of KIO_4 , boil for 5 min, and cool. Transfer to a 100 ml volumetric flask, dilute almost to the mark, and mix. After 24 hours,^(c) dilute to the mark, mix, and determine the optical density at 525 millimicrons in 5 cm cells using distilled H_2O in the reference cell. Obtain the amount of manganese present by comparison with a standard optical density-manganese concentration curve. Manganese can be determined by this procedure when present in amounts between 5 and 600 micrograms. Make proper correction for a reagent blank which is treated exactly as described above.

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(a) The final solution should contain 25 ml H_2SO_4 .

(b) After the second fuming treatment, no more than traces of chloride and fluoride ions remain and the amount of HClO_4 still present will cause no interference.

(c) Full development of color does not always occur immediately but is obtained after 24 hours and remains stable.

Method of Argonne National Laboratory

Dissolution Procedure

Solution of sample is obtained as described under the Argonne method for chromium.

Determination of Manganese

Transfer an aliquot of the H_2SO_4 solution which will contain 20 to 290 micrograms of manganese, ^(a,b) and no more than 0.8 gram zirconium, to a 100 ml beaker, and evaporate to about 10 ml. Add 6 ml HNO_3 plus 4 ml H_2SO_4 , dilute to 25 ml, and heat. Add about 0.2 gram of KIO_4 and keep the solution near boiling for 20 min. Cool in an ice bath, transfer to a 25 ml volumetric flask, dilute to volume, and mix well. Measure the transmittance at 530 millimicrons against a blank on reagents. Obtain the amount of manganese present by comparison with a previously prepared transmittance-concentration curve.

- - - - -

(a) To determine amounts of manganese less than mentioned above, spike the sample with an amount of manganese greater than 20 micrograms and add the same amount to the aliquot reagent blank solution. Use the transmission of this blank solution as the blank for the determination of manganese in the sample solution. By means of this technique manganese may be determined in an amount less than 5 ppm.

(b) These limits for manganese are based on the use of 1.6 cm cells.

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Method of Ames Laboratory

Dissolution of Sample

See under Ames determination of iron.

Determination of Manganese

Transfer 20 ml aliquot of the sample solution to a 250 ml beaker. This aliquot contains 1.00 gram zirconium. Dilute the sample solution to about 75 ml volume, add 5 ml concentrated sulfuric acid, 1 ml of 10%

AgNO_3 solution, and 1.0 gram $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Heat the solution on the hot plate almost to boiling until the purple color develops, and cool.

Transfer the solution to a 100 ml volumetric flask, dilute to volume, and mix well. Determine the transmittancy of the purple solution in a spectrophotometer, using water as a reference solution, at a wavelength of 545 millimicrons. If the color is faint, 5 cm cuvettes should be used for greater sensitivity. With the value found in this manner, determine the manganese content of the solution from a previously prepared standard curve. Manganese may be determined in an amount as low as 2 to 3 ppm in the zirconium metal.

Preparation of Standard Curve

Prepare a standard manganese solution containing 200 micrograms of manganese per ml by dissolving 0.200 gram electrolytic manganese in 50 ml 1:1 H_2SO_4 and diluting the resultant solution to one liter. Mix the solution well and when the standard curve is to be prepared, pipette 100 ml of the standard solution into a liter volumetric flask, add 5 to 10 ml dilute H_2SO_4 , and dilute to volume. This produces a solution containing 20 micrograms manganese per ml. Pipette 1, 2, 3, 4, 5, and 10 ml aliquots of this solution into 250 ml beakers, dilute to about 75 ml volume, and add 5 ml H_2SO_4 . Add 1 ml 10% AgNO_3 solution and 1.0 gram $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and heat the solution almost to boiling on the hot plate until the purple color develops. Transfer the cool solution to a 100 ml volumetric flask and dilute to volume. Determine the transmittancy of the solution in a spectrophotometer at a wavelength of 545 millimicrons using water as a reference solution in both 1 cm or 5 cm cuvettes. Plot the observed points. These curves (for 1 and 5 cm cuvettes) should be straight lines if the solutions were properly prepared.

MOLYBDENUM

Analytical texts^(4,5) discuss a number of colorimetric methods for the determination of trace amounts of molybdenum. The extraction of the molybdenum thiocyanate complex from a sulfuric acid solution with isopropyl ether or butyl acetate has been applied by Center⁽²⁴⁾ to the analysis for microgram amounts of molybdenum in zirconium metal. Crouthamel and Johnson⁽⁴⁰⁾ of the Argonne National Laboratory studied the thiocyanate spectrophotometric procedures for molybdenum and describe a method based on the development of the molybdenum (V)-thiocyanate complex in an acetone medium. Pollock⁽²⁷⁾ has applied this method, with good results, to the determination of microgram amounts of molybdenum in zirconium and Zircalloys. The methods of Center⁽²⁴⁾ and Pollock⁽²⁷⁾ are described.

Method of Battelle Memorial Institute E. J. Center

Reagents

Sulfuric acid - concentrated.

Hydrofluoric acid - 48%.

Sodium thiocyanate solution - 5% aqueous solution.

Stannous chloride solution - add 250 grams stannous chloride and 200 ml concentrated HCl to 1200 ml H₂O.

Butyl acetate.

NOTE: All chemicals are reagent grade.

Procedure

Weigh a sample to contain 20 to 120 micrograms of molybdenum, transfer to a platinum dish, and add 25 ml H₂O and 10 ml H₂SO₄ per gram of sample. Then add HF dropwise to dissolve sample. When sample is in solution

evaporate to fumes of SO_3 and fume vigorously to remove excess fluoride ion. Cool, add 25 ml H_2O , and heat to dissolve salts. Add from a burette 5 ml of sodium thiocyanate solution and transfer the mixture to a 100 ml separatory funnel. Rinse the dish with 10 ml of stannous chloride solution, added from a burette, and transfer this solution to the funnel. Rinse the dish with a final wash of 20 ml butyl acetate. Transfer to the funnel and shake vigorously for 1 min. Draw off and discard the aqueous layer, add, in succession, 5 ml of sodium thiocyanate solution and 15 ml of stannous chloride solution. Shake vigorously and discard the aqueous layer. Transfer the butyl acetate layer to a 50 ml volumetric flask. Rinse the funnel with two 10 ml portions of butyl acetate and add to the flask. Dilute to the mark with butyl acetate and mix thoroughly. Measure the optical density in a Beckman DU Spectrophotometer at 470 millimicrons in 1 cm cells against a reagent blank carried through the procedure. Calculate the molybdenum concentration by reference to a standard curve prepared by carrying known amounts of molybdenum through the entire procedure.

Method of Nuclear Metals, Inc.
E. N. Pollock

Reagents

Acetone.

Ammonium thiocyanate solution (1.0 M in acetone) - 38.1 grams of NH_4SCN in 500 ml acetone. Prepare just prior to use.

Cuprous chloride (0.1 M in HCl) - dissolve 0.495 gram CuCl in 50 ml HCl (conc.).

Hydrochloric acid - concentrated.

Hydrochloric acid - (1:4) mix 1 part of HCl with 4 parts of H_2O .

Hydrofluoric acid - concentrated.

Stannous chloride [10% in HCl (1:4)] - dissolve 5 grams of SnCl_2 in 50 ml HCl (1:4).

Sulfuric acid - concentrated.

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NOTE: All reagents are of analytical grade.

Procedure

Weigh a sample of ca 1.0 to 5.0 grams and place in a platinum dish. Cover sample with H_2O and add 20 drops of H_2SO_4 per gram of sample. Add a total of 40 drops of HF per gram of sample a few drops at a time as the reaction allows. Heat until complete solution of sample is obtained. Evaporate to fumes of SO_3 twice, cool, cautiously add H_2O , and warm to dissolve salts. Cool and transfer to a suitable size volumetric flask, dilute to volume with H_2O , and mix.

Pipette an aliquot no greater than 15 ml, to contain 10 to 40 micrograms of molybdenum, into a 50 ml volumetric flask. As much as 1 gram of zirconium may be tolerated. Adjust the volume to ca 15 ml with H_2O . Adjust the H_2SO_4 content so that the concentration in the final solution will be between 0.3 and 1.0 M. Cool, add 7 drops of CuCl solution and swirl. Add 28 ml of NH_4SCN solution and swirl. Wash down sides of volumetric flask with 2 to 3 ml of H_2O and swirl. Add 15 drops of SnCl_2 solution, dilute to volume with H_2O , and mix.

Determine the optical density in 5 cm cells, after standing one-half hour, in a Beckman DU Spectrophotometer at a wavelength of 460 millimicrons with H_2O in the reference cell. The color is stable for one hour. Correction must be made for a reagent blank treated in the same manner as the sample.

From the corrected optical density, the amount of molybdenum present is determined by reference to a previously constructed standard curve.

Preparation of Standard Curve

Weigh 1.000 gram of molybdenum metal, transfer to a 250 ml beaker, add 20 ml H_2SO_4 , heat to obtain complete solution of the metal, and cool. Transfer to a liter volumetric flask containing 500 ml H_2O , cool, dilute to volume, and mix. This solution contains 1.000 mg/ml. From this stock solution, by proper dilution, prepare a standard solution to contain 5 micrograms of molybdenum per ml.

Into 50 ml volumetric flasks, transfer 0, 1, 2, 4, 6, and 8 ml of the standard (5 micrograms molybdenum per ml) solution. Adjust the volume to ca 15 ml with H_2O . Add 1 ml H_2SO_4 (conc.). Develop the color and determine the optical density as described under procedure. From the data obtained, construct a standard optical density-concentration curve.

NICKEL

A number of colorimetric procedures for the determination of nickel have been described by Read.⁽²⁵⁾ Beaumont and Petretic⁽⁴¹⁾ dissolve the metal in dilute HF solution. After oxidation with bromine water, excess NH_4OH is added, followed by the addition of dimethylglyoxime. The color of the dimethylglyoxime complex is read at 540 millimicrons. Center⁽²⁴⁾ at Battelle Memorial Institute extracted the nickel dimethylglyoxime complex with chloroform and then removed the nickel by shaking with 0.1 N HCl. After oxidation with bromine water, the color was developed in a slightly ammoniacal solution and read at 460 millimicrons. The Argonne National Laboratory oxidized the nickel in a sulfuric acid solution with bromine water, the color was developed in ammoniacal solution and read at 520 millimicrons. Davis⁽²⁶⁾ determined nickel by the diethyldithiocarbamate method, after first extracting the dimethylglyoxime complex from an ammoniacal solution with CCl_4 . Druschel, et al⁽⁴²⁾ employed potassium persulfate in the oxidation of the nickel dimethylglyoxime complex. Other methods are described by Rodden⁽⁵⁾ and Sandell.⁽⁴⁾

Two slightly different procedures are described.

Method of New Brunswick Laboratory
R. H. Beaumont, Jr. and G. J. Petretic

Weigh a 0.500 gram sample of zirconium metal into a 100 ml platinum or bakelite beaker. Completely dissolve the sample in 10 ml of H_2O plus 1 ml of 48% HF. Add 10 ml of 10% citric acid, 5 ml of saturated Br_2 water, and about 5 ml of saturated boric acid (0.85 M). With stirring, add concentrated NH_4OH until the color just disappears. Then add 5 ml in excess. Transfer the solution to a 100 ml volumetric flask and cool to slightly below room temperature. Add 3 ml of 0.1% dimethylglyoxime in alcohol. Approximately 15 min after adding the dimethylglyoxime, dilute the solution to volume. Measure the optical density of the solution in a 1.00 cm cell at 540 millimicrons. Obtain the concentration in ppm by reference to a standard calibration curve.

Nickel in zirconium can be accurately determined in amounts up to 200 micrograms by this method.

Method of Nuclear Metals, Inc.
E. N. Pollock

Reagents

Ammonium hydroxide (NH_4OH) - conc. 28%.

Boric acid (H_3BO_3), 0.85 M - 52.5 grams of H_3BO_3 in 1 liter of H_2O .

Bromine water - saturated solution.

Dimethylglyoxime disodium salt - 1% aqueous solution.

Citric acid - 10% aqueous solution.

Hydrofluoric acid (HCl) - conc. 48%.

Sulfuric acid (H_2SO_4) - conc. 96%.

NOTE: All reagents are of analytical grade.

