

A DILATOMETRIC METHOD

FOR STUDYING

THE TITANIUM-OXYGEN-HYDROGEN SYSTEM

By

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in metallurgical engineering.

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Abstract

A modified Sieverts' apparatus and a Chevenard dilatometer were combined to permit simultaneous observations of equilibrium hydrogen pressures over, and change in length of, titanium or titanium-rich alloy specimens.

The apparatus was tested, using specimens of titanium alloyed with varying amounts of oxygen, and the data obtained made possible the detection of certain phase boundaries of the titanium-oxygen-hydrogen system which previous investigators, using the Sieverts' apparatus alone, had been unable to detect.

The accuracy of the equipment was checked by observing the phase changes in the titanium-hydrogen system and comparing the results with those of previous investigators.

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Introduction and Literature Survey

The methods and apparatus devised by Sieverts (1) for the study of hydrogen-metal systems have proved to possess widespread applicability. A. D. McQuillan (2) has described the technique as "the simplest and most sensitive method by which the phase boundaries occurring in the titanium-rich region of titanium alloy systems at temperatures below 1000°C may be located".

Sieverts' apparatus and its subsequent modifications are designed to permit the admission of measured quantities of hydrogen to a furnace chamber containing a metal or alloy test specimen. Specimen temperature and hydrogen pressures may be measured directly; accurate knowledge of the volumes of the equipment, and precise equilibrium hydrogen pressure measurements make possible the calculation of the composition of the metal-hydrogen alloy.

Phase changes may be detected by the thermodynamic treatment of temperature, pressure, and composition data obtained as a system traverses a temperature or pressure cycle. Thermodynamic methods can be applied to reversible absorption processes -- such as the absorption of

hydrogen by titanium. Under the circumstance of reversibility, the concentration of the absorbed hydrogen is a function only of the pressure of gaseous hydrogen surrounding the specimen and the temperature. (This subject is pursued in greater detail in Appendix 1, and by McQuillan (2).)

Applications of Sieverts' Methods to Ti and Zr Systems

Several early workers, including Sieverts and his colleagues, studied systems involving titanium and zirconium. (Zirconium, as well as titanium studies, are discussed here because the two metals are similar, both metallurgically and in their hydrogen absorption properties.) However, impurities in the metals studied and contamination introduced by experimental procedures hampered these efforts and injected errors into their results. McQuillan (3), and Hepworth (4) have mentioned the purposes of several of these works.

More recent studies using high purity materials and scrupulous experimental methods have been, for our purposes, more productive. Hall, Martin and Rees (5) have studied the solubility of hydrogen in high purity zirconium and have observed the effects of oxygen on rate and extent of hydrogen absorption. A. D. McQuillan has performed investigations of the phase relations of the titanium-hydrogen system using iodide-process titanium (3), and magnesium-reduced titanium (6). He has, as well, extended Sieverts' methods to the study of the phase relations in titanium-rich titanium alloys by observing very small hydrogen pressures over the alloys -- pressures so small that the hydrogen contents of the specimens could be ignored, and the systems

considered to be binary (7).

Of particular interest in this brief review is the study by Hepworth of the ternary titanium-oxygen-hydrogen system. The present work is a sequel to Hepworth's investigation.

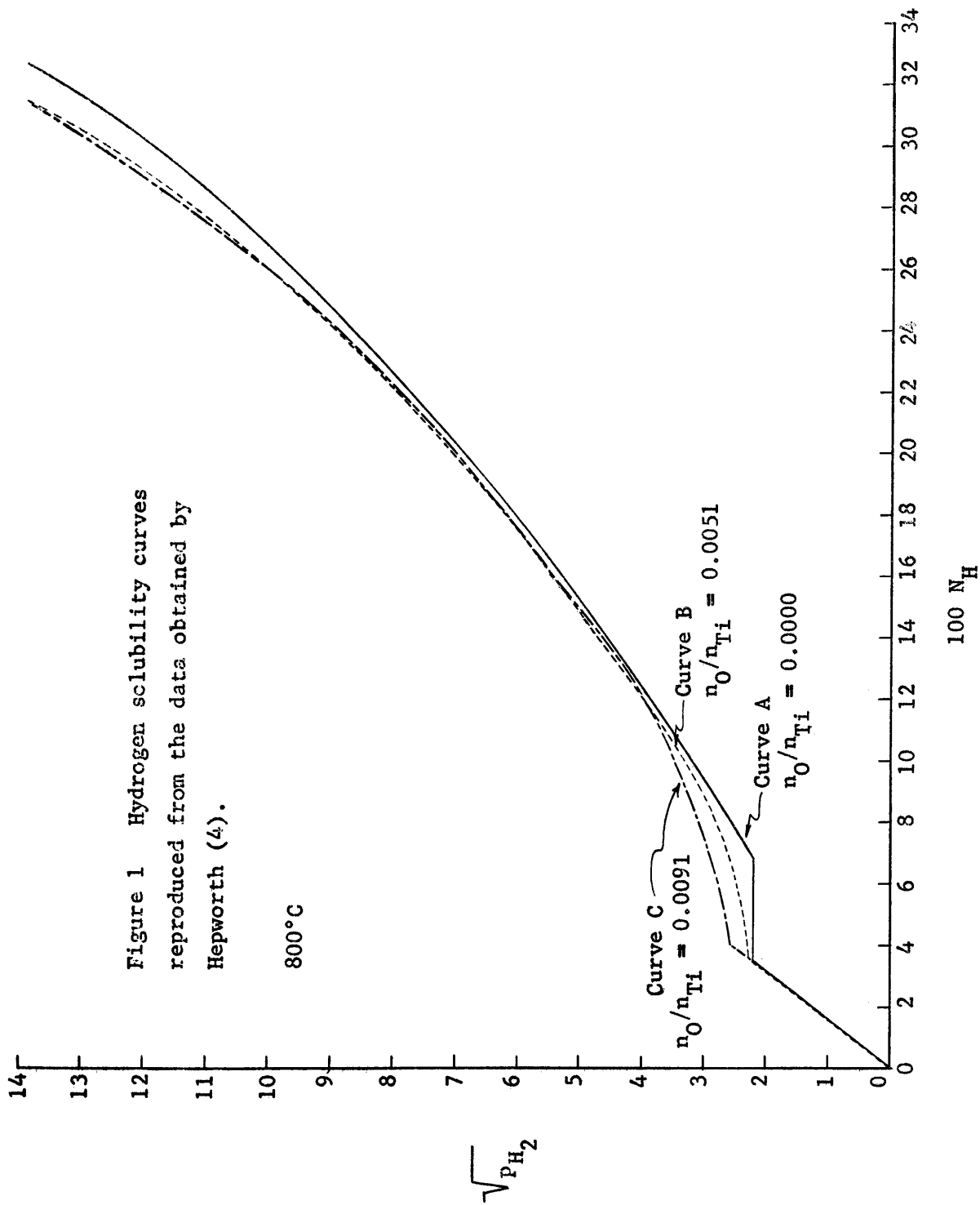
Application of Sieverts' Methods to the Ti-O-H System

Hepworth (4) studied the ternary titanium-oxygen-hydrogen system by observing equilibrium hydrogen pressures over a series of titanium-oxygen alloys varying from 0.000 to 0.1561 in mole ratio of oxygen to titanium. Most data in this investigation was obtained by varying the equilibrium pressure while holding temperature constant. From this isothermal data, phase boundaries were located by observing discontinuities in slope in plots of the square root of the equilibrium pressure against compositions. (Appendix I)

This technique provided a clear indication of the boundary between the α and $\alpha+\beta$ phase regions, and, at low oxygen contents (mole ratio of oxygen to titanium less than about 0.005 at 800°C), of the boundary between the $\alpha+\beta$ and β regions. It did not, however, clearly indicate the latter boundary at higher oxygen contents.

