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DETERMINATION OF OXYGEN IN TITANIUM

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ABSTRACT

Modified vacuum fusion techniques have been employed for the determination of oxygen in titanium. The sample to be analyzed is reacted with powdered graphite, in the presence of tin, to form the stable carbide of titanium and reduce the oxides. The evolved gases are extracted and analyzed. With a furnace temperature of 1900° C, complete reduction is effected within 30 minutes. Good blank conditions are achieved.

The analysis of synthetic standards, prepared by diffusing oxygen gas into hot titanium metal, indicates practically complete recovery of oxygen. Analyses have been made on titanium samples which have been prepared by various commercial processes.

The vacuum apparatus is illustrated and described, and details for the preparation of standard reference samples are given.

PROBLEM STATUS

This is an interim report on work carried out as part of the titanium base alloys program under NRL Problem M01-11R. The vacuum fusion equipment and the method which has been developed will be used to further the studies on titanium alloys.

AUTHORIZATION

NRL Problem No. M01-11R

DETERMINATION OF OXYGEN IN TITANIUM

INTRODUCTION

With the development of improved commercial processes for the production of high purity titanium metal, it has become necessary to devise and to refine analytical techniques for the determination of all elements whose presence might affect the physical properties of the metal. Of primary importance among the contaminating constituents is the element oxygen, which can be introduced during the metal's fabrication as well as during its production. It is generally agreed that oxygen has marked effects upon the physical properties of titanium, but accurate correlations have awaited the development of a dependable method for the evaluation of the oxygen content.

An investigation of oxygen in titanium was undertaken by the Metallurgy Division of the Naval Research Laboratory as a vital supplement to its research program on titanium. A dependable method for the determination of oxygen was considered a prerequisite to an accurate survey of the possibilities and limitations of titanium as a structural metal.

This report presents a modified vacuum fusion method for the determination of oxygen in titanium and describes the apparatus required for the analysis.

BACKGROUND INFORMATION

There are two general types of methods used for determining the oxygen content of metals: *(a) reduction methods, in which the oxides of the metal are reduced by the action of carbon or hydrogen at elevated temperatures, with a subsequent analysis of the gaseous reduction products; (b) residue methods, in which the metals are removed by some chemical action, leaving the residue of unattacked oxides.*[1*]

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[*] *References appear at end of report.*

The method which has had the widest acceptance and has been most versatile in its applications is vacuum fusion, a reduction method. In this method the sample to be analyzed is reacted under vacuum and at high temperatures in a graphite container. The graphite container is heated inductively and supplies the carbon for the reduction of the oxides. The oxygen bearing component of the reduction products is carbon monoxide, which is extracted from the reaction vessel and separated from the other gases evolved by high-vacuum analytical techniques.[2,3]

This method was chosen as a basis for the investigation herein described.

EXPERIMENTAL INVESTIGATION

The analytical investigation was begun along the lines of established vacuum fusion practice, with apparatus which was constructed primarily for the investigation. The gas-pickup characteristics of hot titanium, however, made it impossible to extract more than a small fraction of the oxygen present. Some investigators had reported favorable oxygen recoveries by diluting the titanium with large amounts of iron, but it was impossible in this laboratory to duplicate their achievements or to establish the exact conditions necessary for the complete recovery of oxygen by numerous variations of their technique. No more than 50 percent of the oxygen could be recovered. Even this was not a consistent figure; it varied with the sample size, the physical state of the sample, and the type of oxidation to which the sample had been subjected.

Since it was apparent that a new approach to the problem was needed, attention was given to the possibility of eliminating completely the gas-pickup characteristics of titanium in the reaction crucible. It was felt that this could be done either by removing the mass of the active titanium, after converting it to a volatile salt, as is done in the residue methods for oxygen in metals,[1] or by forming a compound of titanium which would be stable at high temperatures and inert with respect to gas pickup. The latter possibility offered the advantages of simplicity and convenience, in that titanium carbide, which has the desired properties of inertness and stability, could be formed in the reaction crucible with only minor modifications of the existing vacuum equipment. Furthermore, the carbide formation would proceed with a simultaneous reduction of the oxides of titanium. Under there conditions, it seemed reasonable to expect a satisfactory evolution of carbon monoxide without troublesome side reactions.

Preliminary work in which a titanium sample of known oxygen content was reacted with powdered graphite in a graphite crucible, indicated that the reaction between titanium and carbon proceeded quantitatively, forming TiC. The oxygen evolved as carbon monoxide was approximately 75% of the amount added.

In vacuum fusion work with steels containing high percentages of aluminum and manganese some investigators had reported correspondingly low recoveries. This difficulty was overcome to a great extent by the addition of metallic tin to the molten bath.[1] Small additions of tin to the reaction crucible in this work produced an analogous improvement, resulting in oxygen recoveries as high as 90%.

On the basis of the findings of Kroll and Schlechton,[4] it was believed that the remaining 10% was retained within the titanium carbide cinder. These investigators, attempting to reduce metal oxides with carbon under high vacuum, reported that the main difficulty encountered was the sintering of the metal, which sealed up the voids through which the carbon monoxide could escape. It was hoped that this condition could be overcome, if it existed, by fusing the titanium sample with tin before the carbide reaction could be initiated, thus distributing the titanium metal over a greater surface of graphite with a resulting greater porosity of the carbide structure.

This was tried with favorable results. Standard samples, prepared by the addition of pure TiO_2 to titanium metal, as well as samples prepared by the addition of gaseous oxygen, gave recoveries above 97%.

APPARATUS

The vacuum apparatus, pictured in Figure 1 and illustrated schematically in Figure 2, is constructed entirely of Pyrex glass. It consists of a furnace unit and an analytical unit, fused together to form one continuous system. With the exception of the furnace exhaust tube, which has an outside diameter of 25 mm, all other connecting tubing is 15 mm. This large tubing provides for rapid pumping of the gases and contributes to the rigidness and stability of the apparatus. A suspension type supporting framework is used to facilitate flaming of the apparatus and to eliminate the development of strains in the glass.