Procedure

Weigh a sample of ca 1.0 to 5.0 grams and place in a platinum dish. Cover sample with H_2O and add 15 drops of H_2SO_4 per gram of sample. Add a total of 40 drops of HF per gram of sample, a few drops at a time as the reaction allows. Heat until complete solution of sample is obtained. Add 15 ml of H_3BO_3 (0.85 M) per gram of sample. Transfer solution to an appropriate size volumetric flask, cool, dilute to volume with H_2O and mix. Pipette an aliquot^(a) to contain 80 micrograms or less of nickel into a 150 ml beaker and add 2 ml of 10% citric acid solution per 0.1 gram of sample. Adjust volume to ca 45 ml with H_2O . By means of a pH meter, adjust the pH to 1.5 ± 0.1 with NH_4OH . Transfer sample to a 100 ml volumetric flask and chill in an ice bath^(b) to 10°C to 20°C . Add 5 ml of saturated bromine water to each aliquot, swirl to mix, and let stand five minutes. Add NH_4OH dropwise until the color of bromine is destroyed, then add an excess of 5 ml NH_4OH and cool in an ice bath for ten minutes.

Add 3 ml of dimethylglyoxime (1%) aqueous solution, and allow to stand at room temperature for 15 minutes. Dilute to volume with H_2O , and mix.

Determine the optical density in 5 cm cells, within 15 minutes, in a Beckman DU Spectrophotometer at a wavelength of 445 millimicrons with H_2O in the reference cell. Correction must be made for a reagent blank treated in the same manner as the sample.

From the corrected optical density, the amount of nickel present is determined by reference to a previously constructed standard curve.

Preparation of Standard Curve

Prepare a stock solution containing 5 micrograms of nickel per ml as follows: weigh 1.0000 gram of nickel and take in solution with 20 ml HNO_3 . When solution is complete, transfer to a 1 liter volumetric flask, dilute to volume with H_2O , and mix.

From this stock solution, by proper dilution, prepare a standard solution to contain 5 micrograms of nickel per ml.

Into 150 ml beakers, transfer 0, 2, 4, 8, 12, 16, and 20 ml of the standard (5 micrograms of nickel per ml) solution. Add 10 ml citric acid and 5 ml of H_3BO_3 (0.85 M) to each. Develop the color and determine the optical density as described under procedure. From the data obtained, construct a standard optical density-concentration curve.

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(a) As much as 1 gram of zirconium or Zircaloy may be tolerated.

(b) It is advisable that only 6 aliquots be oxidized and carried through the procedure at one time.

TIN

No chemical method is, at present, available for the determination of trace amounts of tin which may be present as an impurity in zirconium metal. Methods which may be applied to the analysis for amounts of tin present in zirconium alloys are described in standard texts.^(1,43,44) These methods, in general, are based upon the oxidation of tin to its quadrivalent state, by means of standard solutions of iodine or potassium iodate, after its reduction to the bivalent state in sulfuric or hydrochloric acid solution. Reduction is accomplished by reducing agents such as granulated lead or iron. The chief precautions in accurate analysis are the complete reduction of the tin to the bivalent state and the prevention of its reoxidation by air. Two methods which have been applied to the analysis for tin in Zircaloy are described. Bryson⁽⁴⁵⁾ et al reduces tin with test lead, and iron is used as the reductant by Bauman.⁽⁴⁶⁾

Method of Westinghouse Atomic Power Division

Scope

1. This method covers the procedure for the determination of more than 0.5% tin in zirconium. It may be used for as low as 0.2% tin but is less satisfactory at this level.

Principle

2. Tin, reduced by lead, is titrated with potassium iodate to a blue end point. Starch is used as the indicator.

Apparatus

- 3.(a) Tin reduction apparatus (ASTM).
- (b) Saturated NaHCO_3 .
- (c) Glass tubing.
- (d) Rubber tubing.
- (e) Ice bath or water connected to a cooler system.
- (f) Hot plate.

Reagents

4. Hydrochloric acid (spec. gr. 1.19).
5. Hydrofluoric acid (48%).
6. Lead metal, granular C.P.
7. Tin metal, 30 mesh C.P.
8. Potassium iodate (approximately 0.05 N) - dissolve 1.788 gram KIO_3 in 50 ml H_2O containing 0.25 gram NaOH and 7.5 gram KI . Dilute to 1 liter, mix, and allow to stand for several days. Standardize this solution by titrating 0.1000 gram tin metal that has been treated as described in paragraphs 12 and 14.
9. Starch solution - make a paste with 5 grams potato starch, C.P., and a few ml H_2O . Add with rapid stirring 500 ml boiling H_2O . Stir until smooth. Store in a refrigerator.
10. Sodium bicarbonate (10% or saturated) - transfer 2 liters H_2O into a beaker containing 200 grams NaHCO_3 and stir.
11. Dry ice.

Procedure

12. Transfer 1.000 gram^(a) of sample into a 300 ml Erlenmeyer flask. Add 50 ml HCl and about 2 ml HF .^(b) When all the metal is in solution, add 50 ml H_2O .^(c)
13. Place the flask containing the sample on a hot plate. Quickly add 1 gram lead metal, 10 ml NaHCO_3 (dry ice) and stopper with a rubber stopper, thus connecting it directly with the NaHCO_3 . Allow to boil gently for 30 minutes. Cool slightly by removing from the direct heat of the hot plate for a few minutes, then place in the ice bath. Allow the solution to cool for about 15 minutes.
14. Remove the rubber stopper and carefully, yet quickly, add a small piece of dry ice. Take the sample from the ice bath, add 2 ml starch solution, and titrate to a blue end point with KIO_3 .
15. Blank - make a blank determination following the same procedure and using the same amounts of all reagents.

16. Calculations - calculate the percentage of tin as follows:

$$\frac{(A-B) C}{D} \times 100 = \% \text{ Sn}$$

A = ml KIO_3 used to titrate the sample.

B = ml KIO_3 used to titrate the blank.

C = tin equivalent of KIO_3 solution in gm/ml.

D = grams of sample used.

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- (a) If less than 2%, tin is present, use 2.000 gram sample.
 - (b) Add HF dropwise in 0.5 ml portions.
 - (c) Core alloy dissolves more quickly in 50 ml 1:1 HCl and HF. When sample is dissolved, add 50 ml more of 1:1 HCl.
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Method of Nuclear Metals, Inc.

F. A. Bauman

Reagents

Iodine solution (0.1 N) - prepare and standardize against National Bureau of Standard Arsenic Trioxide according to directions on the Certificate of Analysis. Standardize each week.

Starch solution (1%) - to 200 ml of boiling H_2O , add 2 grams of soluble starch in 10 ml H_2O . Boil 5 minutes and cool. Prepare fresh each day.

Antimony trichloride (SbCl_3) - 2% aqueous solution.

Plast-Iron powder < 30 mesh - may be obtained from Plastic Metals Division, National Radiator Co.

Hydrochloric acid (HCl) - concentrated.

Hydrofluoric acid (HF) - concentrated.

Boric acid (H_3BO_3), (0.85 M) - 52.5 grams per liter H_2O .

Sulfuric acid (H_2SO_4) - concentrated.

Dry ice (CO_2) - best grade (free from volatile organic matter).

Procedure

Weigh a 1.0 to 5.0 gram sample and transfer to a platinum dish. Add enough H_2O to cover the sample, add 10 ml H_2SO_4 , and then 25 to 50 drops HF a few drops at a time as the reaction permits. Heat gently until complete solution of the metal is obtained. Add 25 ml boric acid solution and cool. Transfer the sample solution to a 250 ml wide mouth erlenmeyer flask and dilute to about 120 ml volume with H_2O .

Add 50 ml HCl, 5 drops 2% $SbCl_3$ solution, and 3 grams plast-iron powder. Place on a hot plate and allow to react until about 75% of the iron has dissolved (about 15 minutes). Before all of the iron has dissolved, assemble in CO_2 apparatus (see Figure 1). Boil on hot plate for 30 minutes (or until all the iron has dissolved). Some metallic antimony may precipitate at this point but will not interfere. Remove from the hot plate and cool the flask in a water bath. After the sample flask is cold, remove plug from stopper and add, by means of a pipet 5 ml of starch solution. Insert the burette^(a) tip in the stopper hole and titrate with 0.1 N iodine solution to the blue end point. Make a reagent blank determination by following the same procedure and using the same amounts of reagents.

Calculate the percentage of tin as follows:

$$\% \text{ Sn} = \frac{(A-B) C}{D} \times 100$$

where:

A = ml iodine solution required to titrate sample.

B = ml iodine solution required to titrate blank.

C = tin equivalent of iodine solution, in grams per ml

D = grams of sample.

 (a) For titration of amounts of tin found in Zircaloy, a 5 ml burette is recommended.

Figure 1

TITANIUM

Microgram amounts of titanium in zirconium metal may be determined by the hydrogen peroxide colorimetric method. The color is usually developed in a sulfuric acid solution. Beaumont,⁽⁴⁷⁾ however, oxidized with H_2O_2 in a hydrofluoric acid solution containing boric acid. Both methods have been found satisfactory if correction is made for interference of microgram amounts of molybdenum and vanadium.⁽²⁵⁾ Two procedures are described in detail.

Method of M.I.T. Metallurgical Project

Transfer a 1.0 gram sample to a platinum dish. Add 20 to 25 ml H_2O , 5 ml H_2SO_4 , and HF dropwise as needed to continue the reaction. After dissolution of sample, add 15 ml 1:1 H_2SO_4 and 1 ml HClO_4 . Evaporate to fumes and fume strongly for a few minutes. Cool, wash down sides of dish with H_2O , add 1 ml HClO_4 , evaporate and heat to copious fumes of SO_3 for several minutes. After cooling, add 50 ml H_2O and heat to dissolve salts. Transfer to a 100 ml volumetric flask, cool, adjust to volume with H_2O , and mix. Pipette 50 ml of this solution into a 100 ml beaker, add 4 drops of 30% H_2O_2 , and mix. Use the solution remaining in the flask as the blank solution. Measure the optical density in a Beckman DU Spectrophotometer at 411 millimicrons in 5 cm cells, with H_2O in the reference cell. Correction must be made for the blank solution. Determine the amount of titanium present by reference to a previously prepared standard optical density-titanium concentration curve.

Preparation of Standard Curve

Weigh 0.1670 gram of ignited TiO_2 (Bakers), place in a porcelain crucible, and add ca 5 gram of prefused potassium bisulfate. Fuse slowly with a final heating over a blast burner. Dissolve the fusion in 500 ml of 20% H_2SO_4 . Transfer solution to a liter volumetric flask, cool, add H_2O to the mark, and mix. One ml of this solution contains 100 micrograms

titanium. To prepare a solution containing 10 micrograms per ml, transfer 50 ml of the original solution to a 500 ml volumetric flask, add 45 ml H_2SO_4 , cool, adjust to volume with H_2O , and mix.

Pipette aliquots of the standard titanium solution containing 0, 20, 40, 60, 80, 100, 200, 500, 1000, 1500, and 2000 micrograms of titanium into 100 ml volumetric flasks and dilute to volume with 10% H_2SO_4 solution and mix. To each of these solutions, add 4 drops of 30% H_2O_2 and mix. Measure optical densities in a Beckman DU Spectrophotometer at 411 millimicrons in 5 cm cells with a 10% H_2SO_4 solution in the reference cell. Construct a standard optical density-titanium concentration curve from the values obtained.

NOTE: Correction must be made if vanadium or molybdenum are present. These corrections are as follows: for every 10 ppm vanadium, subtract 3 ppm from the apparent titanium value, and for every 100 ppm molybdenum present, subtract 8 ppm from the apparent titanium value.

Method of New Brunswick Laboratory
R. H. Beaumont, Jr.

To a 1.0 to 1.5 gram sample of zirconium in a 125 to 300 ml platinum dish, add 25 ml of 3.0 M H_2SO_4 . To this, one or two ml at a time so the solution does not splatter excessively, add a total of 4.0 ml of 48% HF.

After the zirconium has completely dissolved, add 50 ml of 0.85 M H_3BO_3 . If a cover is used on the platinum dish, the droplets of solution splattered on it can be washed off with the H_3BO_3 solution. Then transfer the solution to a 100 ml volumetric flask, add 2.0 ml of concentrated H_2SO_4 , and cool the flask to room temperature before diluting to the mark with H_2O . Any free carbon that may be present can be disregarded. At this point, the HF will no longer etch the glass.

To a 50 ml aliquot, add 0.4 ml of 30% H_2O_2 . The remaining 50 ml of the solution are used for the blank solution. Measure the transmittancy of the solution on a Beckman DU Spectrophotometer at 400 millimicrons using a 10.0 cm cell and a 1.0 millimicron bandwidth. Read the concen-

tration per 100.8 ml from the standard curve. Correct for vanadium and molybdenum if present according to the following formula:

$$\gamma \text{ Ti} = \gamma \text{ apparent Ti} - 0.200 \gamma \text{ V} - 0.087 \gamma \text{ Mo}$$

Preparation of Standard Curve

To platinum dishes containing 4 grams of titanium-free $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, 4.0 ml 48% HF, 25 ml of 3 M H_2SO_4 and 50 ml of 0.85 M H_3BO_3 add 100, 200, 300, and 500 γ of titanium, mix and transfer solutions to 100 ml volumetric flasks. Dilute to the mark with H_2O . Carry out the usual procedure with these solutions. Plot the transmittancy against the concentration on semi-log paper.