Figure 1 shows reproductions of three of the plots prepared by Hepworth. Curve A represents data obtained using a specimen of pure titanium, curves B and C were obtained using specimens of mole ratios of oxygen to titanium of 0.0051 and 0.00905 respectively.

An inspection of curve A in Figure 1 will reveal that in the single phase regions at lower hydrogen contents, the square root of the



hydrogen pressure bears a linear relationship to composition. (References to phases in this paper refer to condensed phases.) At higher hydrogen concentrations deviations from Sieverts' Law are revealed by the curvature of the plot. As required by the Gibbs Phase Rule, the equilibrium pressure is invariant in the two-phase region of the two-component system.

Curves B and C illustrate the effects of increasing quantities of interstitial oxygen in the titanium specimens. With the addition to the system of another component, viz. oxygen, the degrees of freedom are increased by one and the equilibrium pressure in the two-phase region now varies with composition. As a consequence of univariance of the system, the plot in the two-phase region, acquires a finite slope which becomes more appreciable as the oxygen content increases. A second consequence of the introduction of oxygen into the system is a decreased rate of diffusion of hydrogen through the specimen, particularly in the two-phase region where the approach to equilibrium involves lattice rearrangements. The increasing periods of time required to reach complete equilibrium, and the increasingly infinitesimal pressure changes, which attend the latter stages of an approach to equilibrium, have the effect of rounding the otherwise sharp discontinuities between the one- and two-phase regions. The combination of these two effects will be observed, in curve C, to have made the boundary between the $\alpha+\beta$ and β phase regions indistinct.

The Present Study

The purpose of the present study was to devise a method for obtaining additional information about this doubtful region of the titanium-oxygen-hydrogen equilibrium diagram. The relatively large change in volume which accompanies the transition from α to β titanium, and the appreciable lattice distension commonly caused by the presence of interstitial solutes, had suggested the use of dilatometric methods to solve the problem. The Sieverts' apparatus could not be dispensed with in adopting dilatometric methods, but was combined with the dilatometer in order to admit measured quantities of hydrogen to the test specimen. This apparatus had been constructed, tested, and demonstrated in several experimental runs.

Applications of Dilatometric Methods to Ti and Zr Systems

In recent years dilatometric methods have been applied to systems involving titanium, zirconium and their alloys.

McGeary (8) performed dilatometric studies of the phase relations in zirconium, and its binary alloys with uranium, oxygen and nitrogen. Differential dilatometric data were successfully obtained over thermal cycles by means of a quartz differential dilatometer with a Statham Laboratories unbonded strain gauge. The method of sample preparation -- arc-melting, powder methods or machining directly from crystal bar -- was noted to have an effect on the shape of the dilatometric curve obtained. Certain of the specimens, notably the zirconium-uranium alloys, were observed to deform under the compressive forces exerted

by the measuring apparatus. The dilatometric method was found by McGeary to be particularly sensitive to minute amounts of impurities and its results are described by him as "highly sensitive and reproducible continuous records of the volume changes."

Espagno, Azou and Bastien (9) undertook dilatometric studies of portions of the zirconium-hydrogen system which previous investigations by Sieverts' methods had left in doubt. They successfully obtained information about the eutectoid reaction of the system using a Chevenard differential dilatometer equipped with a head having a magnification factor of 600. The specimens were subjected to thermal cycles, and equilibrium hydrogen pressures and changes in length were observed. A study of the effect of the rate of heating and cooling on the phase transformation was also carried out.

Espagno, Azou and Bastien, using the same equipment, performed a subsequent study (10) to determine the boundaries between the single-phase α and δ regions and the two-phase $\alpha+\delta$ region from 20°C to 550°C. They obtained their data by much the same techniques which they had employed in their higher temperature studies, and completed this portion of the zirconium-hydrogen equilibrium diagram. Until their study these phase relations had been arrived at only by indirect methods.

Costa and Cizeron (11) investigated the influence of an axial compression on the $\beta \rightarrow \alpha$ transformation in titanium. Using a Chevenard dilatometer, and by varying the purity of the metal and the axial

compression applied to the specimen, these investigators noted an abnormally large contraction in high purity titanium passing from the β to the α phase while under an axial compression. This phenomenon was attributed by Costa and Cizeron to shearing of the β lattice on a single preferred plane rather than on all possible planes.

Investigations of the Effects of Interstitial Alloying Agents on Titanium Lattice Parameters

Several studies of the effects of interstitial alloying agents on the lattice parameters of titanium have been performed. Clark's investigation (12), according to McQuillan (2), brought forth the most reliable data available. Clark examined the effects of interstitial oxygen and nitrogen on the lattice parameters of iodide titanium at 25°C. Unfortunately, only a relatively small composition range from 0 to 0.5 wt. percent interstitial alloying agent was studied by Clark.

Equipment

The equipment constructed in the course of this study was designed to permit dilatometric observation of a titanium specimen while enclosed in the specimen chamber of a modified Sieverts' apparatus. Figure 2 illustrates the dilatometer and Sieverts' apparatus, the two major pieces of equipment, and shows the device by which they were connected. Among the auxiliary pieces of equipment which may be observed in Figure 4 are a thermocouple, with its associated equipment, a pot furnace, a telescopic micrometer used to measure the magnitude of the specimen expansion as detected and magnified by the dilatometer, and a cathetometer. The cathetometer was used to measure changes in the mercury levels of the manometers.

The Sieverts' Apparatus

The modified Sieverts' apparatus, shown schematically in Figure 3, will be discussed in three sections -- pumping, hydrogen generation and storage, and specimen chamber.