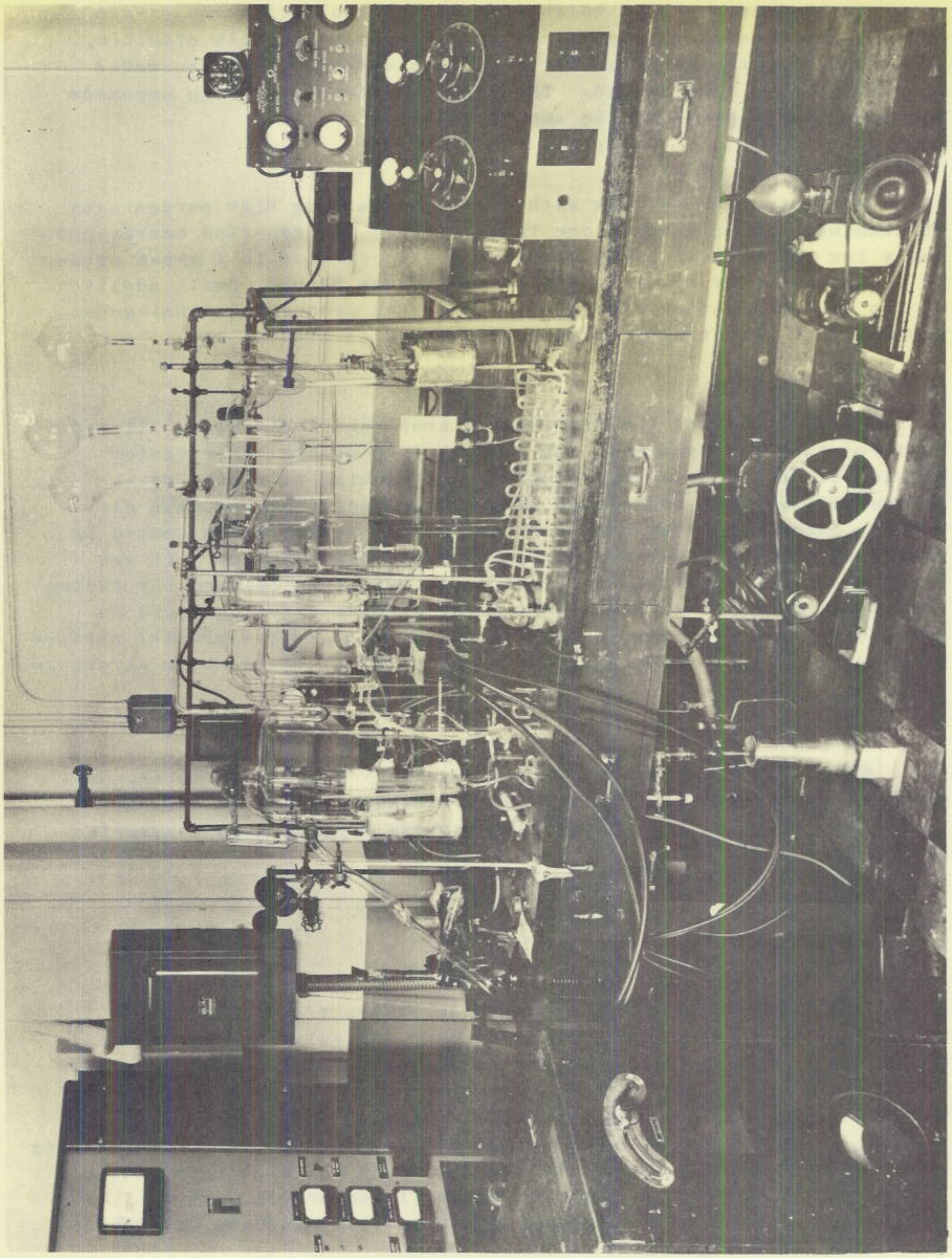

Figure 1 - Photograph of complete apparatus

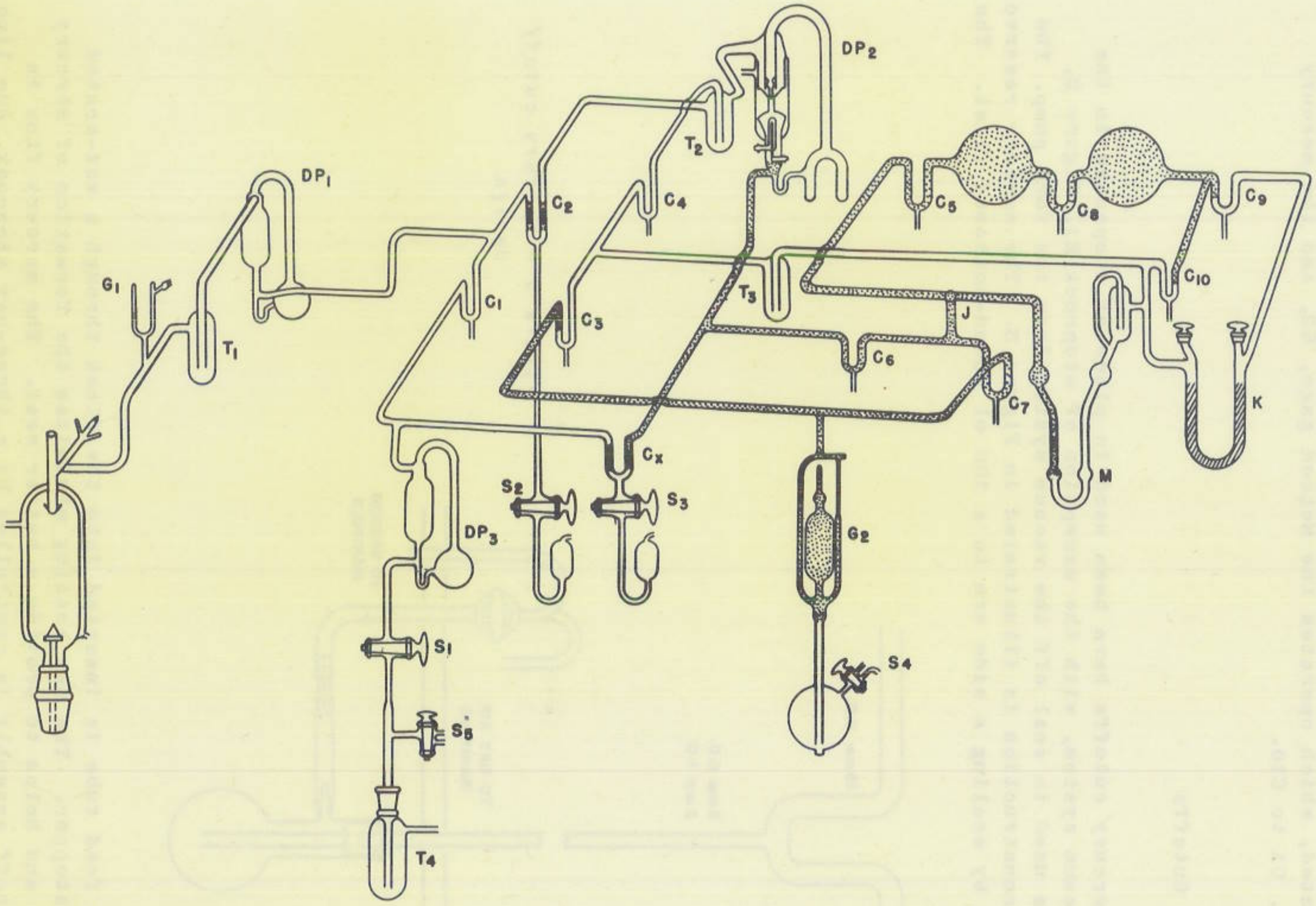

Figure 2 - Schematic diagram of apparatus

Two oil-sealed mechanical pumps are used: a high speed pump, connected to T4, Figure 2, provides the backing for the high vacuum system; and a smaller pump maintains an auxiliary vacuum system, not illustrated, which operates the McLeod gage, G2, and the mercury cutoffs, C1 to C10.

Mercury Cutoffs

Mercury cutoffs have been used in place of stopcocks in the high vacuum system, with the exception of stopcock S1, Figure 2, which is used to seal off the vacuum system from the fore pump. The cutoff construction is illustrated in Figure 3. The mercury reservoir is made by sealing a side arm to a 100 ml round-bottomed flask. The mercury feed tube is inserted into the flask through a wax-coated rubber stopper. The wax coating minimizes the formation of mercury sulfide and helps to provide a better seal. The mercury flow in each cutoff assembly is controlled by a three-way stopcock, one line of which is connected to a dry air manifold at atmospheric pressure, and the other to a vacuum manifold. A short length of capillary

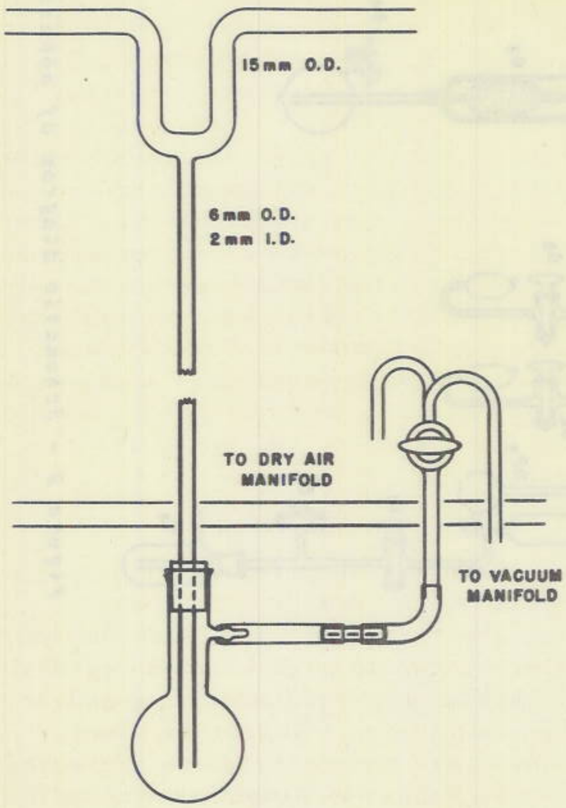

Figure 3 - Mercury cutoff design

tubing is inserted in the line leading from the stopcock to the mercury reservoir to obtain a fine control of the mercury flow. The mercury is triple-distilled grade, which has been further treated to remove greases, oxides, and volatiles. About 50 ml of mercury is required for each cutoff. For ease of support and assembly the reservoirs are located in a common well below the table top. They rest in adjustable supporting rings and can be removed or adjusted individually. The control stopcocks are located in a row, near the front of the table, and all manipulations of the cutoff system can be made from one position. The height of each cutoff assembly, from the mercury level in the reservoir to the top of the U-tube, is slightly greater than the barometric height. If this precaution is observed, there is no danger of the mercury's overflowing into the system.

Two mercury cutoffs of a special design (C2 and Cx, Figure 2) are used in the system to make possible the maintenance of high-vacuum conditions in the analytical unit, while the furnace unit is open to the atmosphere. The simple cutoff arrangement described above cannot be used to separate a pressure differential greater than a few cm of mercury. The cutoff of special design incorporates a carefully ground glass-seat in each arm of the U-tube, into which matching glass check valves are floated by the rising mercury. This provides a gas-tight seal. A conventional type stopcock located in the mercury feed tube controls the mercury flow and prevents mercury from returning to the reservoir when the cutoff is used to seal the analytical unit from the atmosphere. Metal cores are sealed into the glass check valves so that a magnet may be used for freeing the float in the event of sticking.