TUNGSTEN

A number of colorimetric methods for the determination of tungsten are discussed in standard texts.^(4,5) Methods which may be applied to the analysis for microgram amounts of tungsten have been described by Geld and Carroll⁽⁴⁸⁾ and Gentry and Sherrington.⁽⁴⁹⁾ Both methods depend on measurement of the color of the tungsten (V) thiocyanate complex, produced by the reaction of reduced tungsten with potassium or sodium thiocyanate in a strong hydrochloric acid solution. Geld and Carroll⁽⁴⁸⁾ reduced tungsten with stannous chloride. Gentry and Sherrington⁽⁴⁹⁾ used tin amalgam as the reductant. Freund⁽⁵⁰⁾ investigated the variables involved in the stannous chloride-thiocyanate method and recommended a procedure for the determination of microgram amounts of tungsten. Two analytical methods have been applied with good results, to the determination of tungsten in zirconium metal.⁽²⁵⁾ As little as 10 ppm of tungsten may be determined by either method.

Two methods for the determination of tungsten in zirconium or Zircaloy are described.

Method of Bureau of Mines, Albany Laboratory

Reagents

Standard tungsten solution (100 γ W/ml) - dissolve 0.1261 gram WO_3 in 20 ml H_2O containing 5 pellets of NaOH, transfer to a 1 liter volumetric flask, dilute to the mark, and mix.

Standard tungsten solution (10 γ W/ml) - transfer 5 ml of solution above to a 500 ml volumetric flask, dilute to the mark, and mix.

2 M stannous chloride solution - dissolve 113.0 gram $SnCl_2 \cdot 2H_2O$ in warm concentrated HCl, dilute to 250 ml with concentrated HCl.

2 M potassium thiocyanate solution - dissolve 194 gram KCNS in H_2O and dilute to a liter volume.

Reagent grade hydrochloric, sulfuric, and hydrofluoric acids.

Procedure

Transfer 1.000 gram sample to a platinum dish, add 20 ml (1:1) HNO_3 and then HF dropwise until the sample is in solution. Add 10 ml H_2SO_4 and fume twice to insure removal of fluoride. After cooling, add 25 ml H_2O , heat to dissolve salts, and transfer to a 100 ml volumetric flask. Cool the flask under running water for 30 seconds and then add 20 ml concentrated HCl. Add 5 ml SnCl_2 solution, place the stopper loosely in the flask, and immerse the flask in boiling water for 5 minutes to reduce the tungsten. Remove the flask and cool in cold water for 5 minutes without removing the stopper. (Tungsten (V) is very susceptible to air oxidation.)

Add 10 ml KCNS solution, dilute almost to the mark, and mix. Cool in a cold water bath for 5 minutes, remove and let stand on the bench for a few minutes, add H_2O to the mark, and mix. Determine optical density in 5 cm cells (15 minutes plus or minus 2 minutes after the addition of KCNS solution) at 400 millimicrons with H_2O in the null cell. Carry a reagent blank through the entire procedure and make proper correction for this blank. Determine the tungsten present by comparison with a standard optical density-tungsten concentration curve.^(a)

Prepare this curve from data obtained by carrying a series of standard tungsten solutions, containing 0, 10, 25, 50, 100, 200, and 400 micrograms of tungsten, through the entire procedure.

 (a) If molybdenum is present, it must be determined separately and proper correction applied.

Method of Battelle Memorial Institute

Weigh a 0.500 gram sample into a platinum dish. Add 20 ml of (1:1) HCl and about 1 ml HF. When the sample is in solution, add 5 to 10 ml of saturated H_3BO_3 solution and evaporate to about 10 ml. Transfer to a 50 ml volumetric flask, washing out the platinum dish with two 5 ml portions of concentrated HCl.

Add 1 ml of 10% SnCl_2 solution in 6N HCl and 2 ml (from a burette) of tin amalgam. Shake for 2 to 3 minutes. Add 5 ml of 12% NaSCN solution, dilute to the mark, and shake. Allow five minutes for the color to develop, then determine the percent transmittance at 410 millimicrons using a Beckman DU Spectrophotometer or comparable instrument.^(a) A blank is prepared by running the sample through all steps of the above method but omitting the addition of NaSCN.

After correction for the blank, the amount of tungsten is determined by reference to a curve prepared from a standard tungsten solution.

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(a) The range of the determination using 1 cm cells is 0.05 to 0.5 mg of tungsten; 5 cm cells may be used for lower amounts of tungsten.

The HCl concentration should be between 6.0 and 9.0 N for the amalgam reduction. Final acidity should be from 2.0 to 4.0 N.

This method is a modification of a technique of Gentry and Sherrington.⁽⁴⁹⁾

Prepare tin amalgam by heating mercury with excess tin in presence of dilute HCl. Keep in a bottle over solid tin in dilute HCl. Wash used amalgam and return to the bottle.

VANADIUM

The method of Bauman,⁽⁵¹⁾ which has been described by Read,⁽²⁵⁾ has been applied to the analysis for microgram amounts of vanadium in zirconium and Zircaloy. It is an unusually simple and precise analytical procedure and will determine as little as 5 micrograms of vanadium in a gram of zirconium. When a concentrated sulfuric acid solution containing vanadium is treated with a few crystals of potassium chlorate and the solution is heated and fumed vigorously a yellow color develops. The intensity of the color is directly proportional to the amount of vanadium present. Details of this method are given.

Method of M.I.T. Metallurgical Project

F. A. Bauman

Reagents

HF, C.P. 48%.

KClO₃, C.P. Granular.

H₂SO₄, C.P.

HNO₃, C.P.

Procedure

Transfer a 1.0 gram sample to a platinum dish, add enough H₂O to cover the sample, and then add HF a few drops at a time until complete solution is obtained. Add 40 ml 9 M H₂SO₄, evaporate to fumes and fume strongly for a few minutes. Cool, wash down the sides of the dish with H₂O and refume. Cool and add sufficient H₂O to dissolve the salts, warming if necessary. Transfer to a 100 ml volumetric flask, cool, dilute to volume, and mix. Pipette a 50 ml portion of this solution into a 150 ml erlenmeyer flask, add 20 ml of H₂SO₄, and fume vigorously on a hot plate. After cooling, add approximately 0.5 gram KClO₃ by means of a powder funnel. Take care not to leave any crystals adhering to the walls of the flask as these would introduce fresh color if dissolved later while transferring the solution. Fume again vigorously and then cool to room

temperature in a water bath. Between 30 and 45 minutes after the final fuming, measure the optical density at 410 millimicrons, in a 5 cm cell, compared with 30 ml concentrated H_2SO_4 similarly treated. Determine the amount of vanadium present by comparison with a standard curve of optical density vs. micrograms of vanadium.

Preparation of Standard Curve

Prepare a standard vanadium solution containing 100 micrograms vanadium per ml by dissolving a weighed amount of high-purity vanadium in HNO_3 and proper dilution. Dilute 100 ml of this solution to 1 liter to obtain a standard solution containing 10 micrograms vanadium per ml. Use this solution for preparation of the standard curve.

Dissolve 5.0 grams of zirconium metal of extremely low vanadium content in a platinum dish by the addition of HF as described above. To this solution, add 50 ml of 9 M H_2SO_4 , evaporate, and fume twice. Add sufficient H_2O to dissolve the salts and transfer the solution to a 500 ml volumetric flask. Add 150 ml of 9 M H_2SO_4 , cool, dilute to volume, and mix. To 50 ml portions of this solution in 150 ml erlenmeyer flasks, add 0, 1, 2, 3, 4, 5, and 10 ml of the standard vanadium solution. To each solution, add 20 ml concentrated H_2SO_4 and treat exactly as described for the 50 ml aliquot of the sample solution. From the optical density values obtained, construct a standard optical density-vanadium concentration curve.

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NOTE: If the fumings are vigorous but not overly prolonged, not enough H_2SO_4 is lost to warrant closer control of the final volume other than careful addition of the specified volume of acids.

ZINC

Methods for the determination of zinc in zirconium have been described.⁽²⁵⁾ Conditions and complexing agents for the zinc dithizonate colorimetric method are discussed by Sandell⁽⁴⁾ and Rodden.⁽⁵⁾ Two slightly different procedures for the determination of microgram amounts of zinc in zirconium and Zircaloy are described.

Method of Battelle Memorial Institute

Dissolve a sample containing 5 to 25 micrograms of zinc in H_2SO_4 (1:2) by the dropwise addition of HF. Take the sample to fumes to remove fluorides, cool, and dilute to about 50 ml. Add to the sample solution 10 ml of ammonium citrate (40% w/v), 1 ml of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (20% w/v), and 1 ml of $\text{Na}_2\text{S}_2\text{O}_3$ (12.5% w/v). Adjust the pH of the solution to 5.0 to 5.5 with NH_4OH .

Extract the sample in a separatory funnel with dithizone (10 to 20 mg/l of CCl_4), using 5 ml portions. Extraction is complete when the fresh addition of dithizone remains an unchanged green after 2 minutes of vigorous shaking. Wash the combined CCl_4 extracts with 50 ml of 0.02 N HCl by shaking for 2 minutes. Discard the CCl_4 layer and wash the aqueous layer with 10 ml of fresh CCl_4 .

To the aqueous layer, add 1 ml $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution and 1 ml of the $\text{Na}_2\text{S}_2\text{O}_3$ solution. Adjust the pH again to 5.0 to 5.5 and extract with dithizone until an addition of 5 ml of dithizone solution remains unchanged green.

Make the combined CCl_4 extracts to 50 ml volume and wash with 50 ml portions of Na_2S (0.4% w/v) until the sulfide wash remains colorless. (If an emulsion should form at this point, it may usually be broken by adding a "pinch" of dry powdered KCl.)

Filter the washed zinc dithizone solution through a dry filter and read in a 1 cm cell at 535 millimicrons and 0.01 mm slit width against a CCl_4 reference. Carry blanks through all steps of the procedure. Extract

all the reagents (except H_2SO_4 and HF) with dithizone to keep the blank as low as possible.

Determine the amount of zinc present by comparison with a previously prepared standard optical density-zinc concentration curve.

Method of M.I.T. Metallurgical Project

Transfer 2.0 grams of zirconium to a platinum dish, add 40 ml of 1:3 H_2SO_4 and then HF a few drops at a time until complete solution of the sample is obtained. Evaporate to fumes of SO_3 , cool, wash down the sides of the dish with H_2O , evaporate and fume a second time. After cooling, add 50 ml H_2O and heat, if necessary, to obtain solution of the salts. Transfer to a 100 ml volumetric flask, cool, dilute to volume, and mix. Pipette 25 ml of this solution into a 100 ml beaker, add 10 ml 10% ammonium citrate solution and then NH_4OH until the solution is just alkaline to phenolphthalein indicator. Transfer to a separatory funnel and extract with 10 ml portions of 0.01% solution of dithizone in CCl_4 . Extraction is complete when the fresh addition of dithizone remains green after 2 minutes shaking. Extract zinc from the dithizone by shaking with three 10 ml portions of 0.01 N HCl solution. Transfer to a 50 ml volumetric flask, dilute to the mark, and mix.

Pipette an aliquot of this acid solution, containing not more than 5 micrograms of zinc to a separatory funnel. Add 1 ml 25% $\text{Na}_2\text{S}_2\text{O}_3$ solution, 5 ml acetate buffer solution,^(a) and 5 ml 0.001% CCl_4 solution of dithizone. Shake for 2 minutes and filter the CCl_4 layer through a dry filter paper into a 1 cm cell. Cover the cell and immediately measure the optical density at 530 millimicrons compared to H_2O . Determine the amount of zinc present by comparison with a previously prepared standard optical density-zinc concentration curve. Correction must be made for a reagent blank carried through all steps of the procedure. Extract all reagents except H_2SO_4 and HF with dithizone to keep the blank as low as possible.

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(a) Prepared by mixing equal volumes of 2 N acetic acid and 2 N sodium acetate.

BORON

Chemical procedures for the determination of boron in zirconium have been described by Craig and Richmond⁽⁵²⁾ and by Waterbury and Metz.⁽⁵³⁾ Craig and Richmond⁽⁵²⁾ dissolved the metal in dilute hydrofluoric acid in a quartz distilling flask connected to a quartz reflux condenser. The cooled solution was made just alkaline to methyl red by dropwise addition of NH_4OH then made slightly acid by adding HCl dropwise. A solution of 10% CaCl_2 was added to prevent interference by the fluoride present. The boron was distilled over, as methyl borate, into a calcium hydroxide suspension. The boron was determined by a colorimetric method based on its reaction with turmeric extract. Waterbury and Metz⁽⁵³⁾ dissolved zirconium metal in dilute hydrofluoric acid and also in a sulfuric acid solution with SO_3 concentration of about 60 percent and no fluoride present. Good results were obtained by either method of solution. They report excellent agreement with Argonne National Laboratory in the analysis of a sample of zirconium hydride. Argonne National Laboratory used the procedure of Craig and Richmond.⁽⁵²⁾

The method of Craig and Richmond⁽⁵²⁾ is described in detail.