The pumping section, at the left of the diagram, consists of a

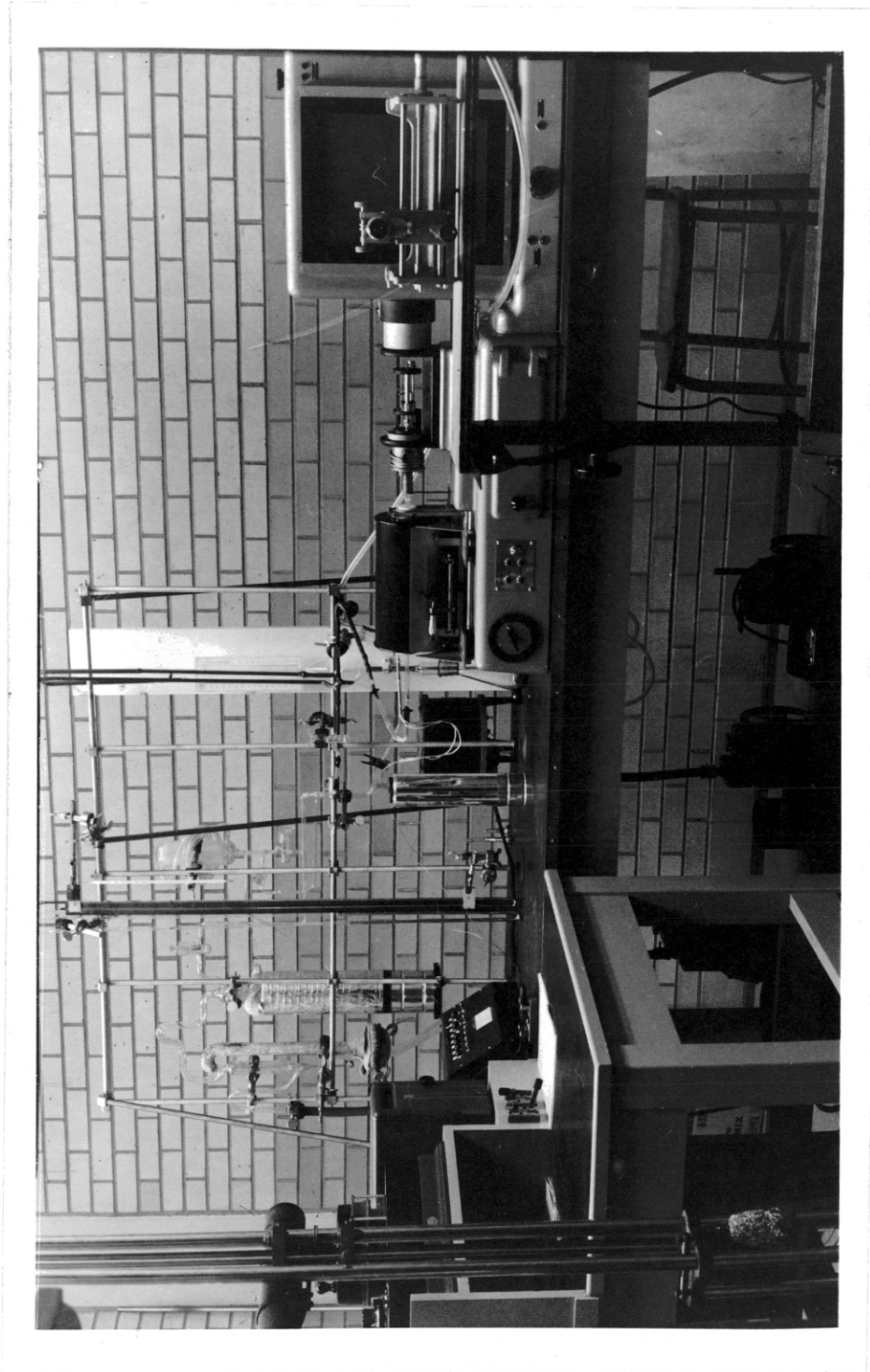
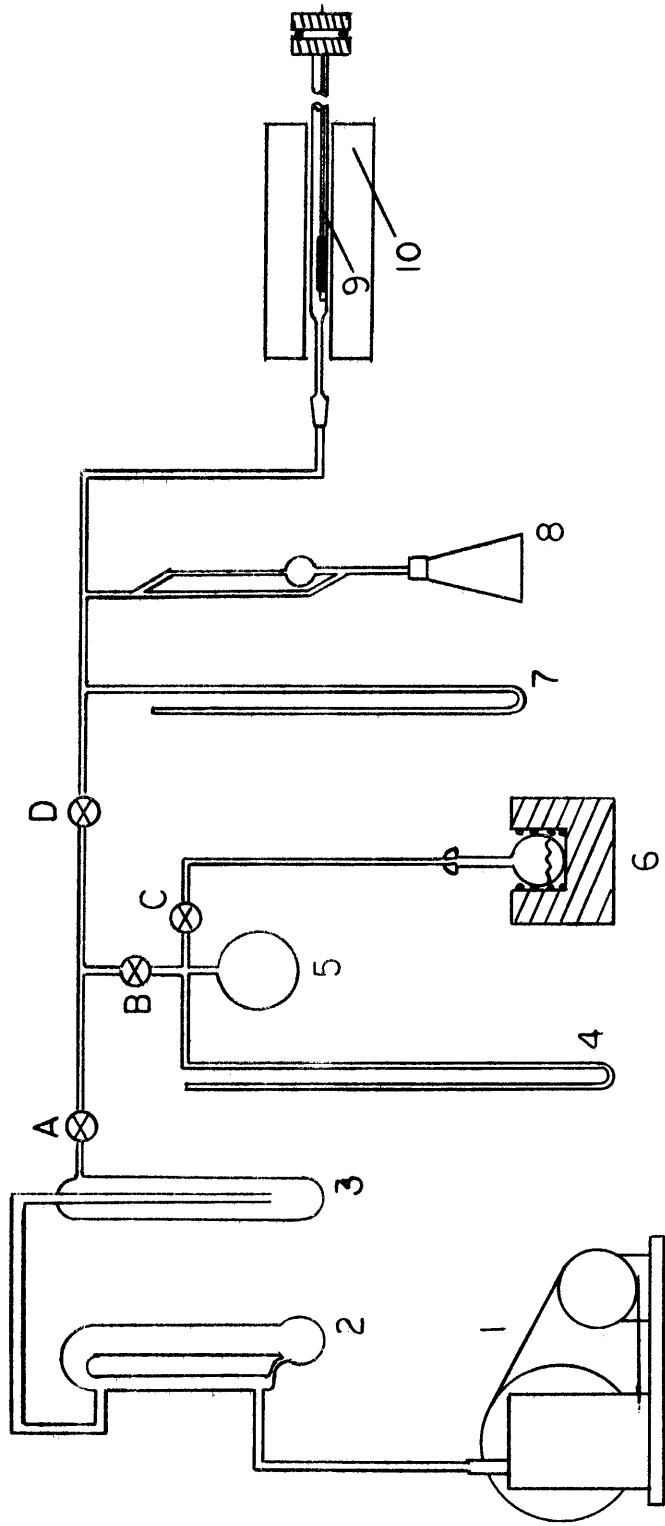


Figure 2 Photograph of the apparatus used in this investigation



Pumping Section

- 1. Mechanical Pump
- 2. Mercury Diffusion Pump
- 3. Cold Trap

H₂ Generation & Storage Section

- 4. Mercury Reservoir
- 5. H₂ Generator
- 6. H₂ Stopcocks

Specimen Chamber

- 7. Mercury Manometer
- 8. McLeod Gauge
- 9. Silica Furnace Tube
- 10. Furnace

A, B, C, D Stopcocks

Figure 3 Diagram of the Sieverts' Apparatus

mercury diffusion pump backed by a mechanical pump. A cold trap, in which a slush of dry ice and isopropyl alcohol was maintained, served to remove condensable vapors from gases passing between the pumping section and the remainder of the apparatus.

Stopcock A (see Figure 3) separates the pumping section from the hydrogen generating and storage section. The latter consists of a hydrogen generator and a reservoir, equipped with a mercury manometer, and bounded by stopcocks B and C. The generator is merely a quartz bulb in which hydrogen can be evolved by heating titanium hydride. The evolved gas is stored in the reservoir, a pyrex bulb, until admitted to the specimen chamber.

The specimen chamber, that portion of the apparatus to the right of stopcock D, is equipped with a mercury manometer and, for precise measurement of pressures below 15 mm Hg, a McLeod gauge. It includes the quartz tube, passing through the furnace, which contains the specimen and dilatometer push rod. The dilatometer end of the specimen chamber terminates at an O-ring seal between the brass fitting in which the quartz tube is mounted and a second brass fitting designed to transmit the motion of the push rod out of the vacuum to the dilatometer head. Both fittings are shown in Figure 4, a plan-section drawing of the motion transmission system. The latter fitting consists of a brass disk through which a stainless steel pin, 1/16 in. in diameter, passes. The pin was carefully lapped into its passageway and the fitting was provided with a grease well which permitted maintenance of a slight pressure of vacuum grease on the pin.