Furnace System

Messrs. W. G. Guldner and A. L. Beach of the Bell Telephone Research Laboratories recently inaugurated the use of an all-glass furnace for vacuum fusion work, in which a quartz tube, suspended from the top of the furnace by platinum wires, is used as a supporting device for the graphite reaction crucible.[5] This convenient arrangement, which provides full visibility and eliminates troublesome metal heads, has been incorporated in the furnace assembly, illustrated in Figure 4. The Guldner-Beach furnace is entirely air-cooled.

For the work described here a water-jacketed furnace tube was used. It consists of a water-cooled Pyrex cylinder, with a 3-inch inside diameter, equipped with a 71/60 Standard-Taper, ground-glass joint at the bottom. A 1-inch tube leading through the top of the cylinder serves as an exhaust tube for the furnace gases, and as a delivery tube for admitting the samples; and provides an optical path for making temperature observations. Three side arms are sealed onto this vertical tube several inches above the furnace jacket. One arm is connected through diffusion pump DP1, to the vacuum system; one accommodates a small iron armature used for manipulating the crucible cover, and the third is used for storing samples to be analyzed. In order to provide access to these latter two side arms, removable caps made from 29/42 Standard-Taper joints are provided; and a similar capping device, into which an optical window is sealed, is provided for the vertical tube which extends to a height of 12 inches above the furnace jacket. These ports of access simplify furnace cleaning operations without greatly increasing inleakage possibilities.

The quartz tube is 6-1/2 inches in over-all length, 2 inches outside diameter, and has two small holes near the open end to accomodate 0.05-inch platinum supporting wires. All of the graphite parts are machined from Acheson AGX grade material, and the millings are screened to obtain 200-mesh powder for an insulating medium around the quartz tube[5] and 20-mesh powder for reaction material inside of the crucible. About 5 cc of the 20-mesh powder is provided for each crucible. Various crucible designs and sizes were tried, but the most efficient and durable proved to be the one of simplest design: 2-1/2 inches in over-all length, with a 7/8-inch outside diameter and a 5/8-inch inside diameter. A thin-walled funnel fits snugly into the mouth of this crucible.

In order to prevent the contents of the crucible from being ejected during the outgassing operations, a graphite plug in the form of a nipple (Figure 4), and having a small hole drilled through the length of it, is provided. This cover is equipped with a bail made from 0.03-inch tantalum wire, to which a thin molybdenum wire is attached. The molybdenum wire extends through the exhaust tube at the top of the furnace and is attached to a soft-iron armature resting in one of the side arms. By moving the armature back and forth in the arm magnetically, the cover is raised and lowered in the mouth of the crucible. Since the pull of the molybdenum wire is slightly off center, the cover is pulled to the side sufficiently far to make optical pyrometer readings possible. An alundum heat shield fitted into the top of the quartz tube is held in place by the same wires that support the tube. In the course of operations this shield becomes coated with tin, and exhibits no tendencies to exhude or absorb gases.

Inasmuch as the quartz tube is relatively inexpensive and fairly simple to assemble, it is good practice to have a number of them on hand, ready to be placed in service at any time. The time required for removing the tube from the furnace and replacing it with another one can, thereby, be reduced to less than 15 minutes.

The quartz tube assembly is inserted into the furnace tube through the joint at the bottom of the furnace. To eliminate the possibility of scratching the ground-glass surface of the inner joint, a paper sleeve is used for protection. A convenient hook for supporting the quartz-tube assembly and inserting it into the furnace is shown to the right of the furnace diagram in Figure 4.

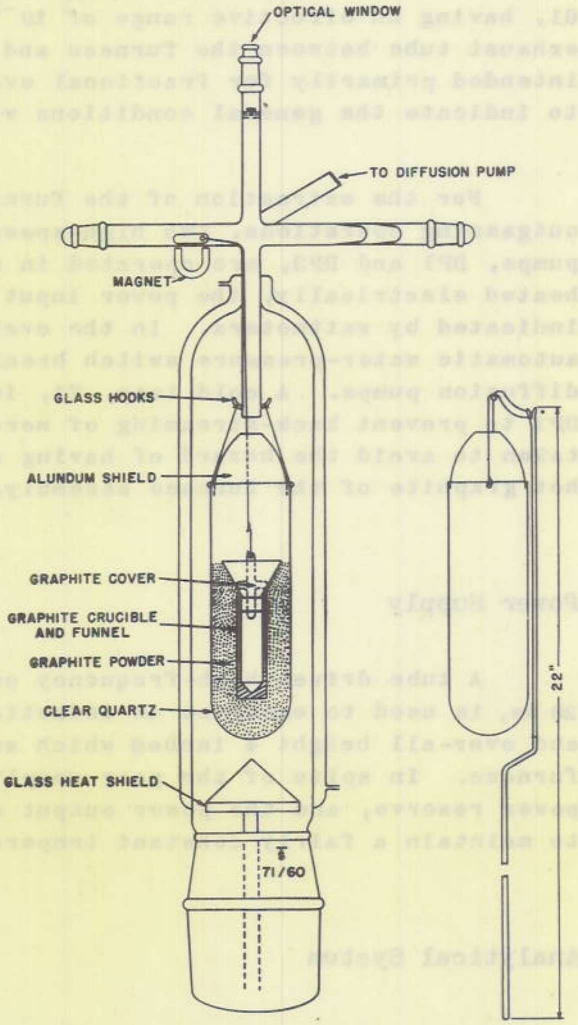

Figure 4 - Detailed furnace design

In spite of all precautions, the optical window becomes coated with a thin film of metal, but a series of baffle plates, located directly below the window and held in place with a nickel-plated spiral spring, tends to minimize this difficulty. A magnetically operated shutter closes the optical path through the baffle plates except when a temperature reading is to be made.

The sample-loading arm has four small side-arms for storing samples to be analyzed, and the nonmagnetic titanium samples are manipulated in this arm by means of a soft iron pusher. In order to minimize the possibilities of sharp, shattering impacts of the hard metal against the glass, the pusher is wrapped in a thin sheet of tin foil. If the need should arise, a mercury lift for introducing samples under high vacuum can be attached to one of the small arms.[6] An ionization gage, G1, having an effective range of 10^{-3} to 10^{-7}mm, is located on the exhaust tube between the furnace and diffusion pump DP1. This gage is intended primarily for fractional evolution studies, but it also serves to indicate the general conditions within the furnace.