Method of New Brunswick Laboratory
J. Craig and M. Richmond

Place 0.4 gram of zirconium in a 60 ml quartz distilling flask containing 5 ml H_2O . Connect the flask to a quartz reflux condenser by means of a 2 hole rubber stopper containing a quartz reagent tube, see Figure 2. Cool the flask in a beaker of cold water and add 5 ml of 1:4 HF through the reagent tube. As soon as the addition of HF is completed, remove the water bath and allow the flask to stand until the reaction ceases.^(a)

After the solution has cooled, remove the flask from the refluxer, add a drop of methyl red and neutralize the excess acid by adding, dropwise, a saturated ammonia solution. During this step, keep the sample

Figure 2

cold and mix carefully to avoid loss of fumes. Finally, make the solution slightly acid by adding HCl dropwise, using 2 drops more than enough to just give a pink color.

After all fumes have settled, add 25 ml of 10% CaCl_2 in methanol and connect the flask to the still which has been provided with a 200 ml receiving dish^(b) and a flask, B, containing 25 ml of methanol and a pellet of KOH or NaOH. The receiving dish is supported in an enclosed cold water bath which consists of a 6-in. crystallizing dish with a plastic (Pittsburgh Plate Glass CR-39) cover and is protected from the heat of the burners by a transite shield. The condenser tube passes through a hole in the center of the cover almost to the bottom of the receiving dish, see Figure 3.

Immediately after connecting the sample flask to the still, add 5 ml of 0.1 N lime to the receiving dish. Immerse each flask in a beaker of hot water, heated gently so as to keep beaker B at 80°C to 82°C and beaker A at 76°C to 78°C . As the alcohol in flask B distills over, add successive portions to flask B until a total of 125 ml has been added. Keep the volume of solution in flask A at about 40 ml by controlling the difference in temperature between the two beakers, and the depth to which the flasks are immersed in the water baths. After all the alcohol has been distilled from flask B, discontinue heating, loosen the stoppers in the flasks, and wash the end of the condenser tube with 10 ml of H_2O . Add immediately an extra 5 ml of lime to the distillate and evaporate to dryness on the steam bath.

Remove the dry sample from the steam bath and cool to room temperature.^(c) Add 2 ml of dilute oxalic-hydrochloric acid reagent. Manipulate the dish so as to bring the reagent into contact with all the lime. Add 2 ml of a 1% turmeric extract and twirl until all reagents are mixed thoroughly. Add each of these reagents rapidly from a coarse-tipped pipet. Place the dish in a water bath, kept at $55 \pm 1^\circ\text{C}$, containing enough water to nearly or just float the dish. Allow to remain there until just dry and then for 30 or 45 minutes longer. Remove the dish and cool. Extract the precipitate with about 20 to 25 ml of 90% ethanol added in about 5 ml portions using a rubber-tipped rod to stir the precipitate.

Figure 3

Decant the extracts into a 25 ml graduate, dilute to 25 ml with 90% ethanol, mix and filter through a dry No. 42 Whatman filter paper. With a Beckman Spectrophotometer, measure the transmittancy of the solution at 540 millimicrons, using as a reference the color development blank obtained by carrying 5 ml of lime through the above procedure, beginning with evaporation on the steam bath. With each group of samples, obtain a transmittancy-concentration curve by adding known amounts of boric acid (0.5 to 1.5 γ of boron) to 5 ml 0.1 N lime and taking through the color development. Determine the boron content of the test solution from this transmittancy-concentration curve and correct for a "reagent" blank which is run through all steps of the procedure and which amounts to about 0.1 γ of boron. Make a correction also for the average loss through the solution, neutralization, and distillation steps (this may amount to 10% and is determined by analyzing samples both alone and with added amounts of boron.)

Reagents

Sodium hydroxide (or potassium hydroxide) C.P.

Boric acid C.P.

Hydrochloric acid C.P.

Oxalic acid C.P.

Ammonia, Saturated Solution

Prepare in quartz from tank NH_3 .

Methanol, Purified

Distill the reagent absolute (or synthetic) methanol from KOH or NaOH in a quartz apparatus.

Calcium Chloride, 10% in Methanol

Clean^(d) a piece or two of distilled calcium weighing about 35 to 70 grams by washing with distilled H_2O and scraping off the oxide formed. Weigh the clean metal and transfer to a large silica dish, placed in a large pan of ice and water. Add 100 to 300 ml of H_2O , then add, rather rapidly, 4.4 ml of HCl per gram of calcium taken (the large ice bath is used to control the rate of reaction.) After all the calcium has

reacted, add methyl red and a quartz boiling tube and enough HCl to give an acid reaction that is permanent even when the solution is heated to boiling. Boil to evaporate solution to a volume of about 3.5 (between 3.0 and 3.8) ml per gram of calcium taken. Cool the solution and then dilute with purified methanol to 28 ml of solution per gram of calcium used.

Calcium Hydroxide, 0.1 N Suspension

Drop about 0.80 gram of distilled calcium, cleaned as above, into a 500 ml quartz flask containing 0.5 ml of H_2O for each mg of calcium. After the metal has decomposed, close the flask with a rubber stopper containing a quartz tube which can be used for transferring approximately 5 ml portions of the suspension. When the tube is not in use, close the top of it with a small rubber bulb. The suspension should be mixed well immediately before each portion is pipetted.

Dilute Oxalic-Hydrochloric Acid Solution

Add 270 ml of H_2O and 160 ml of 95% ethanol to 40 grams of $(COOH)_2 \cdot 2H_2O$ in a 500 ml quartz flask. After the oxalic acid dissolves, add 50 ml of HCl and mix well. This solution may be used for several months.

Turmeric, 1% Extract

Prepare by stirring two grams of turmeric in 200 ml of boron-free 95% ethanol for 4 hours and filtering through Whatman No. 42 filter paper from which boron has been removed previously by washing with ethanol (or by washing with dilute HCl and then with H_2O until free of acid in which case the paper is dried before use). The extract is prepared and stored (in the dark) in boron-free flasks.

Ethanol 95%

That used for dissolving turmeric or for washing filter paper should be stored in boron-free glass; that used after color development may be stored in Pyrex if desired.

-
- (a) No heat is applied. If there is a residue, it can be separated by filtration, through boron-free filter paper and examined further. Before ashing a residue to remove filter paper, it should be washed
(Cont'd. on next page)

free of acid, covered with 5 ml of 0.1 N lime, and evaporated to dryness. Subsequent ashing, and fusion with Na_2CO_3 (0.5 gram) cause no apparent loss of boron.

- (b) The receiving dish, which is also used for evaporation and color development, must be of a standard size and composition. Well-glazed Coors No. 4A porcelain dishes and Amersil No. 7 quartz dishes are equally satisfactory. Great care must be taken before color development to avoid contamination from glassware, filter paper, etc. Unless specifically stated otherwise, fused quartz should be used throughout the work for carrying out reactions and storing reagents.
- (c) The dry sample may be analyzed immediately or if desired may be stored until later in a dessicator containing a small dish of NaOH pellets and sealed with vaseline.
- (d) To avoid the possibility of surface contamination, the metal pieces may be cleaned first by washing with distilled H_2O followed by scraping off the oxide with a clean knife reserved for that purpose.

CARBON

For the determination of carbon in zirconium and zirconium-base alloys, the standard combustion method is in general use. Three methods are described which differ with respect to temperature of combustion, oxygen purification trains, the oxidant to convert CO to CO₂, and the final measurement (gravimetric, volumetric, or conductometric) of the carbon dioxide. Since gravimetric methods are familiar to all analytical chemists, the procedure, which has been in use by Bane⁽¹³⁾ at the Argonne National Laboratory, is not described in detail.

Gravimetric Method

Place 1 to 2 grams of zirconium chips on a bed of 60 mesh alundum in an alundum boat. Ignite in O₂ at about 1150°C in a quartz combustion tube. Purify the O₂ by bubbling it through H₂SO₄, then over hot CuO (~700°C) and through absorption tubes containing magnesium perchlorate and ascarite. Pass the exit gases through hot CuO, silver wool, magnesium perchlorate, and ascarite. Weigh the tube containing the ascarite before and after the run. The increase in weight represents the CO₂ absorbed. Calculate the carbon content from this weight.

Volumetric Method

Burelbach⁽⁵⁴⁾ has described a volumetric method used for the determination of carbon in thorium at the New Brunswick Laboratory. This may be applied to the analysis for carbon in zirconium and Zircaloy with slight revision of the procedure. The revised procedure is described.

Reagents

Barium hydroxide solution - a 0.04 to 0.05 N solution, 0.5 M in barium chloride, is prepared by dissolving 7.7 grams of barium hydroxide octahydrate and 122 grams of barium chloride dihydrate in water and diluting to 1 liter.

Standard hydrochloric acid - a 0.05 N solution is prepared by diluting 4 ml of concentrated hydrochloric acid to 1 liter. This solution is standardized against sodium carbonate in the usual manner.

Carbon dioxide-free water - distilled water is boiled to remove carbon dioxide.

Thymolphthalein indicator - a 0.1% solution in 95% ethyl alcohol.

Procedure

Heat the combustion tube (see Figure 4) to 1200°C with oxygen passing through it. Check for leaks by observing the bubbler with the stopcock on the titration apparatus turned off momentarily. If bubbles still appear, recheck the apparatus for leaks.

Fill the burette, 12, with the standard hydrochloric acid solution. Add 10 ml of the barium hydroxide solution and 4 drops of indicator to the absorption column, 11. Insert an ignited Zircofrax boat in the combustion tube. Start the oxygen flow, open the stopcocks, and allow the oxygen to flow through the train for 30 minutes. With the oxygen still flowing momentarily, run the barium hydroxide solution into the receiving flask. Wash the absorption column down twice with 5 ml portions of carbon dioxide-free water. Shut off the oxygen flow. Titrate with the standard hydrochloric acid slowly, and with continued stirring, to the disappearance of the blue color.

Place a 2 gram sample of metal chips in an ignited Zircofrax boat. Fill the burette and absorption column. Insert the boat into the combustion tube. Turn on the oxygen immediately, open the stopcock, and sweep out for 30 minutes. Run the barium hydroxide solution into the receiving flask and carry on as above.

Calculate the carbon content from the difference between the volume of the titrant used in the blank and in the sample run,

$$\% C = \frac{(V_{\text{blank}} - V_{\text{sample}}) (N_{\text{HCl}}) (0.6)}{\text{Sample Weight in grams}}$$

where V_{blank} and V_{sample} are the volumes in ml of standard acid used in titrating the blank and sample respectively, and the Sample Weight is expressed in grams.

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Figure 4

1. Pressure Regulator
(Pressure maintained at 4" Hg.)
2. Sulfuric Acid Overflow Trap
3. Drierite Guard Tube
4. Vycor Combustion Tube (filled with copper oxide and heated to 600-650°C)
5. Preheater
6. U-tube (half filled with Ascarite; the balance contains $\text{Mg}(\text{ClO}_4)_2$ plus a little indicating Drierite.)
7. McDaniels or Zircofrax Combustion Tube (1-1/4" I.D. with tapered end. Inlet end closed with a rubber stopper having a steel inlet tube with steel and asbestos baffles. This end is always water cooled.)
8. Burrell High Temperature Furnace
9. Sulfur Trap (gas washing bottle 2/3 filled with conc. H_2SO_4 saturated with chromic acid.)
10. Titration Apparatus (A three-way stopcock leads from combustion tube to a Zackerl-Kralnick Absorption buret which in turn drains into the receiving flask. A 10 ml buret also leads into the flask.)

The performance of the train is checked occasionally by analyzing a standard steel sample.

Conductometric Method

Bryson⁽⁵⁵⁾ has described a conductometric method for the determination of carbon in zirconium and zirconium-base alloys. Details of this method are given below.

Principle

The sample is combusted in an oxygen stream and the carbon dioxide in the evolved gases is absorbed by a dilute barium hydroxide solution. The amount of carbon present in the sample is determined by measuring the change in conductance of the absorbing solution and comparing this change against a standard curve.^(a,b)

Scope

The method is set up to cover a concentration range from 0.0005 to 0.035% carbon based on a 1 gram sample. However, good results have been obtained on sample portions as low as 0.1 gram, thus extending the upper limit to 0.350% carbon. Sample segregation must be taken into consideration whenever smaller samples are used.

Known interferences include sulfur compounds and the halides. Both are removed by traps, located between the combustion tube and the absorption cell.