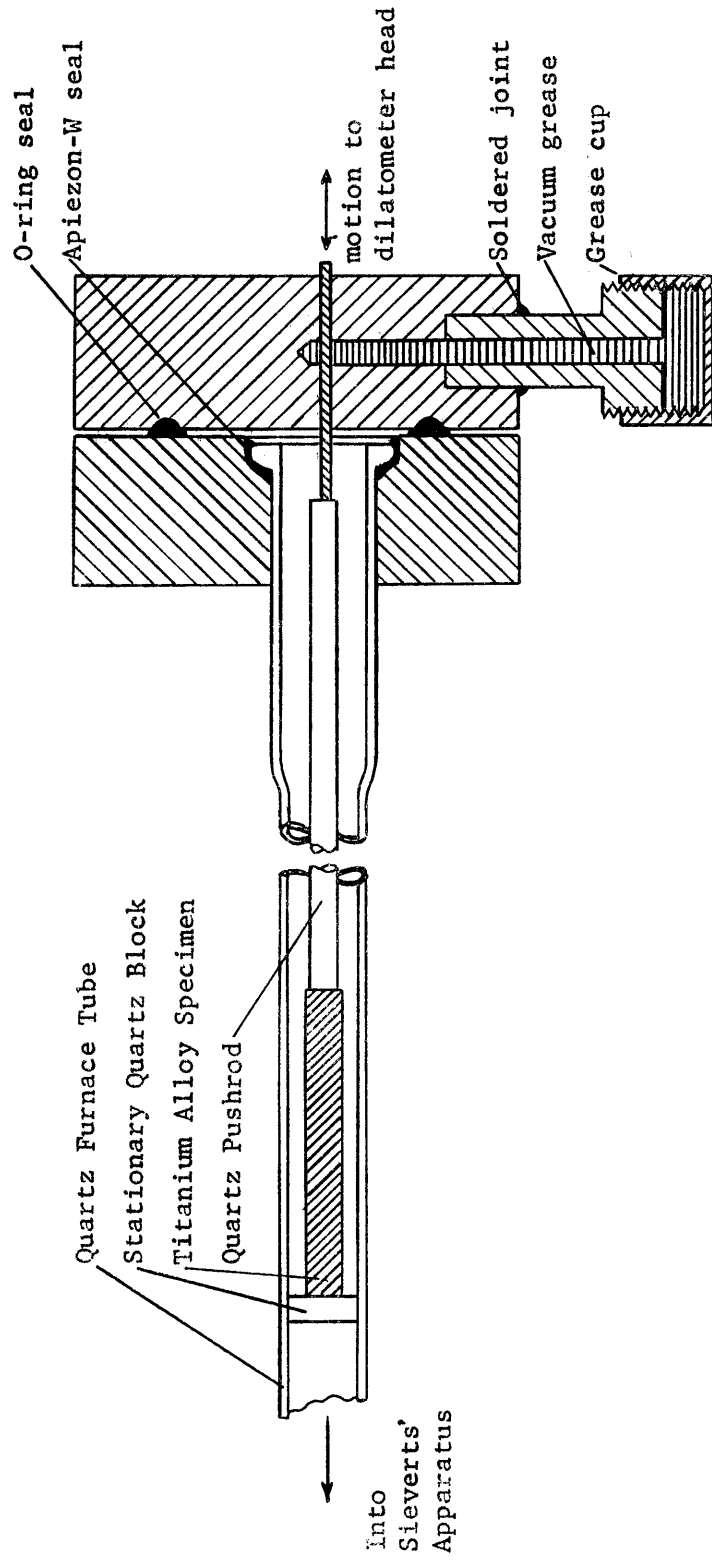


Figure 4 Plan-section drawing of the mechanism for transmitting motion due to changes in specimen length to the dilatometer head.

The Dilatometer

A Chevenard Photographically Recording Dilatometer, Model No. 55, equipped with dilatometric head No. SN 35 and slightly modified, was used in this study. The Chevenard Model 55 Dilatometer, pictured in Figure 5, is a unit designed to automatically subject test specimens to any preset thermal cycle (temperatures not to exceed 1150°C), and to continuously record the resulting changes in specimen dimensions. Silica pushrods bearing against the specimen transmit dimensional changes to the dilatometer head where they are magnified by means of an optical tripod. A beam of light, reflected from the optical tripod, passes through a series of mirrors where it is focused to a pinpoint approximately 0.1 mm in diameter. A photographic film or a ground glass screen may be placed in the focal plane. The trace of this light spot on the film or ground glass provides an accurate record of the expansions and contractions of the specimen as it passes through the thermal cycle.

Dilatometric head No. SN 35, the only one available for this work, was designed for differential dilatometry. Two corners of the optical tripod are arranged to receive motion from pushrods -- one bearing on the test specimen, the other bearing on a standard specimen of accurately known thermal expansion properties. The third corner rests on a fixed plate, providing a fixed reference point on which the motion of the other two corners can be based.

For this study the pushrod, intended to bear on the standard specimen, was removed and the leg of the optical tripod which it

actuated was also allowed to bear on a fixed plate. This modification in effect converted the dilatometric head to measure true expansion. By substituting a micrometer head for the test specimen, the magnification factor of the resulting modification was measured and determined to be 318.9.

The Furnace

The furnace, provided as a part of the standard equipment of the Chevenard Model 55 dilatometer, proved, with minor modifications, to be very satisfactory. The mechanically operated drum, provided with the equipment for programming thermal cycles, was replaced with a Starrett micrometer head graduated to read to 1×10^{-4} in. This modification, shown in Figure 5, permitted precise control of the furnace temperature during isothermal runs. After approximately 90 minutes equilibrating time, fluctuations in furnace temperature due to operation of the controller (an off-on type mechanism) or to drift with time, could not be detected with the potentiometer-galvanometer combination used (a Leeds and Northrup type K-2 potentiometer and a Leeds and Northrup galvanometer.) A sleeve, fashioned out of sheet Inconel, was inserted in the furnace tube to flatten the temperature gradient and the ends of the furnace were closed with plugs carved from fire brick.

The device which was designed and constructed to transmit the motion of the single pushrod out of the vacuum envelope to the dilatometric head has been described and pictured in Figures 4 and 5. Its construction and satisfactory operation represent the solution to the most difficult mechanical problem encountered in the investigation.



Figure 5 Photograph of the Chevenard Model 55 dilatometer used in this investigation. Shown in the picture are the motion transmitting vacuum seal, the telescopic micrometer used to measure light spot motion and the modification made to the furnace controller.

Experimental Procedure

Preparation of Dilatometric Specimens

Titanium-oxygen alloy specimens in a form suitable for dilatometric study were needed for this investigation. Because of the extreme embrittlement of titanium caused by even small quantities of interstitial oxygen, conventional methods of forming which involve machining were considered to be undesirable. Specimens of the required dimensional uniformity were, instead, prepared by arc-casting into a copper chill-mold. The procedure by which this was accomplished was developed by Professor M. T. Hepworth and is described in Appendix 2.

The castings, as taken from the mold, were cylindrical in form, approximately 0.25 in. in diameter, and to each was appended the button of metal which remained when the mold was filled. Out of these cylinders the specimens were hand-cut to a length of 1.6 in.

Each specimen was etched, using hydrofluoric acid, to remove outer surfaces which could possibly have been contaminated by contact with the copper mold or by the subsequent cutting operation. The finished specimens were weighed and their lengths, measured with a micrometer,

were recorded.

Calibration of Equipment

The hydrogen reservoir, specimen chamber and connecting passageways were volumetrically calibrated by observing the pressure change as gas at a known pressure was released from an accurately known volume into the evacuated system. The ideal gas law was used in carrying out these calculations. For those portions of the apparatus equipped with manometers, volume varies with pressure as the mercury level in the manometers rises and falls. Because of this dependence of volume on pressure, numerous measurements were necessary, in calibrating these variable volumes, to accurately determine the functional relationships.

The magnification factor of the dilatometer was measured by substituting a Starrett micrometer head, graduated to read to 1×10^{-4} in., for the specimen. The pushrod was then moved a measured amount by means of the micrometer head, and the corresponding motion of the light spot on the ground glass screen was observed. The dilatometer head was found to magnify changes in specimen length 318.9 times.

Because of the relatively large volume of the specimen chamber, the quantity of gaseous hydrogen necessary to establish the equilibrium hydrogen pressure became an appreciable portion of the total quantity admitted from the hydrogen reservoir. In order to calculate the quantity of gaseous hydrogen remaining in the specimen chamber after equilibrium was established, the effect of holding a portion of that hydrogen at the temperature of the dilatometer furnace had to be

determined. This effect was measured by observing the change in specimen chamber pressure as the furnace was cycled between room temperature and the temperature at which the run was to be made. By carrying out this procedure several times, each with a different quantity of gas in the chamber, the pressure of the gas with the entire chamber at 25°C was determined to be a linear function of the pressure in the chamber with the furnace at a given temperature. The constant relating these pressures varied with furnace temperature.