For the extraction of the furnace gases during the preliminary outgassing operations, two high-speed single-stage mercury diffusion pumps, DP1 and DP3, are operated in series. The diffusion pumps are heated electrically, the power input being controlled by Variacs and indicated by wattmeters. In the event of a water-pressure drop, an automatic water-pressure switch breaks the electrical circuit to the diffusion pumps. A cold trap, T1, is located between the furnace and DP1 to prevent back-streaming of mercury vapor. All precautions are taken to avoid the hazard of having a mercury globule fall into the hot graphite of the furnace assembly.

Power Supply

A tube driven high-frequency oscillator, having a power input of 20 kw, is used to energize an induction coil (inside diameter 4 inches and over-all height 4 inches) which surrounds the water jacket of the furnace. In spite of the poor coupling afforded, there is an ample power reserve, and the power output can be controlled closely enough to maintain a fairly constant temperature under operating conditions.

Analytical System

The portion of the apparatus to the right of C2 and Cx (Figure 2) constitutes the analytical system. Cutoffs C2 and Cx are of the special design previously described and are used for maintaining the analytical system at high vacuum when the furnace is open for recharging.

A two-stage mercury diffusion pump, DP2, constructed after the design of Naughton and Uhlig,[7] is used both to collect and to circulate the gases to be analyzed. The gases are collected in one of three calibrated volumes. The largest volume, 2755 ml, is represented by the shaded area in Figure 2. The volume can be confined to 1730 ml by closing C8 or to 680 ml by closing C5. All pressure measurements in the course of an analysis are made with the McLeod gate, G2, which is always part of the calibrated volume. The range of the gage is 0 to 1700 microns, with the most accurate range lying between 0 to 175 microns. When gases are being collected, the calibrated volume is so chosen that, if possible, the final pressure of the gases is less than 175 microns. In order to evacuate the gage during the circulation of the gases, it is connected through C3 to the low pressure side of DP2. A magnified deflection-type manometer, M, having mercury in the arm that is open to the calibrated volume and Amoil-S in the other, is incorporated in the system to provide rough indications of the pressure.[6]

The catalyst in K, (used for oxidizing the hydrogen to water vapor and the carbon monoxide to the dioxide) is a mixture of cupric oxide, rare-earth oxides, and kaolin.[8] It is prepared by dissolving 150 grams of pure copper and 23.5 grams of rare-earth oxides in nitric acid. (The rare-earth oxides should have a cerium content not less than 35 percent.) The two solutions are mixed and evaporated to dryness. The dry mixture is heated to drive off the acid fumes and then brought to a temperature of 800° C and maintained there for 24 hours. The ignited mixture is crushed and put through an 80-mesh screen, mixed with 36 grams of pure kaolin and moistened with water to form a plastic mass. This mixture is dried and baked at 800° C for four hours, after which it is broken into small lumps and reduced in a stream of hydrogen at a temperature of 300°-400° C. It is reoxidized at the same temperature. The processes of reduction and oxidation are repeated. After the final oxidation, the material is crushed and put through a 10-mesh screen. The material retained on a 20- mesh screen is placed in the catalyst U-type, K.

The catalyst tube is maintained at a temperature of 325° C by means of a small, electrically heated, pot-type furnace. Provision has been made at the extremities of the U-tube for removing the catalyst for reactivation. The same catalyst has been used in this apparatus for over a year, however, without the need of reactivation and without evidence of loss of efficiency.

The trap, T3, is used for separating the oxidation products of the catalysis by differential freezing. A mixture of dry ice and acetone, supercooled to -90° C by subjecting it to reduced pressure, is used for freezing out the water vapor. Liquid nitrogen (-195° C) is used for freezing out the carbon dioxide.

At junction J, a 29/42 Standard-Taper joint is provided for attaching a small calibrated volume to the analytical system. This small volume is used for the original calibration of the analytical system and for recalibration in the event changes are made in the system which affect the volume. It is at this point also that the apparatus used for the preparation of standard samples is joined to the system.

STANDARDIZATION

The lack of titanium metal of known oxygen content made it necessary to prepare standards which would simulate as nearly as possible the actual conditions of combination encountered in analytical investigations. Titanium metal, prepared by the thermal decomposition of the tetraiodide, was chosen as the base metal to which additions of oxygen would be made.

Gas Addition Apparatus

The apparatus illustrated in Figure 5 provides for the addition of nitrogen, oxygen, and hydrogen to metal samples. Three 1-liter flasks of the pure gases (99% +) are connected by means of Standard-Taper joints, through three-way T-bore stopcocks a, b, and c, to a