Apparatus

Resistance-type (glo-bar) tube furnace (Burrell T-2-9).

Conductometric carbon determinator (Leco No. 515).

Carbon determinator accessories as listed in the Leco Instruction Manual.^(a)

Reagents

Ascarite (8-20 and 20-30 mesh).

Magnesium perchlorate (anhydrous).

Sulfuric acid (Sp. Gr. 1.84).

Manganese dioxide.

Silver wire.

Barium hydroxide (Baker analyzed - $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$).

Gelatin (U.S.P.).

2-ethyl-1-hexanol.

Trichlorethylene.

Ether (reagent grade).

Accelerator iron (Burrell plast-iron).

Combustion boats (Burrell 24-405).

Bureau of Standards steel samples Nos. 55d, 166, 170.

Barium hydroxide solution - approximately one week before needed, prepare the barium hydroxide solution as follows: bubble carbon dioxide free air through 18 liters of distilled water for at least one day. Dissolve 18 grams of barium hydroxide in 500 ml of carbon dioxide free water. Filter through Whatman No. 40 filter paper into the carbon dioxide free water prepared above. Dissolve 2 grams of gelatin in 500 ml of warm carbon dioxide free water. Add 5 ml of 2 ethyl hexanol (octyl alcohol). Add this solution to the barium hydroxide solution, stopper, and mix thoroughly.

The one-week limit should always be observed. This allows the barium hydroxide solution time to stabilize so that consistent results can be obtained.

Procedure

Calibration Curve

Combust 1 gram samples of Bureau of Standard Nos. 55d, 166, and 170 using the same procedure, including accelerator, as that outlined for the unknown samples. Plot the resistance readings for these samples against their known carbon content on linear co-ordinate paper. The graph is a straight line up to 0.035% carbon for a 1 gram sample. The curve must be checked daily.

Sample Preparation

Degrease approximately 3 grams of the sample chips three times with trichlorethylene, rinse three times with ether and allow to dry.

Analysis of Samples

Place 1 gram of the prepared sample in the combustion boat and cover with 1 gram of accelerator iron. Introduce the loaded boat into the combustion tube. Combust the sample at 1350°C in a 250 to 300 ml/min flow of oxygen. After the combustion tube, pass the gas through the sulfur and halogen traps and the barium hydroxide absorption cell. The conductance of the absorbing solution changes as the barium hydroxide absorbs the evolved carbon dioxide. Ten minutes after the sample is placed in the combustion tube, stop the gas flow and measure the resistance change of the absorbing solution.

Calculations

Concentrations based on 1 gram samples are read directly from the standard curve.

Concentrations based on fractional gram samples are calculated as follows:

$$\% C = \frac{A}{B}$$

A = concentration reading from curve.

B = sample weight in grams.

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- (a) Instruction Manual for Operation of Leco No. 515 Conductometric Carbon Determinator, Laboratory Equipment Corporation (1954).
 - (b) Bennet, E. L., Harley, J. H., and Fowler, R. M., Analytical Chemistry, 22, 445 (1950).

CHLORINE

Chlorine in zirconium sponge may be determined by gravimetric or volumetric methods of analysis. Nephelometric or turbidimetric methods of analysis are more suitable for the determination of the microgram amounts of chlorine present in vacuum melted zirconium or Zircaloy metals. A comprehensive discussion of many types of procedures for the determination of chlorine is found in "Analytical Chemistry of the Manhattan Project."⁽⁵⁾ Read⁽²⁵⁾ describes a nephelometric method which has given reliable results for the determination of microgram amounts of chlorine in zirconium. From 5 to 200 micrograms of chlorine in 1 gram of zirconium may be determined. AgNO_3 solution is added to a dilute solution of the metal in the mixed acids H_2SO_4 , H_3BO_3 , HF , and HNO_3 . The turbidity of the solution is measured in a spectrophotometer. Thomason and Kelley⁽⁷⁷⁾ describe an automatic potentiometric titration method which will determine 5 to 250 micrograms of Cl in zirconium. Beiter⁽⁵⁶⁾ et al describe a nephelometric method for the determination of microgram quantities of chlorine in zirconium and Zircaloy and note that reproducibility of analytical data is erratic when less than 20 micrograms of chlorine is present. This was also observed by Bauman.⁽⁴⁶⁾

The method of Nuclear Metals, Inc. is described.

Method of Nuclear Metals, Inc.

Reagents

All chemicals are "Reagent Grade" and all glassware should be pyrex brand glass.

Water (H_2O) - water previously passed through a mixed bed ion exchange resin and then distilled.

Sulfuric acid [(1:3) H_2SO_4] - add 50 ml concentrated H_2SO_4 to 150 ml H_2O .

Nitric acid [(1:1) HNO_3] - add 100 ml concentrated HNO_3 to 100 ml H_2O .

Silver nitrate solution^(a) (AgNO_3) 1% - dissolve 1 gram AgNO_3 in 100 ml H_2O .

Boric acid (0.85 M) - dissolve 52.5 grams H_3BO_3 in 900 ml hot water, cool, dilute to 1 liter and mix.

Hydrofluoric acid (HF) - 48%.

Standard chloride solution (10 micrograms Cl/ml) - dissolve 0.3297 gram NaCl in water, transfer to a liter volumetric flask, dilute to volume, and mix. Transfer a 50 ml aliquot of this solution to a liter volumetric flask, dilute to volume, and mix. This solution will contain 10 micrograms Cl per ml.

Procedure

Transfer 1.0 gram sample^(b) of zirconium or Zircaloy to a platinum dish, add 20 ml H_2O and 5 ml (1:3) H_2SO_4 . Dissolve the metal by the addition of 2 to 3 ml HF, a few drops at a time, as the reaction permits. After complete solution of the metal is obtained, add 25 ml 0.85 M boric acid solution and transfer to a 100 ml volumetric flask. Add, by means of a pipet, 2.0 ml of the standard chloride solution,^(c) 5 ml (1:1) HNO_3 , and 5 ml 1% AgNO_3 solution, dilute to volume, and mix. Heat in a water bath at 40°C for 30 minutes. (Do not expose to strong light at any time.) Remove from the warm water bath and let stand in water at room temperature for 30 minutes.

Measure the percent transmission in 5 cm cells at 500 millimicrons in a suitable spectrophotometer.^(d) Make correction for a reagent blank, treated in the same manner as the sample solution.^(c) Determine chlorine by reference to a standard transmittance-chlorine concentration curve.

Preparation of Standard Curve

Add 0, 2, 4, 6, 8, and 10 ml of the standard (10 micrograms Cl/ml) solution to 1 gram samples of zirconium metal of low (< 5 ppm) chlorine content and treat exactly as described in the procedure for the sample solution. From the data obtained construct a standard transmittance-chlorine concentration curve.

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- (a) Prepare fresh each day and do not expose to bright light.
- (b) Sample should contain no more than 100 micrograms Cl.
- (c) 20 micrograms Cl is added to the sample solution and to the blank solution to insure the presence of at least 20 micrograms Cl in each solution.
- (d) The turbidity may be measured in a nephelometer.

PHOSPHOROUS

For the microgram quantities of phosphorous found in zirconium metal a sensitive colorimetric method is required. Rodden⁽⁵⁾ discusses methods based on the formation of molybdenum blue by the reduction of phosphomolybdic acid.

Davis⁽²⁶⁾ adapted the method of Boltz and Mellon⁽⁷⁸⁾ to the determination of phosphorous in zirconium, and his procedure has been found to be reliable. This procedure is described.

Method of M.I.T. Metallurgical Project

W. A. Davis

Reagents

Sodium molybdate (2.5% in 10 N H_2SO_4) - 2.5 grams of sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) is added to about 50 ml of H_2O plus 28 ml H_2SO_4 . After complete solution of the salt, dilute to 100 ml volume.

Hydrazine sulfate solution - 0.15 gram of hydrazine sulfate dissolved in 100 ml of H_2O .

Indicator solution (0.1% 2,4 dinitrophenol in ethyl alcohol) - 0.1 gram of 2,4 dinitrophenol is dissolved in 100 ml of ethyl alcohol.

Reductant solution - this solution is made just before using by mixing 25 ml of 2.5% sodium molybdate in 10 N H_2SO_4 , 10 ml of 0.15% hydrazine sulfate solution and enough H_2O to make 100 ml.

Procedure

To a platinum dish, add 1.000 gram of zirconium, 25 ml H_2O , 25 ml HNO_3 and HF dropwise. Following solution of the metal, add 5 ml of H_2SO_4 and evaporate to fumes. Add 1 ml HClO_4 and fume. Wash down sides of dish with H_2O and fume again. Repeat this operation again. Dissolve salts with H_2O and transfer to a 100 ml volumetric flask, dilute to volume and mix well.

Transfer 25 ml of the solution to another 100 ml volumetric flask and add 10 drops of indicator solution. Add NH_4OH (conc) until a yellow color appears and then add H_2SO_4 (conc) dropwise until yellow color disappears. Add 40 ml of reductant solution and dilute to 100 ml volume with H_2O and mix well. Heat in a water bath until the temperature of the solution reaches 90°C and hold at $90^\circ \pm 5^\circ\text{C}$ for 10 minutes. Cool the flask to room temperature and measure the optical density of the solution at 760 millimicrons with H_2O in the reference cell. Use either 1 cm or 5 cm cells depending upon the amount of phosphorous present. Determine the amount of phosphorous present by reference to a standard curve of optical density versus micrograms of phosphorous. This curve is prepared by adding known amounts of phosphorous (as a solution of KH_2PO_4) to 0.25 gram of zirconium in a dilute solution of H_2SO_4 and treating as above.

COMMENT: Phosphorous may be determined by this method when present in the metal in amounts between 20 and 1000 ppm.

SILICON

Colorimetric methods for the determination of silicon have yielded good results in analysis of zirconium metal.⁽²⁵⁾ A modification of the method which Boyle and Hughey⁽⁵⁷⁾ used to determine silicon in magnesium metal was used by Read and Martin⁽⁵⁸⁾ to determine silicon in zirconium. The zirconium metal was dissolved in a solution containing HNO_3 and a carefully measured volume of 10% HF solution (15 ml of HF per gram of zirconium). A great excess of 0.85 M boric acid was added, and the pH was adjusted to 2.5 with ammonium carbonate. Ammonium molybdate solution was then added, and the pH was adjusted to 2.3 with 6 N HCl. The molybdenum-blue color was developed by adding sodium sulfite solution and finally ammonium tartrate solution. The color developed was a clear molybdenum blue, and the optical density was read at 710 millimicrons after the solution was diluted to a 200 ml volume (the pH of the diluted solution was 6 to 7). All operations were carried out in platinum or plastic beakers with a minimum amount of contact with glass until the ammonium tartrate had been added. As little as 10 ppm of silicon in zirconium can be determined by this method. It is imperative that the amount of HF used be carefully measured since this acid contains fluosilicic acid in amounts which may vary appreciably from lot to lot. Albright⁽⁵⁹⁾ analyzed four lots of 48% HF from the same manufacturer and found that the silicon content varied from 12 to 125 micrograms/ml. One lot from a second manufacturer contained 13 micrograms/ml.

Carlson and Banks⁽⁶⁰⁾ obtained good results for silicon in analyses by a different procedure. The metal was dissolved in a dilute solution of sulfuric acid by the slow addition of a measured amount of hydrofluoric acid. After the addition of boric acid and molybdic acid, the pH was adjusted to 1.2 to 1.3 with a specially prepared 20% NH_4OH solution. Tartaric acid was added, and the heteropoly blue complex was obtained by adding a reducing solution prepared by dissolving 27 grams of sodium bisulfite, 2 grams of sodium hydroxide, and 0.5 gram

of 1-amino-2-naphthol-4-sulfonic acid in 250 ml of distilled water. The color was read at 815 millimicrons.

Two methods for the determination of silicon in zirconium and Zircaloy are described. The method of Goward and Wilson⁽⁶¹⁾ is adapted from the procedure of Carlson and Banks.⁽⁶⁰⁾ The procedure of Read and Hicks⁽⁶²⁾ is a variation of the method of Read and Martin.⁽⁵⁸⁾

Method of Nuclear Metals, Inc.
E. B. Read and P. R. Hicks

The spectrophotometric determination of silicon in zirconium and Zircaloy is based upon the solubility of silicon tetrafluoride in a very dilute nitric acid solution, and the complexing of the fluorides with boric acid. If sufficient boric acid is not present, silicon may be picked up from contact with the glass electrodes of the pH meter and glass containers. The presence of free HF, however, inhibits the development of color. It is, therefore, essential that the requisite quantity of boric acid be present; considerable excess has no apparent effect.

Reagents

Hydrofluoric acid (10% by weight) - weigh 104 grams of 48% reagent HF into a polyethylene HF bottle. Dilute to 500 ml with H₂O and mix well.