Measurement of Hydrogen Solubility

Two series of measurements, over a range of hydrogen pressures, were made on each specimen. All readings, on any particular specimen, were made at a constant temperature.

First, by successive additions of measured quantities of hydrogen to the specimen chamber, equilibrium hydrogen pressures were measured as the hydrogen content of the alloy increased and the specimen passed from α , through $\alpha+\beta$ to the β phase. With the exception of a series of readings made with a pure titanium specimen, dilatometric measurements were not attempted during this procedure -- instead the dilatometric pushrods were retracted and held out of contact with the specimen. The data thus obtained were used to prepare plots of mole fraction hydrogen, N_H , versus the square root of the equilibrium pressure, $\sqrt{p_{H_2}}$.

Such plots, which have Sieverts' Law for their theoretical basis, were used by Hepworth to reveal phase boundaries in the titanium-oxygen-hydrogen system. As observed by Hepworth, the transition from

$\alpha+\beta$ to β becomes indistinct as the oxygen content of the specimen becomes greater than about 1 atomic percent. Above this point the transition is marked only by a smooth curve. This observation was born out by the results of this series of equilibrium pressure runs.

The second series of measurements was made by pumping successive, unmeasured quantities of hydrogen out of the specimen chamber. The pushrods of the dilatometer were placed in contact with the specimen and for each increment of hydrogen removed, the equilibrium pressure, p_{H_2} , and the contraction of the specimen, Δl , were read. By reference to the Sieverts' Law plots previously prepared as hydrogen was added to the system, N_H , the mole fraction hydrogen in the specimen, was determined for each equilibrium pressure obtained as the hydrogen was removed. Finally, plots of N_H versus $\Delta l/l$, where l is the length of the specimen, were prepared in order to detect the $\alpha+\beta - \beta$ phase boundary.

Outgassing of Specimen and System

In preparation for each series of readings, the apparatus was assembled, as shown in Figure 2, and evacuated for at least 48 hours. Then, following the method of Hall, Martin and Rees (5) for outgassing the specimen and furnace tube, the specimen chamber was twice flushed with hydrogen at room temperature, the furnace was heated to 1050°C with a small hydrogen pressure in the specimen chamber, and the specimen was vacuum annealed for approximately 30 min. at this temperature. The specimen chamber was then isolated from the pumps and allowed to

cool to the operating temperature.

Measurement of Pressure and Length Changes

Hydrogen pressures in the specimen chamber, below 15 mm of Hg, were measured with the McLeod gauge. Measurements of higher pressures in the specimen chamber and all pressures in the hydrogen reservoir were made by means of mercury manometers. A cathetometer was used to read the levels of the mercury in the manometers, and all manometer pressure readings, with the exception of specimen chamber pressure readings, were corrected to a standard temperature basis for changes in mercury density and scale expansion. Corrections to the specimen chamber pressure were found to have an insignificant effect on the experimental data.

Changes in specimen length were revealed, through the optical system of the dilatometer, by motion of a pinpoint light spot on a ground glass screen. The motion of the light spot was measured by means of a telescopic micrometer.

Sources of Materials for Study

Titanium hydride, obtained from Metal Hydrides, Inc., was heated to generate high purity hydrogen for the study. The iodide-process titanium used was obtained in crystal bar form from the Foote Mineral Company, and the titanium dioxide, used as a source of alloying oxygen, was a Baker Reagent. Analyses of these materials, where available, are summarized in Appendix 3.

Analysis of Prepared Specimens

The dilatometric specimens were analyzed for oxygen and nitrogen by the Denver Research Institute using vacuum fusion techniques. For financial reasons analyses could not be performed on the specimens before and after each dilatometric run. The analyses reported for each specimen represent its composition after undergoing the pressure cycle previously described and, therefore, include contamination acquired in both alloying and casting operation and the dilatometric run.

Experimental Results

Three experimental runs have been performed to determine the usefulness of the apparatus devised. Test specimen compositions for these runs were planned with the purpose of providing an effective test of both the accuracy of the data being obtained and the ability of the method to detect the phase boundaries being sought. A pure titanium specimen, machined from the iodide-process crystal bar, was studied in order to test the accuracy of the calibrations. The data of McQuillan (3) and Hepworth (4) were used as a standard for comparison. A second specimen was studied in order to test the ability of the equipment to detect the $\alpha+\beta - \beta$ phase boundary under conditions of higher oxygen concentrations. The third run was intended to compare the effectiveness of the dilatometric and equilibrium pressure methods in the range of oxygen concentrations where the $\alpha+\beta - \beta$ phase boundary is indistinct when observed by the pressure method alone.

The experimental data pertaining to the three runs performed has been tabulated in Table I. The mole ratio of oxygen to titanium, $n_{\text{O}}/n_{\text{Ti}}$, calculated for each specimen from the TiO_2 addition represents

Table I
Experimental Data

I Run No. 1

Furnace temperature:	800°C
Duration of run:	53 hours
Specimen weight:	4.264 grams
Vacuum fusion analysis results:	470 ppm oxygen 118 ppm nitrogen
* n_O/n_{Ti} (calculated from TiO_2 addition):	0.0000
** $n_O + n_N/n_{Ti}$ (calculated from analysis results):	0.0018
n_O/n_{Ti} (estimated by comparison of plots with those of Hepworth):	0.002
Equilibrium pressure and dilatometric data:	

*** 100 N_H	$P_{H_2}^{1/2}$ (mm ^{1/2})	$10^3 \Delta l/l$
1.69	1.06	0.42
3.86	2.12	1.27
4.38	2.14	1.39
5.21	2.18	1.50
6.13	2.20	1.57
7.02	2.25	1.71
7.54	2.31	1.79
8.50	2.61	2.04
10.20	3.14	2.63
12.62	3.76	3.58
16.07	4.92	4.56
	4.39	3.57
	4.00	3.13
	3.86	2.86
	3.36	2.13
	2.90	1.37
	2.62	0.92

Table I (continued)

*** 100 N_H	$P_{H_2}^{1/2}$ (mm ^{1/2})	$10^3 \Delta \mathcal{L}/\mathcal{Q}$
	2.36	0.49
	2.25	0.22
	2.20	0.00
	2.18	-0.21
	2.14	-0.31
	2.08	-0.39

* n_O = moles interstitial oxygen

n_N = moles interstitial nitrogen

n_{Ti} = moles titanium

** moles oxygen and moles nitrogen are combined to arrive at total moles α -stabilizing interstitial alloying agent

*** N_H = mole fraction interstitial hydrogen (for Run No. 1, 100 N_H calculated from vacuum fusion analysis data and by assuming the specimen to be pure Ti differ by no more than 0.01)

II. Run No. 2

Furnace temperature:	700°C
Duration of run:	63 hours
Specimen weight:	5.501 grams
Vacuum fusion analysis results:	780 ppm oxygen 213 ppm nitrogen
n_O/n_{Ti} (calculated from TiO_2 addition):	0.1270
$n_O + n_N/n_{Ti}$ (calculated from analysis results):	0.0030
n_O/n_{Ti} (estimated by comparison of plots with those of Hepworth):	(insufficient comparable data)

Equilibrium pressure and dilatometric data:

* 100 N _H	** 100 N _H	P _{H₂} ^{1/2} (mm ^{1/2})	10 ³ Δl/l
1.09	1.01	0.47	
2.84	2.64	1.18	
5.18	4.81	2.14	
7.35	6.85	3.04	
8.36	7.79	3.26	
9.29	8.66	3.36	
10.45	9.76	3.41	
11.62	10.86	3.54	
13.43	12.57	3.70	
14.53	13.63	3.82	
15.52	14.52	3.90	
17.60	16.53	4.25	
19.39	18.24	4.55	
21.11	19.87	4.86	
23.09	21.79	5.30	
25.56	24.13	5.94	
30.37	28.78	7.83	
		7.44	-0.34
		6.68	-0.74
		6.35	-2.67
		5.85	-3.49
		5.44	-4.16
		4.90	-5.14
		4.59	-5.67
		4.35	-6.28
		4.04	-7.09
		3.78	-7.75
		3.61	-8.40
		3.43	-9.97
		3.35	-10.34
		3.27	-10.72

* from vacuum fusion analysis results

** from TiO₂ addition

III Run No. 3

Furnace temperature:

800°C

Duration of run:

41 hr. 9 min.