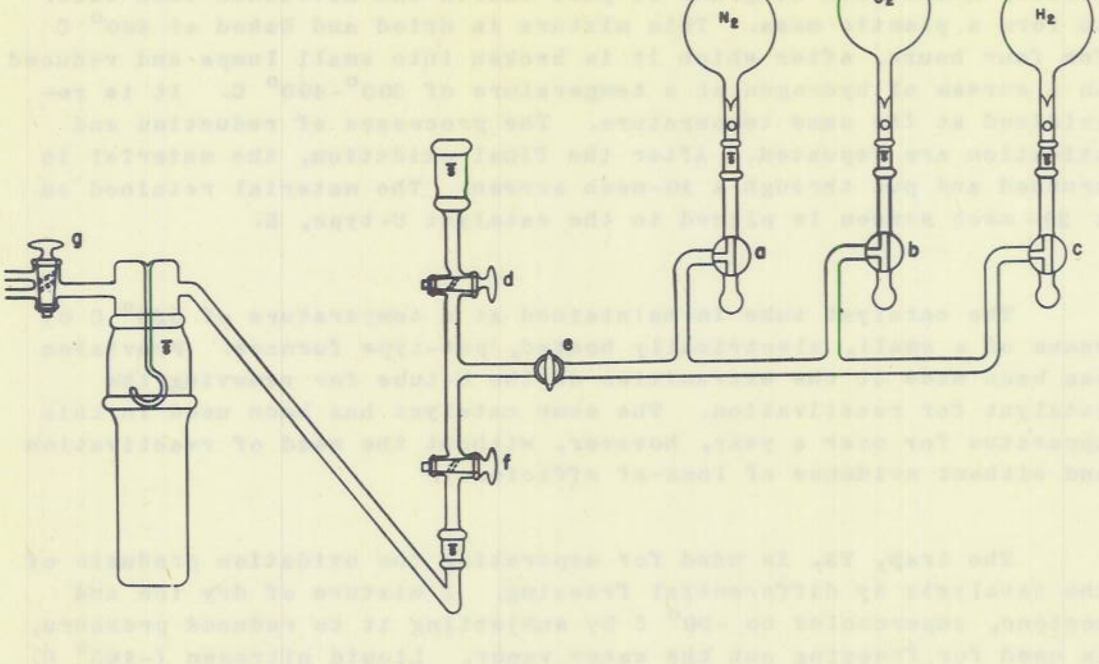

Figure 5 - Gas addition apparatus

common manifold. One arm of each stopcock is sealed off, as illustrated, to provide a volume of approximately 0.5 ml. A small steel ball is placed in the neck of each flask for breaking the glass seal. An absorption chamber (extreme left in Figure 5) 1-1/4 inches outside diameter and 8 inches long, is connected to the apparatus by means of a 34/45 Standard-Taper joint. The outer joint, which constitutes the head of the absorption chamber, is equipped with: a glass hook, from which samples are suspended; a three-way capillary stopcock, g, for bleeding gas into the system and for the initial evacuation of the system; and a connecting tube for joining the absorption chamber to the gas manifold. Three stopcocks, d, e, and f, are placed as illustrated to provide for versatile handling of the addition gases.

The addition apparatus is connected to the analytical system at point J, Figure 2, by means of a 29/42 Standard-Taper joint. The volume of the addition apparatus represented by the area to the left of stopcock e (Figure 5), and below stopcock d, is 175 ml. By adding this volume to the calibrated volume of the analytical system, the addition gases are measured in the same volumes and with the same gage used later for measuring the gases evolved in the course of the analysis. This cancels any slight errors which might exist in the calibration of the gas volumes and the basic accuracy of the McLeod gage.

Preparing Standard Samples

With the addition apparatus connected to the analytical system and the analytical system maintained at high vacuum, stopcock d being closed, a piece of titanium metal prepared by the iodide methods and weighing about 0.5 gram is attached to a piece of thin platinum wire. The wire is attached to the glass hook in the chamber head so that the titanium sample will be suspended near the middle of the chamber. The apparatus is assembled and evacuation is begun through stopcock g with the larger mechanical pump; stopcocks a, b, and c are turned to the position shown in Figure 5; and e and f are opened.

When the pressure in the system is reduced to the ultimate obtainable with the mechanical pump, and it is ascertained that there is no inleakage at the joints and stopcocks, the addition system is opened to the analytical system, and the evacuation is continued with the diffusion pumps. For this purpose, g is closed and d is opened; C1, C2,C3, and C6 (Figure 2) are closed; Cx and S1 are opened. Diffusion pumps DP2 and DP3, are running. When the pressure is reduced to the 10^{-4} mm range, stopcocks a, b, and c are given a quarter turn in the counterclockwide direction, and the steel ball in the neck of the oxygen flask is raised magnetically, breaking the glass seal.

The oxygen expands into the neck of the flask and the stopcock is never again turned into the position shown in Figure 5. The other flasks of gas remain sealed until such a time as they are needed.

Cutoff C5 is now closed; C6 and C3 remain closed. A reading is taken on the McLeod gage. If the pressure is still in the 10^{-4}mm range, stopcock b is given a quarter turn in the counterclockwise direction, permitting gas to expand into the small volume in the sealed off arm of the stopcock. The stopcock is then given a quarter turn in the clockwise direction, permitting the gas in the small volume to expand into the addition system. The pressure is measured on the McLeod gage. If a smaller amount of oxygen is desired, C6 is opened for a moment, permitting the excess to be pumped off. If a larger amount is desired, another volume is admitted through b. When the desired quantity is obtained, e is closed. This gives an exact volume of 630 ml. of gas available for addition to the sample.

The titanium sample is now heated inductively, by a small high-frequency spark-gap generator having a power input of 3-kw. The addition chamber is cooled with a blast of air. The maximum temperature that can be obtained using this power unit with a 0.5-gram sample is about 1100° C, as observed with an optical pryometer. The oxygen pickup begins well below this temperature, however, and at temperatures above 1000° C, the pickup is almost instantaneous for the small amount of oxygen involved. The temperature is maintained at a maximum for 15 minutes after the pickup is complete to give the oxides an opportunity to diffuse through the metal and attain homogeneity. If the addition temperature is much lower than 1000° C, the pickup is slow and the diffusion of the oxygen through the sample is not complete, as indicated by discoloration of the metal surface. After the 15-minute diffusion period, the power is turned off, the sample permitted to cool, and the residual pressure measured. With samples containing appreciable amounts of hydrogen, it is good practice to heat the sample to 1100° C, with the diffusion pumps running, before the oxygen is admitted to the system. If hydrogen is to be added to the titanium metal for experimental work, it is added after the oxygen additions have been made.

When the gas additions have been made, d and f are closed, and dry helium is admitted to the system through g. The sample is removed, and is ready for analysis. A series of standards can be prepared in one afternoon or while the outgassing operation on the furnace is being conducted.

A piece of titanium metal, cut from the same stock as that used for the preparation of standards is always analyzed with the standards as a blank.