Boric acid (0.85 M) - dissolve 52.5 grams H₃BO₃ in 1 liter of H₂O.

Ammonium carbonate solution (20%) - dissolve 20 grams in 100 ml H₂O in a porcelain casserole. Warm to hasten solution (make up fresh every day).

Ammonium molybdate solution (10%) - dissolve 25 grams in 250 ml H₂O (may be stored in glass for 3 to 4 days).

Sodium sulfite solution (17%) - make up fresh solution in H₂O each day in a porcelain casserole.

Ammonium tartrate solution (40%) - dissolve in hot H₂O (may be stored in glass for 3 to 4 days).

Nitric acid - concentrated.

Hydrochloric acid (1:1) - equal volumes of HCl and H₂O.

NOTE: All reagents are of analytical grade.

Procedure

Solution of Sample

Weigh a sample of 1 gram or less^(a) into a 250 ml platinum dish provided with a platinum cover. Add 25 ml H_2O , 3 ml HNO_3 (conc.) and 15 ml HF (10%).^(b) After solution is complete heat (not above $70^\circ C$) for 1 hour. Wash off cover with H_2O from wash bottle. Add 150 ml H_3BO_3 (0.85 M) and mix well with a platinum rod. Transfer to a 200 ml volumetric flask,^(c) dilute to the mark with H_2O , mix well and immediately pour back into the platinum dish. Pipette a 50 ml aliquot into a platinum or suitable plastic dish (150 to 250 ml).

Development of Color

Adjust the pH of the aliquot solution to 2.5 with ammonium carbonate solution^(d) stirring with a platinum rod. Add 5 ml ammonium molybdate reagent and adjust to pH 2.3 with HCl . Let stand 10 minutes plus or minus one-half minute.^(e) Add 25 ml of sodium sulfite solution and stir well. After standing 10 minutes plus or minus one-half minute, add 10 ml ammonium tartrate solution and stir. Pour into a 200 ml volumetric flask, add H_2O to the mark, and mix well. Let stand 1 hour.^(f)

Determine the optical density at 710 millimicrons with a Beckman DU Spectrophotometer using 50 mm cells^(g) with distilled water in the comparison cell. The silicon content of the sample solution is obtained from a standard optical density-concentration curve. Make proper correction for a reagent blank which must be carried through the above procedure.

Preparation of Standard Curve

Prepare a stock solution containing 40 micrograms of silicon per ml as follows: fuse 0.0862 gram of N.B.S. No. 81 glass sand with 10 grams of sodium carbonate in a platinum crucible. Dissolve the cooled melt in 500 ml hot H_2O in a large porcelain casserole. After cooling transfer the solution to a 1 liter volumetric flask. While swirling the solution in the flask, add very slowly 180 ml HNO_3 (1:1). Cool, dilute to the mark with H_2O , and mix well. From this stock solution prepare two solutions containing respectively 10 and 20 micrograms of silicon per ml.

NOTE: These solutions remain stable for 2 to 4 months.

To several 250 ml polyethylene beakers add 15 ml H_2O , 1 ml (1:1) HNO_3 , 15 ml HF (10%), and 150 ml H_3BO_3 (0.85 M). Mix well with a platinum rod. As described in the above procedure, dilute to 200 ml volume. Transfer 50 ml aliquots to 250 ml polyethylene beakers. From previously prepared standard silicon solutions, add to these aliquots 10, 20, 30, 40, 60, 80, 100, 150, 200, and 300 micrograms of silicon, respectively. Develop the color in these solutions and measure the optical densities as described in the above procedure. From these measurements construct the standard optical density-concentration curve.^(h)

- - - - -
- (a) Best results are obtained with a 250 mg aliquot. With greater amounts of sample present there is a tendency to "salt out" when the sodium sulfite is added.
 - (b) Due to the appreciable amount of silicon in hydrofluoric acid, this reagent must be measured as accurately as possible in a plastic graduate.
 - (c) Glass contact must be avoided before complexing free HF with boric acid. Subsequent necessary contact with glass, when diluting samples and measuring pH, should be for as short a period as possible.
 - (d) Most of the required amount of ammonium carbonate solution may be added in advance of pH measurement to speed up this operation and shorten glass electrode contact.
 - (e) It is essential that the interval of time between additions of the reagents be controlled to obtain uniform color development.
 - (f) The solutions may be transferred to glass containers after the addition of ammonium tartrate. No appreciable change may be noted after standing two hours.
 - (g) Fifty mm cells may be used when silicon present is 300 micrograms or less. With more than 300 micrograms of silicon present, 10 mm cells may be used.
 - (h) This curve will duplicate almost exactly one prepared from solutions containing no HF or H_3BO_3 .

Method of Westinghouse Atomic Power Division
G. W. Goward and B. B. Wilson

1. Method

(a) Principle

Hydrofluoric acid is used both to dissolve the sample and convert the silicon to a reactive form. The silicon is reacted with molybdic acid to form molybdisilicic acid. The sensitivity of the method is increased by reduction of the molybdisilicic acid to a heteropoly blue complex. The maximum absorbance of the complex is at 815 millimicrons.

(b) Scope

The method covers the determination of silicon as an impurity in zirconium metal and Zircaloy. The range of the method is from 5 to 50 micrograms of silicon as measured in 1 cm cells.

2. Apparatus

- (a) Platinum beakers (200 ml) with lids.
- (b) Polyethylene bottles for storage of solutions.
- (c) Plastic burette for dispensing hydrofluoric acid.
- (d) Beckman Model B or DU Spectrophotometer or similar instrument.

3. Reagents

(a) Ammonium hydroxide (Spec. Gr. 0.92) - prepare by bubbling tank ammonia through distilled water contained in a polyethylene bottle in an ice bath until the above specific gravity is obtained.

(b) Molybdic acid solution (10%) - dissolve 25 grams of ammonium molybdate tetrahydrate in about 200 ml of water. Add 20 ml of concentrated sulfuric acid. Cool and dilute to 250 ml.

(c) Tartaric acid solution (20%).

(d) Reducing solution - dissolve 27 grams sodium bisulfite, 2 grams of sodium hydroxide, and 0.5 gram 1-amino-2-naphthol-4-sulfonic acid in water. Dilute to 250 ml.

(e) Boric acid solution (saturated) - dissolve 52.5 grams boric acid in warm water and dilute to 1 liter.

(f) Standard silicon solution (0.5 mg/ml) - place C.P. silicic acid in a platinum crucible in a muffle furnace. Ignite at 1100°C to 1150°C to constant weight. Weigh 1.072 gram of the SiO_2 into a platinum crucible. Fuse with 5 grams sodium carbonate. Dissolve the melt and dilute to 1 liter in a volumetric flask. Dilute a 10 ml aliquot to 500 ml in a volumetric flask. Each ml of solution is equivalent to 0.01 mg silicon. Standardize the concentrated stock solution by the usual gravimetric procedure for the determination of silicon. Store these solutions in polyethylene bottles.

4. Procedure

(a) Calibration Curve

Transfer 0 (blank), 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 ml aliquots of standard silicon solution into 20 ml platinum beakers. To the standard solutions and reagent blank add 40 ml of saturated boric acid and 4 ml of 10% molybdic acid. Adjust the pH to 1.2 to 1.3 using the special ammonia reagent. After 8 to 12 minutes, add 4 ml of 20% tartaric acid and mix the solution. Immediately thereafter, add 1 ml of the reducing solution and mix. Transfer to 100 ml volumetric flasks, mix, dilute to volume, and mix. After 20 minutes determine the absorbance of the solutions in 1 cm cells at 815 millimicrons using water in the reference cell. Correct for the blank and plot the photometric readings of the calibration solutions against the milligrams of silicon in the solutions.

(b) Analysis of Samples

Weigh samples of suitable size so that the amounts of silicon present fall on the calibration curve. Place in platinum beakers and add 10 ml of distilled H_2O and 0.5 ml of 1:1 sulfuric acid to each. Cover the beakers with platinum lids and dissolve the samples by the dropwise addition of 2.0 ml of HF. Let samples sit until solution is complete.

In order to prepare a reagent blank, weigh out a portion of the zirconium sample that is to be analyzed for silicon. This portion should weigh the same as the samples to be analyzed. Add 10 ml of water, 4 ml of H_2SO_4 and dissolve the sample by the dropwise addition of HF.

Evaporate and fume the sample nearly to dryness. Cool and dissolve the salts in 10 ml H_2O and 2 ml H_2SO_4 . Add 20 drops HF. Take sample through this HF addition and fuming procedure three more times in order to be certain that all the silicon has been driven off. Finally, take up the salts in 20 ml of distilled H_2O and 0.5 ml of 1:1 H_2SO_4 . Add as much HF as is used in dissolving actual samples. Let stand as long as normal samples.

Prior to color development, oxidize all reducing ions by titration of both samples and blank to a faint pink tinge with 0.004 N KMnO_4 . Develop the color in the samples and blank as in 4(a) starting with the addition of boric acid. Take the photometric readings of the sample and blank solutions as described in 4(a).

5. Calculations

Convert the photometric readings of the sample and blank solutions to milligrams of silicon by means of the calibration curve. Calculate ppm of silicon as follows:

$$\text{ppm Si} = \frac{(A - B) 1000}{C}$$

A = milligrams of silicon found in sample.

B = milligrams of silicon found in the reagent blank.

C = grams of sample.

NITROGEN

The nitrogen present in zirconium and Zircaloy metal is readily determined by micro-Kjeldahl distillation as ammonia from solutions of the metal. The metal samples are dissolved in dilute solutions of hydrofluoric acid or mineral acids containing HF. By careful control of reagents, atmosphere, distillation conditions, etc., it is possible to obtain precise measurement of nitrogen when present in zirconium in amounts as low as 5 ppm.

The methods applied to the determination of nitrogen consist briefly in: (1) solution of the metal in acid, (2) steam distillation of ammonia after excess NaOH solution has been added, (3) absorption of the ammonia in a boric acid solution, and (4) measurement of the nitrogen by titration with a standard acid solution or by a colorimetric method employing Nessler's reagent to develop the color. Distillation methods which have been found satisfactory are discussed by Rodden⁽⁵⁾ and Read.⁽²⁵⁾ Beeghly⁽⁶³⁾ describes a micro-Kjeldahl steam-distillation unit which was applied to the analysis for nitrogen in steel. Rodgers⁽⁶⁴⁾ made slight changes in the Beeghly⁽⁶³⁾ apparatus and analyzed for trace amounts of nitrogen in zirconium metal. Nitrogen was determined by measuring the ammonia-Nessler color complex. Two types of Micro-Kjeldahl Distillation Apparatus are described by Steyermark et al.⁽⁶⁵⁾ One is the Pregl Type (Parnas-Wagner) and the second is a "One-Piece Model" similar to the apparatus which is commercially available from Scientific Glass Apparatus Co., Inc., Bloomfield, N. J.

Three methods of analysis for microgram amounts of nitrogen are described. Goward and Perrine⁽⁶⁶⁾ of Westinghouse Atomic Power Division have adapted the method described by Beeghly⁽⁶³⁾ and by Rodgers.⁽⁶⁴⁾ The Battelle Memorial Institute Laboratory uses the Parnas-Wagner nitrogen apparatus and the Scientific Glass Apparatus Co., Inc. Micro-Kjeldahl distillation apparatus is applied in the M.I.T. Metallurgical Project Method.

Method of Westinghouse Atomic Power Division
G. W. Goward and A. W. Perrine

The sample is dissolved in hydrochloric and hydrofluoric acids. The resulting solution is made basic with strong sodium hydroxide solution and nitrogen is removed as ammonia by steam distillation. Ammonia is determined spectrophotometrically in the distillate with Nessler's reagent.

Scope

The method covers the determination of nitrogen in zirconium-base alloys^(a) in the range of 5 to 120 ppm of nitrogen in a 1 gram sample. Range and sensitivity of the method can be varied by varying sample size and wavelength and depth of solution used for photometric measurement.

Reagents

Hydrofluoric acid (48%).

Hydrochloric acid (1:1).

Sodium hydroxide (37.5%) - dissolve 600 grams of NaOH in 1000 ml H₂O.

Nessler reagent - dissolve 50 grams of potassium iodide in a minimum volume of cold H₂O (about 35 ml). Add a saturated solution of mercuric chloride slowly, until the first slight precipitate of red mercuric iodide persists and then 400 ml of a clarified 9 N solution of alkali (potassium or sodium hydroxide). Dilute the solution to 1 liter with ammonia-free water and allow to clarify. Remove the clear supernatant liquid for use. The reagent does not deteriorate and can be stored indefinitely.

Standard ammonia solution - dissolve 3.818 grams of NH₄Cl in H₂O and make to 1 liter. Dilute 10 ml of this stock solution to 1 liter to give a solution, 1 ml of which contains 0.010 mg of nitrogen.