Specimen weight: 5.037 grams

Vacuum fusion analysis results: 615 ppm oxygen
137 ppm nitrogen

$n_{\text{O}}/n_{\text{Ti}}$ (calculated from TiO_2 addition): 0.00900

$n_{\text{O}} + n_{\text{N}}/n_{\text{Ti}}$ (calculated from analysis results): 0.00231

$n_{\text{O}}/n_{\text{Ti}}$ (estimated by comparison of plots
with those of Hepworth): 0.005

Equilibrium pressure and dilatometric data:

* 100 N_{H}	** 100 N_{H}	$P_{\text{H}_2}^{1/2}$ ($\text{mm}^{1/2}$)	$10^3 \Delta l/l$
1.85	1.84	1.31	
3.16	3.15	1.96	
5.27	5.30	2.48	
6.09	6.07	2.62	
7.21	7.20	2.80	
8.72	8.72	3.06	
10.35	10.35	3.42	
12.06	11.99	3.92	
14.17	14.13	4.59	
16.08	16.04	5.20	
19.92	19.86	6.88	
23.57	23.52	8.55	
		7.46	2.43
		6.42	4.06
		5.56	5.36
		4.71	6.74
		3.99	7.86
		3.46	8.87
		3.26	9.32
		3.02	9.69
		2.80	9.97
		2.58	10.21
		2.39	10.43
		2.18	10.63
		2.06	10.72
		1.82	10.87
		1.45	11.11
		0.99	11.44
		0.148	11.78

* from vacuum fusion analysis results

** from TiO_2 addition

Run No. 1
 800°C
 $n_O/n_{Ti} = 0.002$

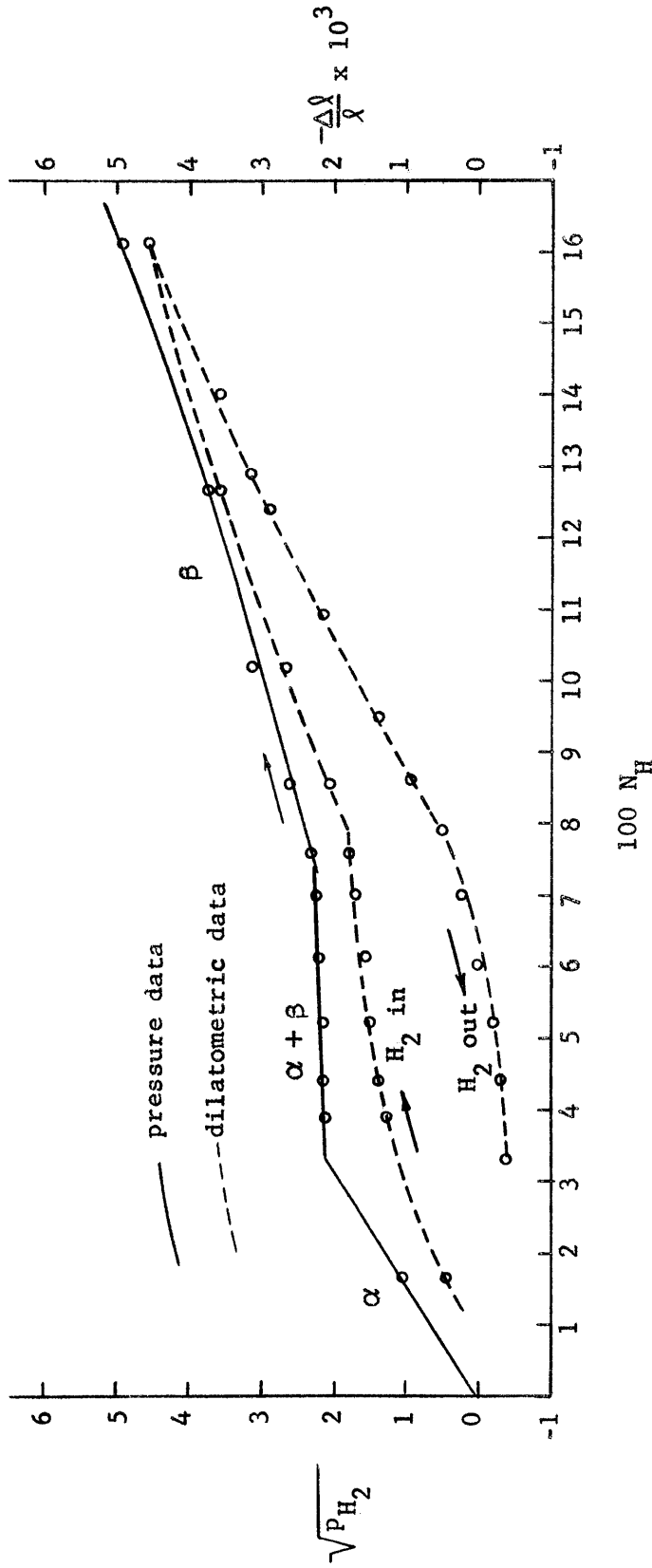


Figure 6 Equilibrium hydrogen pressure and dilatometric curves prepared from data obtained using a titanium specimen machined from a crystal bar.
 (Note: $-\frac{\Delta l}{l} \times 10^3$ is plotted in this curve. Δl , the specimen contraction, is negative here because a zero point of zero H content was used.)