ANALYTICAL PROCEDURE

Preparation of the Sample

A solid piece of titanium is cut from the stock metal in such a way as to obtain a section that is representative of the whole cross-section. The cutting, preferably with a jeweler's saw, is done slowly enough to keep the heating of the sample to a minimum. The samples are washed in carbon tetrachloride. The weight of the samples should fall between 0.2 and 0.5 grams, and a piece of clean, stick tin having a weight approximately twice that of the titanium is provided for each sample. The titanium-tin sample pairs are pressed together until they adhere sufficiently to be handled as one sample. If small pieces of titanium are to be analyzed (or powdered titanium) the samples are wrapped in bright tin foil of the appropriate weight. Tin foil is more convenient to use than stick tin, but the blanks run slightly higher due to the greater surface area.

Preparation of the System

With the furnace and analytical systems outgassed and static conditions maintained throughout, the procedure is as follows: Cutoffs C2 and Cx are closed, and control stopcocks S2 and S3 turned to the cutoff position, thus isolating the furnace from the analytical system. Cutoff C1 is opened, and helium is admitted to the furnace system through S5. The mercury column below the U-tube of C1 serves as a manometer, indicating the pressure within the system. After the pressure rises to atmospheric, the ground-glass plug at the bottom of the furnace tube is removed, the quartz tube assembly is extracted by means of the forked rod illustrated in Figure 4, and a freshly-assembled quartz tube is inserted.

After the optical window has been cleaned, the samples to be analyzed are loaded in the appropriate side arm in the order in which they are to be analyzed, the pusher is enclosed, and the system is again sealed. It is important that the initial evacuation of the system proceed slowly enough to prevent the fine insulating graphite powder from being lifted from the quartz tube and to give the operator an opportunity to seat the glass joints properly. This is accomplished by operating the smaller mechanical pump which, by proper manipulation of the valves of the pumping system, is connected to the furnace system through stopcock S5. Again the mercury column of C1 serves as a manometer and indicates the progress of the evacuation. When the pressure drops to a few cm of mercury, the larger mechanical pump is started and S5 is closed.

Outgassing

When the pressure within the furnace system drops to a few microns, the diffusion pumps are started. Mixtures of dry ice and acetone are placed around T1 and T4. With the diffusion pumps operating at their maximum pumping speed, the high-frequency oscillator is started and the heating of the crucible is begun. The heating is done slowly at first, until the major volume of the easily liberated gases is extracted and the graphite powder within the crucible no longer has a tendency to be ejected. The temperature is then allowed to rise slowly until a crucible temperature of 2300°-2400° C is reached. This temperature is maintained for 4 hours or until such a time as blank conditions are favorable.

While the outgassing is in process, DP2 is started and the catalyst is brought up to temperature (325° C). A small amount of gas which evolves from the catalyst while it is being heated, is pumped off continuously by operating DP2 with C3 and C6 closed and Cx open.

Determining the Blank

The ionization gage is used to indicate the progress of the outgassing operation. When the gage shows that the pressure is reduced to the 10^{-4} mm range, with a crucible temperature of 2300° C, a blank is collected as follows: the temperature is dropped to 1900° C. After a few minutes, cutoffs C3, C4, Cx, C9, and C10 are closed; C2 is opened; C1 is closed; and the timing is begun. The pressure is read on the McLeod gage at 5-minute intervals. Unless analyses of unusual accuracy are to be made, a total blank of 5 microns per 15-minute period is satisfactory. The carbon monoxide usually constitutes about 1/3 of the total gas collected, which represents a blank of approximately 0.025 ml (N.T.P.) of carbon monoxide per hour at the above rate.

The first blank collected is measured and pumped out of the system without being analyzed. If it indicates that conditions are satisfactory for the beginning of the analytical work, the temperature is lowered to 1200° C, and a 2-gram piece of tin is dropped into the crucible. The temperature is then raised slowly until the activity of the tin-graphite mixture subsides, after which the temperature is allowed to rise to 2000° C. This first charge of tin is necessary to condition the crucible and to obtain a blank under operating conditions.

The blank to be applied in the analysis of a piece of titanium metal is collected over the same temperature cycle used in the course of an analysis. Normally, the initial crucible temperature is 1200° C, rising to 1900° C at the end of the run, the total time being 30-40 minutes. The analysis of the blank gases is conducted in the same manner as that described in the next section.

Analysis of Sample

After the crucible has been conditioned with tin and a satisfactory blank has been collected and analyzed, the analytical system is pumped down to 10^{-4}mm. (Any initial pressure less than a micron is negligible, since it is impossible to read the final pressure of the collected gases closer than ± 1 micron). The cutoffs are in the same position as specified for the collection of the blank, the temperature is lowered to 1200° C, and a piece of titanium is dropped into the furnace along with a piece of tin. The cover of the crucible is raised slightly to permit the metals to drop into the crucible and is then replaced. The power is turned on with the controls set to give a maximum temperature of 1900° C. Pressure measurements are made every two minutes with the McLeod gage to follow the progress of the evolution. All of the hydrogen is evolved by the end of the first two minutes, after which there is no further evolution of gas until a crucible temperature in the 1700° C range is reached. From observations made of the reactions when no tin was present in the crucible, the TiC is formed exothermically at about 1650° C, and the carbon monoxide begins to evolve at about 1750° C. In the presence of tin, however, the temperatures at which the reactions take place are more difficult to observe. The temperature at which carbon monoxide begins to evolve is somewhat lower when tin is present, but is still several hundred degrees above the temperature at which the hydrogen evolution is complete. Analysis shows that little or no nitrogen is evolved from the titanium sample under these conditions. Since some of the graphite powder may be ejected from the crucible in spite of the cover, it is necessary occasionally to raise the cover slightly to permit the powder to fall back into the crucible. The heating is continued until the rate of increase in pressure is equivalent to the blank.