Ammonia-free water - prepare water that is free of ammonia by running distilled H₂O through a mixed bed resin demineralizer.

Prepare all solutions in ammonia-free atmosphere and store in carefully stoppered pyrex bottles. Boil all rubber stoppers used for 30 minutes in a 10% NaOH solution and then rinse with ammonia-free H₂O.

Procedure

Calibration Curve

Pipette 0 (blank), 2, 4, 6, 8, 10, and 12 ml of ammonium chloride standard (0.01 mg (10 γ) N/ml) into 50 ml Nessler tubes containing 25 to 30 ml of ammonia-free H_2O , thus making a series of solutions containing 0 (blank), 20, 40, 60, 80, 100, and 120 γ of nitrogen. Add 1 ml of Nessler reagent to each tube. Dilute to the mark. Insert rubber stoppers in the tubes and shake well. Determine the optical density, or percent transmission of the standard solutions at 430 millimicrons in 2 cm cells.^(b) Correct for the blank and plot these readings against the mg, or γ , of nitrogen in 50 ml volume.

Samples

Dissolve 1 gram of sample^(c) in a 100 ml distillation flask, used with the Beeghly Kjeldahl unit (see Figure 5) using 10 ml of 1-1 HCl and 2 to 3 ml HF added 8 to 10 drops at a time. Heat in a water bath until solution is complete and cool.

While the samples are dissolving, fill the steam-generating flask of the distillation unit with ammonia-free H_2O . Apply heat and pass steam through the distillation flask and into the condenser. Collect 50 ml portions of distillate and add 1 ml of Nessler reagent to each. When this test shows the apparatus to be free of ammonia, add 25 ml of NaOH to the sample cautiously, so as to form two layers in the flask. Immediately connect to the distillation apparatus. Distill for 7 minutes or at least until 35 to 40 ml of distillate is collected. Remove the distillation flask and Nessler tube from the unit and add 1 ml of Nessler reagent to the tube. Dilute to the mark, shake well, and measure the optical density, or percent transmission at 430 millimicrons in 2 cm cells. Determine the amount of nitrogen in the solution from the calibration curve.

Carry a reagent blank through the whole procedure using the same amounts of reagents as are used with the samples. Correct the amount of

Figure 5

nitrogen found in Samples above for this blank and calculate ppm of nitrogen in the sample.

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- (a) The method as written is usable for most simple zirconium-base alloys and hafnium. Variations of acids, time of dissolving and addition of reagents such as hydrogen peroxide extend the method to cover uranium and uranium-base alloys.
 - (b) Either a filter photometer or spectrophotometer may be used. It is convenient to adapt the instrument for direct color measurement in the Nessler tubes.
 - (c) Because of the variable amounts of nitrogen picked up during machining of chip samples, solid samples are the preferred form.
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Method of Battelle Memorial Institute

All H_2O must be of low combined nitrogen content. Such H_2O may be obtained by distillation under properly controlled conditions or by ion exchange purification.

Reagents

HF, 48%, reagent grade or HBF_4 .

NaOH, 38% - dissolve 1.5 lb NaOH in 2000 ml H_2O , add 0.5 gram de Varda's alloy, boil until volume is 1800 ml.

HCl, 1:1 - dilute the 37% reagent with an equal volume of H_2O .

H_3BO_3 - dissolve 40 grams of H_3BO_3 in 1000 ml of H_2O . Prepare 0.18% H_3BO_3 solution by diluting 40 ml of the above (4% solution) to 1000 ml with H_2O . More concentrated H_3BO_3 solution may be used.

Indicator - dissolve 0.166 gram of methyl red and 0.0834 gram of brom cresol green in 100 ml of neutral alcohol. Other mixed indicators with sharp end point are acceptable.

HCl, 0.01 N - standardize against standard steels or carbonate-free NaOH solution which has been standardized against NBS Standard Sample 84C, acid potassium phthalate.

Procedure

Transfer 0.5 to 1.0 gram of sample^(a) to a 50 ml Griffin beaker and treat with 25 ml 1:1 HCl and 1/2 ml HF.^(b) After rapid hydrogen evolution subsides, heat, without boiling, until bubbling stops. Complete solution of the metal should be obtained. If insoluble residue is present, this should dissolve if a few drops of 30% H_2O_2 ^(c) is added and the solution heated. Any residue remaining should be checked for nitrogen. This may be done by decanting and fuming the insoluble matter with H_2SO_4 using selenium as a catalyst. Prepare one or more reagent blanks with each set of samples and treat these solutions in exactly the same manner as the sample solution. Transfer the cool sample solution to a Parnas-Wagner nitrogen apparatus (shown in Figure 6) with a minimum of wash H_2O . Add 25 ml of 38% NaOH solution and steam^(d) distill. Collect 10 ml of condensate in a 50 ml erlenmeyer flask containing 5 drops of indicator solution and 10 ml of 0.16% H_3BO_3 (use 4% H_3BO_3 if sample contains 0.1% or more nitrogen). Adjust the flame so that 5 minutes after the condenser head gets hot, 10 ml of condensate has been collected. When distilling a sample, immerse the discharge end of the condenser in the H_3BO_3 solution for 3 minutes then lower the receiving flask so that the delivery tip is above the level of the solution for the remaining 2 minutes. Titrate the reagent blank with 0.01 N HCl to the first appearance of pink. Using this blank for comparison, titrate the sample to the same color, and correct for the reagent blank. A burette calibrated in 0.01 ml divisions is recommended for this titration.

$$\% N = \frac{\text{ml HCl} \times N \text{ HCl} \times 1.401}{\text{Sample Weight (grams)}}$$

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- (a) Sample should be etched to remove any surface contamination caused by cutting or machining. For very low nitrogen metal a 2.0 gram sample is recommended.
 - (b) Sample may be dissolved in dilute HF alone or dilute H_2SO_4 with the addition of HF. A lower reagent blank titration will result if only HF is used for sample dissolution.
 - (c) It is imperative that the same amount of H_2O_2 be added to the reagent blank since this reagent is seldom free from nitrogen.
 - (d) A few drops of H_2SO_4 will eliminate a possible blank from the steam.

Figure 6 Kjeldahl Distillation Apparatus

1. Steam Generator
2. Steam Trap
3. Distilling Flask
4. Introduction Funnel
5. Silver Tube Condenser
6. Condenser Jacket
7. Erlenmeyer Flask

Method of M.I.T. Metallurgical Project

Reagents

Boric acid (H_3BO_3) - 2% aqueous solution.

Hydrochloric acid (HCl) - (0.01 N) standardized gravimetrically as silver chloride.

Hydrofluoric acid (HF) - 48%.

Hydrogen peroxide (H_2O_2) - 30%.

Sulphuric acid (H_2SO_4) - concentrated.

Sodium hydroxide solution - 50 w/o aqueous solution of purified NaOH . Filter the solution through glass wool into a polyethylene bottle.

Indicator solution - dissolve 0.1 gram of brom cresol green in 50 ml 95% ethyl alcohol. Dissolve 0.1 gram methyl red in 100 ml 95% ethyl alcohol. Combine 25 ml of brom cresol solution with 35 ml of methyl red solution, and mix.

Apparatus

Micro-Kjeldahl Distillation Apparatus obtained from Scientific Glass Apparatus Co., Inc.

Glas-Col heater, obtained from Glas-Col Apparatus Co.

Steaming of Still

Before samples are to be analyzed, the still should be steamed for at least 1 hour as follows. Rinse and fill flask F (see Figure 7) with H_2O , add a few E and A Boileezers to insure an even boil and add a few drops of H_2SO_4 . Clean and grease all stopcocks and flask connection. Place flask F in position, start water running through cooling system J, and place heater beneath flask F. Place a beaker under the delivery tip to catch the distillate. To prevent overflow into flask F, drain water from jacket G by opening stopcock D occasionally and replenish H_2O in flask F as required.

After steaming the still for 1 hour, prepare reagent blank solutions. Treat as described under Procedure until a consistent low blank is obtained. Blank should be equivalent to about 5 micrograms of nitrogen.

Figure 7

Procedure

Dissolution of Metal Sample

Weigh a sample^(a) of 1.5 to 2.0 grams and place in a clean, rinsed platinum dish provided with a platinum lid. Cover sample with about 15 ml H_2O , add 1 ml H_2SO_4 , HF a few drops at a time as reaction allows (about 40 drops per gram sample) and heat gently to obtain complete solution of the sample. If a residue remains, add 2 to 4 drops of H_2O_2 and heat to the disappearance of the peroxide boil.

Distillation

With stopcock B open, transfer sample solution to funnel A, wash down sides of dish with H_2O , and transfer washings to funnel A. Add 20 ml of the NaOH solution and wash funnel with H_2O . Place heater under flask F, after the H_2O in flask F begins to boil close stopcock B, and place the 125 ml erlenmeyer flask H containing 10 ml of 2% boric acid and 3 drops of indicator solution at the delivery tube. The flask H is placed so that the delivery tip is immersed in the solution as far as possible without touching the bottom of the flask. After the first drop of distillate enters flask H set a time clock for 10 minutes. At the end of the 10 minute distillation period lower flask H and, using a wash bottle reserved for this purpose, wash down the end of the delivery tube with H_2O .

Titrate^(b) distillate with the standard 0.01 N HCl solution. The color change is from green to pink. Compare the end point to that obtained when running the blank.

Correction must be made for a reagent blank carried through the entire procedure.

$$\text{Calculation: } \frac{\text{ml HCl} \times \text{Normality HCl} \times 14.008 \times 10^3}{\text{Sample Weight (grams)}} = \text{ppm N}$$

Flushing Still

Remove heater and open stopcock D to drain chamber C. After all of the solution has been drained off, close stopcock D immediately and place a 125 ml erlenmeyer flask filled with H_2O at the delivery tip, holding

flask so that the delivery tip is about two-thirds down in the flask.

As the system cools a partial vacuum is produced that will cause the H_2O in the flask to be drawn into chamber C, then into area G. Open stopcock D and drain off rinse solution. Fill funnel A three times with H_2O , waiting each time until the H_2O has been expelled from chamber C into area G, and drain as before. The still is then ready for the next distillation.

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- (a) The determination should be performed on solid pieces of metal that have been previously etched with a 1:1 HNO_3 solution containing a few drops of HF, rinsed with H_2O , then acetone and dried. This treatment will remove surface contamination which usually occurs when the sample piece is cut.
- (b) A 5 ml burette calibrated in 0.02 divisions is satisfactory for this titration.

OXYGEN

Oxygen in zirconium is usually determined by the hydrogen chloride volatilization method in which the metal is volatilized, leaving the oxygen in the residue as ZrO_2 . This method was described by Read and Zopatti⁽¹⁴⁾ and later by Read.⁽²⁵⁾

Tighe et al⁽¹⁶⁾ describe an HCl volatilization method modified to provide for reverse flushing of the reaction tube with inert gas during and after introduction of samples. Metal halides are removed without opening the system. Movement of the samples in and out of the reaction zone was accomplished by means of a magnet. Results comparable to those obtained by the Read and Zopatti⁽¹⁴⁾ method are reported.

The application of vacuum-fusion techniques to the analysis for oxygen in zirconium have, in general, not been successful. Kroll and Schlechten⁽⁶⁷⁾ reported that, when ZrO_2 was intimately mixed with 100 mesh graphite and heated at 1960°C , about 7.5% O_2 remained in the sample. It was suggested that a stable carbide is formed and that deoxidation stops after equilibrium is reached. Stanley et al⁽⁶⁸⁾ reported obtaining results by vacuum-fusion which were in good agreement with the HCl method. The zirconium sample, wrapped in iron foil, was introduced into 15 to 20 grams of molten iron. The reaction temperature was 2000°C . Addition of tin aided reduction.

Sloman and Harvey⁽⁶⁹⁾ discussed fundamental reactions in the vacuum-fusion method and its application to the determination of O_2 , N_2 , and H_2 in a number of metals including zirconium. Results for oxygen in a number of Bureau of Mines zirconium metal samples were reported. An iron bath at 1750°C was used for reduction.

Derge⁽⁷⁰⁾ determined oxygen in titanium using a bath of 25 grams iron and 5 grams tin, the sample was added at 1800°C . Walter⁽⁷¹⁾ wrapped the titanium sample in tin foil and dropped it into a crucible containing thin shavings of graphite. No information is available concerning the application of the Derge⁽⁷⁰⁾ and Walter⁽⁷¹⁾ methods to the determination

of oxygen in zirconium.