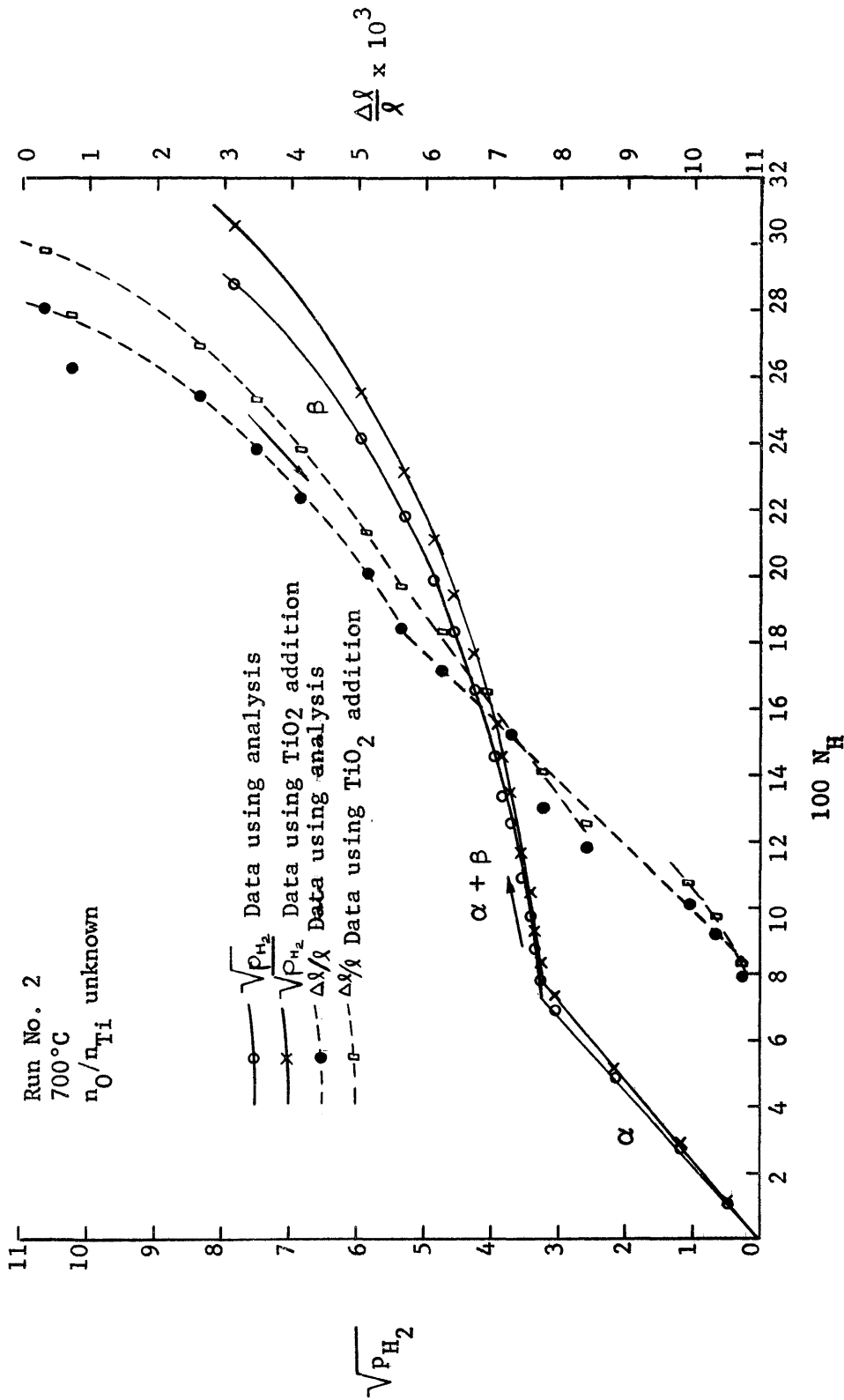


Figure 7 Equilibrium hydrogen pressure and dilatometric curves for Run No. 2 calculated for the theoretical composition and the composition obtained by vacuum fusion analysis.

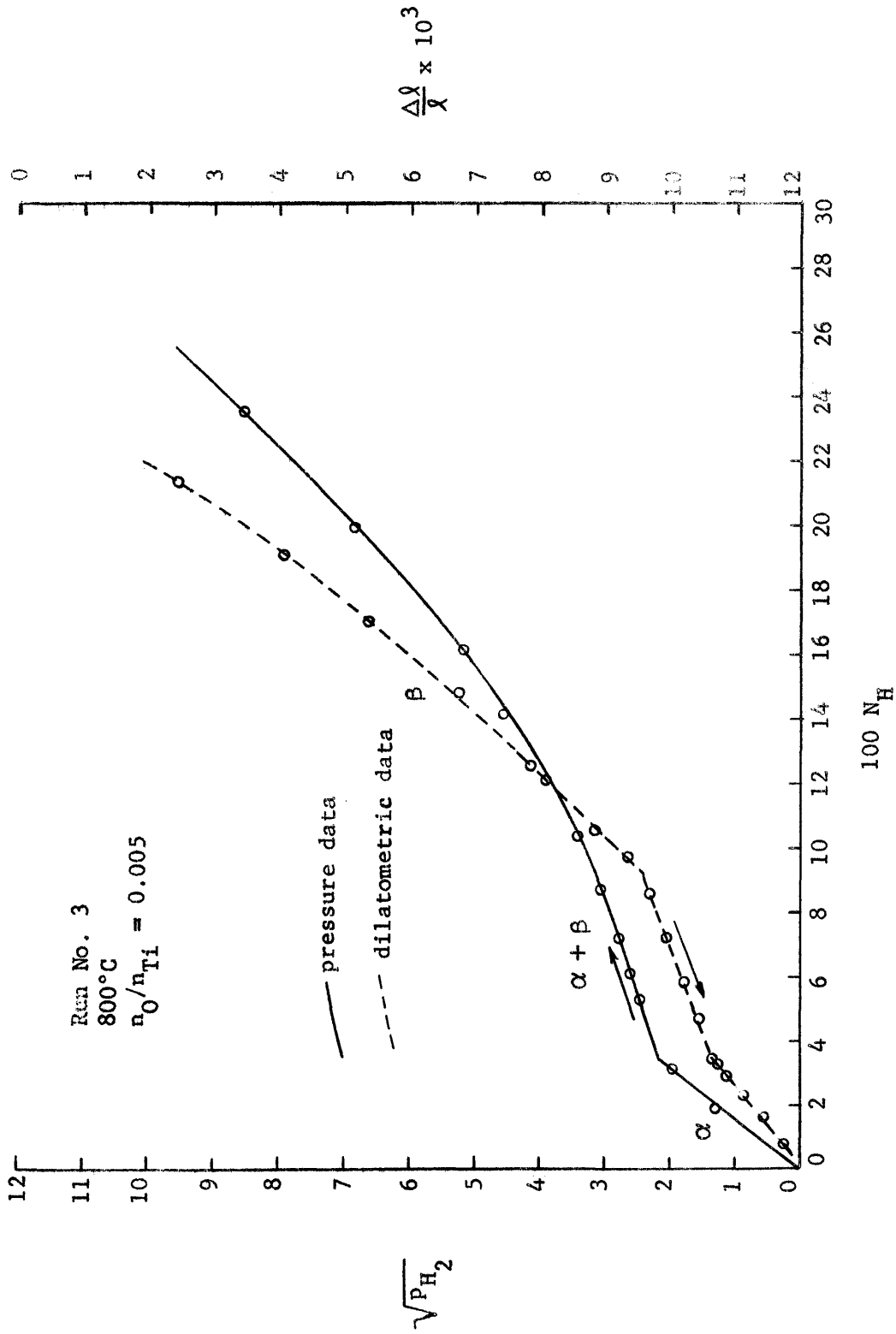


Figure 8 Equilibrium hydrogen pressure and dilatometric curves for Run No. 3. Composition data have been calculated using the results of the vacuum fusion analysis.

the composition which was preferred for the purpose of the particular test. The vacuum fusion analyses, performed on each specimen, and the mole ratio of oxygen to titanium calculated from the results of these analyses are shown. Where possible, an estimated composition, based on a comparison of the equilibrium pressure data with that obtained by Hepworth (4), is shown.

For each run, mole fraction interstitial hydrogen, N_H , has been calculated using the analysis results and, for comparison, using the oxygen concentration which the TiO_2 addition had been intended to produce. Because of the appreciable quantity of nitrogen found in each specimen, the moles of oxygen and nitrogen have been added together in performing composition calculations and together are treated as moles of α -stabilizing interstitial alloying agent. With the exception of Run No. 2, the difference in the values obtained never exceeded 0.0001. These results, increased by a factor of 100, are shown in Table 1 for Run Nos. 2 and 3.

Appendix 4 contains sample calculations which illustrate the method by which the quantities N_H , $\sqrt{P_{H_2}}$ and $\Delta l/l$ were calculated.

Figures 6, 7 and 8 show plots, prepared from data in Table 1, of square root of equilibrium hydrogen pressure, $\sqrt{P_{H_2}}$, and specimen contraction per unit length, $\Delta l/l$, versus atomic percent interstitial hydrogen, $100 N_H$. The pressure and dilatometric data have been plotted together over a common $100 N_H$ axis in order to compare discontinuities in slope of the two curves. For Run No. 1, $-\Delta l/l \times 10^3$ has been

plotted because the dilatometric zero point was chosen as the length at $N_H = 0$. For subsequent runs the dilatometric zero point was chosen at the maximum N_H attained. Positive values of $\Delta l/l$ then indicated specimen contractions as hydrogen was removed. The curves prepared for Run No. 2 have been plotted using N_H calculated both from the analysis results and from the TiO_2 addition. For Runs Nos. 2 and 3 curves plotted using the two values of N_H were, for the purposes of this investigation, indistinguishable. Arrows on each curve indicate the direction of change in N_H as the data were taken.