At this point, C2 is closed, C1 is opened, the furnace temperature is raised several hundred degrees, and maintained there for ten minutes in preparation for the next sample. During this period, the analysis of the collected gases is begun. A Dewar flask of liquid nitrogen is placed around T3; cutoff C7 is closed; C3, C4, and C9 are opened. This permits the gases to circulate over the catalyst and through the freezing-out trap, at the same time evacuating the McLeod gage. The circulation is continued for ten minutes; C10 is then opened and the circulation continued for five minutes more. At the end of this period, C3, C9, and C10 are closed, and C7 is opened. The gases are allowed to collect for two minutes, and the pressure is measured. The reading should be a micron or less; if it is not, the circulation is continued for a few minutes more. When the pressure is of the order of a micron, the liquid nitrogen is removed from T3 and replaced with a mixture of dry ice and acetone (-90° C). After a minute, the pressure is again observed. The pressure measured is that of carbon dioxide, which represents the oxygen content of the sample. This pressure, subtracted from the total pressure of the gases collected, represents the pressure due to hydrogen. A reasonably accurate estimate of the hydrogen and oxygen content of a sample can be made without analyzing the gases by observing the amount of each gas evolved in its characteristic temperature range during the heating cycle.

In the event that the amount of gases collected is larger than is desired for an analysis, an aliquot is easily taken. With the gases occupying the volume represented by the shaded area in Figure 2, C8 is closed, and Cx is opened. This permits the exhausting of all the gases, except those trapped by C8, C9, and C10. When the pressure of the system drops to a micron or less, Cx is closed and C8 is opened, thus expanding the entrapped volume into the total calibrated volume. The pressure is again observed. The pressure of the gases will now be about 1/3 of the original pressure.

After the analysis is completed, C1 and C6 are closed, and Cx, C9, and C10 are opened. The cold mixture is removed from T3, and the system exhausted. After this is done, another sample can be analyzed. As many as five samples have been run in the same crucible with one charge of graphite powder. The crucible can be cleaned upon removal from the furnace and reused, since there is very little attack on the crucible walls.

An analysis is always run on the tin used for fluxing. The amount of oxygen and hydrogen is usually small if clean tin is used, but for a high degree of accuracy and precision, this analysis, plus the analysis of the blank furnace gases, is applied as a correction against the analysis of each titanium sample.

ACCURACY AND REPRODUCIBILITY OF THE METHOD

Table 1 shows the oxygen recovery on a series of standards when no tin was used to alloy with the titanium. The sample weight is approximately the same in each case, but the amount of oxygen varies. The fraction of oxygen recovered, although only about 90 percent of the amount added, is nearly the same for each sample.

Table 2 shows the oxygen recovered on a series of standards when tin was used to alloy with the titanium. No attempt was made

TABLE 1

Analysis of Titanium Standards. No Tin Fusion

Sample No.	Sample Weight (Grams)	Oxygen Added (%)	Oxygen Recovered (%)
1	0.327	0.65	0.60
2	0.385	0.50	0.45
3	0.364	0.39	0.36
4	0.364	0.18	0.16

TABLE 2

Analysis of Titanium Standards. Tin Fusion

Sample No.	Sample Weight (Grams)	Oxygen Added (%)	Oxygen Recovered (%)
5	0.636	0.32	0.31
6	0.205	0.27	0.27
7	0.534	0.105	0.106
8	0.616	0.065	0.065

to correlate sample weight and oxygen concentration. By this method the recovery is practically complete. Sample 6 was prepared by making an addition of spectrographically pure TiO_2 to titanium metal; all others were prepared by making gaseous additions to the hot metal.

Table 3 shows the reproducibility that is obtainable. The analyses were made on titanium samples prepared by different commercial processes. The series serves to illustrate also the range of oxygen concentrations which may be expected in analytical work and gives some indication of the pickup tendencies of the metal during fabrication. No oxygen analyses were available on these samples from other sources for comparative studies.

Samples 9 through 12 were taken from different sections of a large titanium filament prepared by the thermal decomposition of the

TABLE 3

Analysis of Various Types of Titanium Metal

Sample No.	Sample Weight (Grams)	Method of Preparation	Form of Sample	Oxygen Analysis (%)
9	0.369	Iodide	Solid	0.011
	0.349			0.011
10	0.690	"	"	0.007
	0.627			0.011
	0.690			0.012
11	0.569	"	"	0.006
	0.603			0.005
12	0.300	"	"	0.014
	0.275			0.015
13	0.247	"	Wire	0.021
	0.416			0.021
	0.367			0.019
14	0.330	Reduction	Sponge	0.128
	0.542			0.132
15	0.434	"	Spg. Vac. Annealed	0.175
	0.419			0.160
16	0.433	"	"	0.152
	0.391			0.144
17	0.344	"	Spg. Mlt. in Argon	0.31
	0.371			0.29
18	0.372	"	Solid	0.117
	0.450			0.118
19	0.640	"	"	0.118
	0.321			0.119
20	0.550	"	"	0.094
	0.547			0.096
21	0.663	"	"	0.129
	0.471			0.122

iodide. Number 13 was 0.04-inch wire drawn from the same stock. It shows a pickup of about 0.01 percent. Sample 14 was untreated sponge. Samples 15 and 16 were taken from the same stock as number 14 and heated in different zones of a vacuum annealing furnace. Sample number 17 was taken from the same stock as number 14 and melted in argon. Sample number 17 also contained a considerable amount of hydrogen, indicating that water vapor was probably present in the argon. Samples 18 through 21 were taken from small ingots prepared by arc-melting sponge in high vacuum.

LIMITATIONS OF THE METHOD

It is impossible to determine the lower limit of oxygen concentrations detectable by this method, since the most nearly oxygen-free titanium obtainable to date has analyzed 0.005 percent. If there is a residual quantity of oxygen that is not evolved, it escapes present methods of detection. No attempt has been made to establish an upper limit. For the present work, an upper limit of 0.5 percent has provided a safe margin, and standardization work was not carried beyond that order of concentration.

CONCLUSIONS

A method developed for the determination of oxygen in titanium yields analyses of satisfactory accuracy and precision. It eliminates the use of troublesome metal baths, with a resulting longer life for crucibles, and provides for simplicity in the analysis of the evolved gases. Conventional vacuum fusion equipment can be adapted to utilize the method with only minor modifications. The method provides a foundation for further oxygen-titanium investigations.

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