Codell and Norwitz⁽⁷²⁾ determine oxygen in titanium by reaction of the metal with carbon, and bromine in a silica tube at 825°C. Helium is used as a carrier gas. The oxygen in the sample combines with carbon to form CO which is oxidized to CO₂ with hot copper oxide. The CO₂ is absorbed into a weighed bulb containing ascarite. Smiley⁽⁷³⁾ determined oxygen in samples of iron, steel, aluminum, and thorium without high vacuum by dropping the sample into molten platinum in a graphite crucible. Oxygen in the sample reacts to form carbon monoxide which is swept out by a stream of argon at atmospheric pressure. A modified form of Schütze reagent oxidizes the CO to CO₂ which is condensed in a capillary trap and measured with a capillary manometer. No information is available concerning the application of the Codell⁽⁷²⁾ or Smiley⁽⁷³⁾ methods to the determination of oxygen in zirconium.

For the determination of oxygen in zirconium and Zircaloy the method described is a revision of the Read-Zopatti procedure. Three samples are volatilized by hot HCl at the same time. More precise measurement of oxygen is obtained by determination of the zirconium present in the residue. Zirconium is determined by measurement of the color of its alizarin red S complex as described by Wengert.⁽⁷⁴⁾

ANALYSIS FOR OXYGEN IN ZIRCONIUM AND ZIRCALOY

Method of Nuclear Metals, Inc.
E. B. Read and L. P. Zopatti

Reagents

Nitric acid (HNO₃) - concentrated.

Nitric acid [(1:1) HNO₃] - equal volumes of HNO₃ and H₂O.

Hydrofluoric acid (HF) - 48% solution.

Sodium chloride - fine crystals.

Argon gas - welding grade.

Sulfuric acid (H₂SO₄) - concentrated.

Fusion mixture - 1 part sodium carbonate (Na_2CO_3) to 4 parts sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) by weight.

Hydrochloric acid (HCl) - concentrated.

Hydrochloric acid (pH 1.0) - to about 500 ml H_2O add HCl dropwise so as to obtain a solution of pH 1.0.

Alizarin red S solution 0.05% - dissolve a pellet of sodium hydroxide in about 25 ml H_2O . By means of a dropper, add this NaOH solution to about 600 ml H_2O so as to obtain a solution of pH 9.5. Dissolve 0.25 gram alizarin red S in 500 ml of the alkaline (pH 9.5) solution. This solution may be stored for several weeks.

 NOTE: All reagents are analytical grade.

Preparation of Sample

Transfer a solid piece of zirconium metal (cut so as to weigh approximately 1 gram) to a 250 ml beaker. Add 50 ml (1:1) HNO_3 and heat to about 80°C then add 5 to 10 drops HF and swirl to mix. When H_2 evolution is rapid and brown fumes appear, pour off the acid and immediately rinse thoroughly with H_2O . This treatment removes surface contamination and leaves a bright shiny surface on the metal piece.

Hydrogen Chloride Volatilization^(a)

Weigh the sample piece, place in a small platinum or quartz boat (1-1/2 in. x 1/2 in. x 3/8 in.), set in a large quartz boat (6 in. x 5/8 in. x 7/8 in.) and transfer to the cold end of the Vycor combustion tube (see diagram of Volatilization Apparatus - Figure 8). Transfer 300 grams of NaCl crystals (previously dried at 130°C) to the HCl generator.

With the tube containing copper chips at a temperature of 400°C to 450°C and while the "Hevi Duty" Electric Furnace is heating to proper temperature 650°C , replace the air in the HCl generator with oxygen-free argon gas in the following manner. Remove the three clamps at A_1 , A_2 , and A_3 , close stopcocks D and E and remove clamp at C. Adjust stopcock B so as to allow argon to enter HCl generator and flow out through C. Adjust

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Schematic Diagram of The Hydrogen Chloride Volatilization Apparatus.

Figure 8

the regulator on the argon tank so the gas will flow at a rate of 100 to 150 ml per minute. After 20 minutes, open stopcocks E and D and close tube at C with screw clamp. After 15 minutes, close stopcock D, open ball and socket joint under stopcock E and, by means of a glass funnel, add 250 to 300 ml concentrated H_2SO_4 to the acid reservoir. Close and clamp ball and socket joint making certain that stopcock E is open. Allow argon to flush through E for 10 minutes. Close stopcock F and clamp G and adjust stopcock B so as to allow the argon gas to enter Vycor tube at A_3 . Close stopcock E immediately. Allow argon to flow through the combustion tube for 1 hour, open stopcock F for a few seconds and close again.

Close the valve on the argon tank and turn stopcock B so as to permit HCl gas to flow from the HCl generator through the Vycor combustion tube. Allow the H_2SO_4 to drip through stopcock D so as to maintain a steady flow of HCl gas (approximately 150 ml per minute). By means of the stainless steel push rod, place the large boat in the hot zone of the combustion tube and withdraw the rod immediately.

The primary trap will be filled with a white cloud of ZrCl_4 soon after initiating the generation of HCl gas, but will clear after the zirconium metal has been completely volatilized. Continue flow of HCl gas for 15 minutes after the disappearance of white fumes in the primary trap, then close stopcock D. When flow of HCl gas has almost stopped, set stopcock B so as to allow argon to flow through the Vycor combustion tube and immediately open stopcock E. Adjust the valve on the argon tank so the gas will flow at the rate of 100 to 150 ml per minute and allow the "Hevi Duty" furnace to cool for about 30 minutes. Close the valve on the argon tank, remove the boat from the Vycor tube, and cool.

Transfer the residue from the boat to a weighed platinum crucible. Ignite over a Meker burner, cool in a dessicator, and weigh. The residue will be ZrO_2 with some contamination by iron, nickel, chromium, and other impurities. Analyze this residue for zirconium and calculate the oxygen content of the metal as described below.

Analysis of Residue for Zirconium Content

To the platinum crucible containing the ignited residue, add 1.0 gram of fusion mixture and mix intimately by stirring with a glass or platinum rod. Cover with a platinum lid, fuse over a blast burner to obtain a clear melt, and allow to cool. Place crucible and lid in a 150 ml beaker, add 50 ml H₂O and 5 ml HCl and heat to dissolve the melt.

By means of a stirring rod, remove the crucible and lid, washing thoroughly with a stream of H₂O, and cool. Transfer the solution to a 250 ml volumetric flask, dilute to the mark with H₂O, and mix.

Pipette an aliquot of this solution (to contain 0.05 to 0.3 milligrams zirconium) into a 100 ml volumetric flask. Dilute to about 75 ml volume with pH 1.0 hydrochloric acid, add 5 ml 0.05% alizarin red S solution, dilute to the mark with pH 1.0 HCl and mix. Let stand for 1 hour and determine optical density of the solution in 5 cm cells at 510 millimicrons in a Beckman DU Spectrophotometer. Correct for a reagent blank prepared by treating 1.0 gram of fusion mixture in the same manner as the sample melt. Determine the zirconium present by reference to a previously prepared standard optical density-zirconium concentration curve. From the amount of zirconium present in the aliquot solution, calculate the oxygen present in the metal as follows:

$$\frac{0.3508 \times \text{milligram Zr} \times 100}{\text{milligrams sample in aliquot}} = \% \text{O}_2 \text{ in metal}$$

Preparation of Standard Optical Density-Zirconium Concentration Curve

Transfer 135.1 mg of pure ZrO₂ to a platinum crucible, add 1.0 gram of fusion mixture, and mix thoroughly by stirring with a platinum rod. Cover with a platinum lid and fuse over a blast burner to obtain a clear melt and allow to cool. Place the crucible and lid in a 150 ml beaker, add 50 ml H₂O and 5 ml HCl and heat to obtain solution of the melt. Remove the crucible and lid, washing carefully with a stream of H₂O. Transfer the solution to a liter volumetric flask, dilute to volume with pH 1.0 HCl solution and mix. This standard solution contains 100 micrograms zirconium per ml.

Pipette aliquots of the standard solution to contain 0, 50, 100, 150, 200, and 300 micrograms of zirconium into 100 ml volumetric flasks. To each flask, add 75 ml pH 1.0 HCl solution, 5 ml 0.05% alizarin red S solution, dilute to the mark with pH 1.0 solution, and mix. After 1 hour, determine the optical densities of these solutions in 5 cm cells at 510 millimicrons. From data obtained, construct a standard optical density-zirconium concentration curve.

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(a) Three samples may be treated at the same time.

HYDROGEN

Hydrogen may be determined in zirconium and Zircaloy by use of vacuum fusion, hot vacuum extraction, or combustion methods. Rodden⁽⁵⁾ discusses in detail the determination of hydrogen by ignition in oxygen in a microbustion tube. Gregg et al⁽⁷⁵⁾ describe a method of analysis for hydrogen in zirconium by burning chips of the metal at 1200°C in a standard carbon combustion train, absorbing the water in a tube of anhydrous magnesium perchlorate, and weighing as H₂O. Sloman and Harvey⁽⁶⁹⁾ determined hydrogen in zirconium by vacuum fusion, McGeary⁽⁷⁶⁾ describes a method for vacuum extraction of hydrogen from 0.1 to 1.0 gram zirconium samples heated at 1200°C in an inductively heated graphite capsule. Hydrogen was determined by measuring its pressure in a calibrated volume with a McLeod gauge. The precision of this method was estimated to be ± 0.5 ppm. The method which is described is an adaptation of the McGeary method.

Method of Westinghouse Atomic Power Division R. K. McGeary, P. Elbling, and G. W. Goward

Principle

Hydrogen is extracted from the metal or alloy by induction heating at 1150°C in a graphite crucible in vacuo. The gas is transferred from the furnace to a calibrated volume by means of a diffusion pump. Hydrogen present in the original sample is calculated from the pressure increase in the calibrated volume as measured with a McLeod gauge.

Scope

The method covers the determination of hydrogen in zirconium and Zircaloy in the range of 1 to 3000 ppm in a 0.5 gram sample. The upper limit is determined by the maximum pressure which can be read on the McLeod gauge. The upper limit may be increased by the use of smaller samples but only at the expense of losses in precision due to segregation.

Apparatus

Hot vacuum extraction apparatus (Figure 9) as described by McGeary.⁽⁷⁶⁾
Graphite crucibles (United Carbon Products).

Figure 9
Hot Extraction Apparatus for Hydrogen Analysis of Zirconium

Reagents

Acetone (Reagent Grade).

Procedure

Sample Preparation

Cut a 0.2 to 0.4 gram solid sample from the specimen to be analyzed making certain that the sampling area is removed from any sheared edges or those areas which have been heavily worked or heated. File or sand off any heavy oxide coating. Degrease the sample with acetone and then weigh.

Blank Rate of Apparatus

Insert a graphite crucible in the furnace and seal the furnace tube to the apparatus. Load the samples in the sample tube, seal and evacuate the apparatus to about 0.05 microns. Outgas the graphite crucible by heating at 1500°C . When the crucible is sufficiently outgassed lower the temperature to 1150°C and evacuate to 0.001 microns. Determine blank rate of the calibrated volume in microns per minute by isolating the system from the evacuating diffusion pump and forepump. Measure the pressure increase with the McLeod gauge at intervals of 5 minutes for 20 minutes. If the blank rate is greater than 0.05 microns per minute, continue the outgassing procedure until the desired blank rate is obtained.

Analysis of Samples

When a satisfactory blank rate is obtained, open the calibrated volume to the evacuating diffusion pump and forepump and again evacuate to 0.001 microns. Manipulate a sample into the graphite crucible heated to 1150°C and simultaneously isolate the calibrated volume from the evacuating diffusion pump and forepump. Read the pressure on the McLeod gauge at 5 minute intervals until the pressure increase equals the blank rate. This concludes the analysis of the first sample. Open the system to the evacuation diffusion pump and forepump and again evacuate to 0.001 microns. Repeat the procedure for successive samples.

Calculations

$$\text{ppm H} = \frac{10^6 \text{ PVM}}{760 \text{ RTW}}$$

P = corrected pressure from McLeod gauge
in mm of mercury.

V = volume of calibrated volume used in ml.

M = molecular weight of hydrogen.

R = gas constant (82.05 ml atm/°K mole).

T = temperature of volumes °K.

W = sample weight in grams.

RARE EARTH ELEMENTS

Hettel and Fassel⁽³⁹⁾ have reported a method for the determination of fractional parts per million amounts of the rare earth elements dysprosium, gadolinium, holmium, samarium, and terbium when present in zirconium.

A 100.0-gram sample of zirconium is dissolved in a polyethylene beaker by the addition of measured amounts of distilled water and hydrofluoric acid. A hydrochloric acid solution of 20.0 mg of 99.5% pure yttrium oxide is added, the solution is cooled, diluted to a definite volume, and mixed well. This solution is passed through an ion exchange column containing Dowex 50 ion exchange resin, to separate the rare earth elements from the zirconium.

Additional separations are made so that the rare earth oxides are obtained in relatively pure state in a matrix of Y_2O_3 and their concentrations are determined by spectrographic analysis.

Complete details of the method are described by the authors.

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