Discussion and Conclusions

Each of the three runs was performed for a specific purpose and each revealed certain characteristics of the equipment and method. Accordingly, the results will be discussed separately and in the order in which the runs were made.

Results of Run No. 1

The purpose of the first run as outlined previously was to check, by comparing the data obtained with that reported by other investigators (3, 4), the accuracy of the system volume calibrations and the vacuum system integrity.

As may be observed by inspecting the equilibrium pressure plot in Figure 6 and the vacuum fusion analysis results, the specimen was slightly contaminated. The presence of nitrogen in the specimen indicates some atmospheric contamination, probably the result of gettering of gases from the inner surfaces of the system as the specimen compartment was brought to its operating temperature. McQuillan (2) states that to prevent specimen contamination from this

source, the silica furnace tube must be baked out at 1000°C for 24 hours under a vacuum of 10^{-6} mm Hg before introduction of the specimen. He was able to bring his specimen into the furnace tube, after carrying out this procedure, by using a magnetic pusher. Unfortunately, because of the requirement that the specimen be engaged with the dilatometer pushrod, this technique could not be used in the present investigation. The fact that the analysis indicates a higher oxygen than nitrogen concentration seems to indicate another source of contamination -- possibly oxygen present in the iodide crystal bar before machining or acquired by high temperature reaction with the silica furnace tube. The latter possibility could be eliminated by wrapping the specimen in molybdenum foil. An oxygen analysis of the iodide bar as received would have been most informative, and will be requested for subsequent study of this method.

The accuracy of the volumetric calibration of the equipment is indicated by a comparison of the data obtained with that reported by McQuillan (3) and Hepworth (4). The hydrogen compositions, as determined in each of the investigations, at which the first β phase appeared and at which the transition to the β phase was completed are tabulated below.

	100 N _H at β appearance	100 N _H at all β
McQuillan (3)	* 3	* 7
Hepworth (4)	3.61	* 7
Present study	3.35	7.4

* approximate values

The hydrogen concentration necessary to bring about the $\beta \rightarrow \alpha$ transition in the present study may be expected to be slightly higher than normal because of the presence in the specimen of α -stabilizing contaminants.

Dilatometric readings, for this first run only, were taken during both the addition and removal of hydrogen. Comparison of the resulting curve in Figure 6 with those for the following runs in Figures 7 and 8, readily shows that the specimen expansion was badly constrained by the dilatometric pushrods. The plot describes a hysteresis loop which indicates a net specimen contraction over the cycle of almost 3 mils. McGeary's observation (8), that unmelted Zr crystal bar ordinarily undergoes a net increase in length over a thermal cycle, would seem to emphasize the abnormality of the shortening in this instance.

The positions of the $\alpha+\beta$ - β phase boundary, as indicated in Figure 6 by the two dilatometric curves and the pressure curve, are interesting to note. The fact that the dilatometric and pressure data which were obtained at the same time, indicate phase boundaries approximately 0.5 atomic percent apart, eliminates any possibility of attributing the difference to accumulating contamination.

Costa and Cizeron (11) have noted that high purity titanium, when placed under axial compression, exhibits an abnormally large contraction in passing from β to α . Because of the effect of the constraint of the pushrods in this run, and in order to obtain any possible advantages from the phenomena noted by Costa and Cizeron, the decision was made to take dilatometric data only on removal of hydrogen.

Results of Run No. 2

The interstitial α -stabilizer concentration in the specimen studied in the second run is indicated by the analysis results to be much lower than that indicated by the equilibrium pressure data. For this reason two complete sets of curves were plotted for this run -- one set based on the analysis results and a second set based on a composition calculated from the weight of TiO_2 alloyed into the specimen. The two equilibrium pressure curves are quite similar. The dilatometric curves differ significantly, however, particularly near the two-phase region where a small change in equilibrium pressure corresponds to a large change in composition. The dilatometric curve based on the TiO_2 addition is noted to be linear from approximately 8.6 to 18.4 atomic percent hydrogen. A sharp discontinuity in slope marks the transition from the $\alpha+\beta$ to the β region at the latter point. In contrast, the dilatometric curve based on the analysis results shows only scattered points below approximately 19.6 atomic percent hydrogen. This comparison and the form of the equilibrium pressure curve lead the author to believe that the composition based on the TiO_2 addition is a better approximation than that calculated from the analysis results.

The several points of the dilatometric curves which are abnormally high are attributed to binding of the pin in the motion transmitting vacuum seal. A high grease pressure was inadvertently allowed to build up in this fitting and difficulty in moving the push-rods was experienced for the remainder of the run.

Results of Run No. 3

The third run illustrates the effectiveness of the dilatometric method at oxygen concentrations which render the $\alpha+\beta$ to β transition indistinct, if not entirely indistinguishable. For the specimen studied, a slight discontinuity in slope is discernable in the pressure curve, but a far more obvious discontinuity occurs in the slope of the dilatometric curve. In contrast to the previous runs the compositions corresponding to the changes in slope of the two curves in Figure 8 agree quite closely. Once again, however, the form of the equilibrium pressure curve indicates a higher concentration of α -stabilizing interstitial alloying agents than is indicated by the vacuum fusion analysis results. Comparison of the hydrogen concentration at which the $\alpha+\beta$ to β transition was observed, with data reported by Hepworth, indicates that the mole ratio of α -stabilizer to titanium was actually about 0.005, a value approximately midway between the two values calculated. Assuming the mole ratio to be 0.005 as indicated, the hydrogen concentration at which the α to $\alpha+\beta$ transition occurred is observed to agree with Hepworth's data to within 0.1 atomic percent. The author is again lead to the conclusion that the vacuum fusion analysis results are in error.

Conclusions

As pointed out in the two preceeding paragraphs, the results of the analyses performed on at least two of the three specimens must be placed in doubt. This unfortunate circumstance hinders the drawing

of sound conclusions from the data, however the following observations may be made:

a. Run Nos. 2 and 3 indicate that the dilatometric technique described is capable of detecting the $\alpha+\beta$ to β transition in the Ti-O-H system at oxygen concentrations above those at which the equilibrium pressure method fails.

b. The apparatus developed for this study is capable of accurate hydrogen solubility measurements as indicated by Run No. 3, however refinements of the method are considered to be necessary before any extensive work is undertaken. A modification of the dilatometric equipment to permit measurement of specimen length without exerting a force on the specimen would permit taking pressure and dilatometric data simultaneously. Substitution of pressure transducers for the necessary manometers and McLeod gauge would eliminate numerous problems encountered in the operation and maintenance of the system and would greatly simplify the calculations involved in putting the data in use.

c. Because Hepworth's data for the $\alpha+\beta$ to β transition region was used in determining the compositions of the specimens, the only available check on his results is comparison of the atomic percent hydrogen at the α to $\alpha+\beta$ transition. Although this is a rather insensitive check, it has been carried out and indicates close agreement with his data.

Appendix 1

Metallurgical Background

Titanium Metallurgy

Pure titanium exists in two allotropic forms, viz., the hexagonal close-packed configuration, α , which is stable at temperatures below $882.5 \pm 0.5^\circ\text{C}$ (3) and the body-centered cubic form, β , which is stable at higher temperatures. Each form exhibits its own unique set of physical properties (such as density, resistivity, coefficient of thermal expansion and others) which, for each form, are continuous functions of temperature. Abrupt discontinuities in these functions should, therefore, be expected at the transformation temperature; the strength of the discontinuity in any particular property, of course, depends on the difference in the magnitudes of the property in the two allotropic forms at the transformation temperature.

Figures 9, 10 and 11 illustrate the phase relations of those parts of the binary systems titanium-hydrogen, titanium-oxygen and titanium-nitrogen which are pertinent to this study. As may be observed, by reference to these equilibrium diagrams, the allotropic transformation may be induced by the addition of small amounts of any

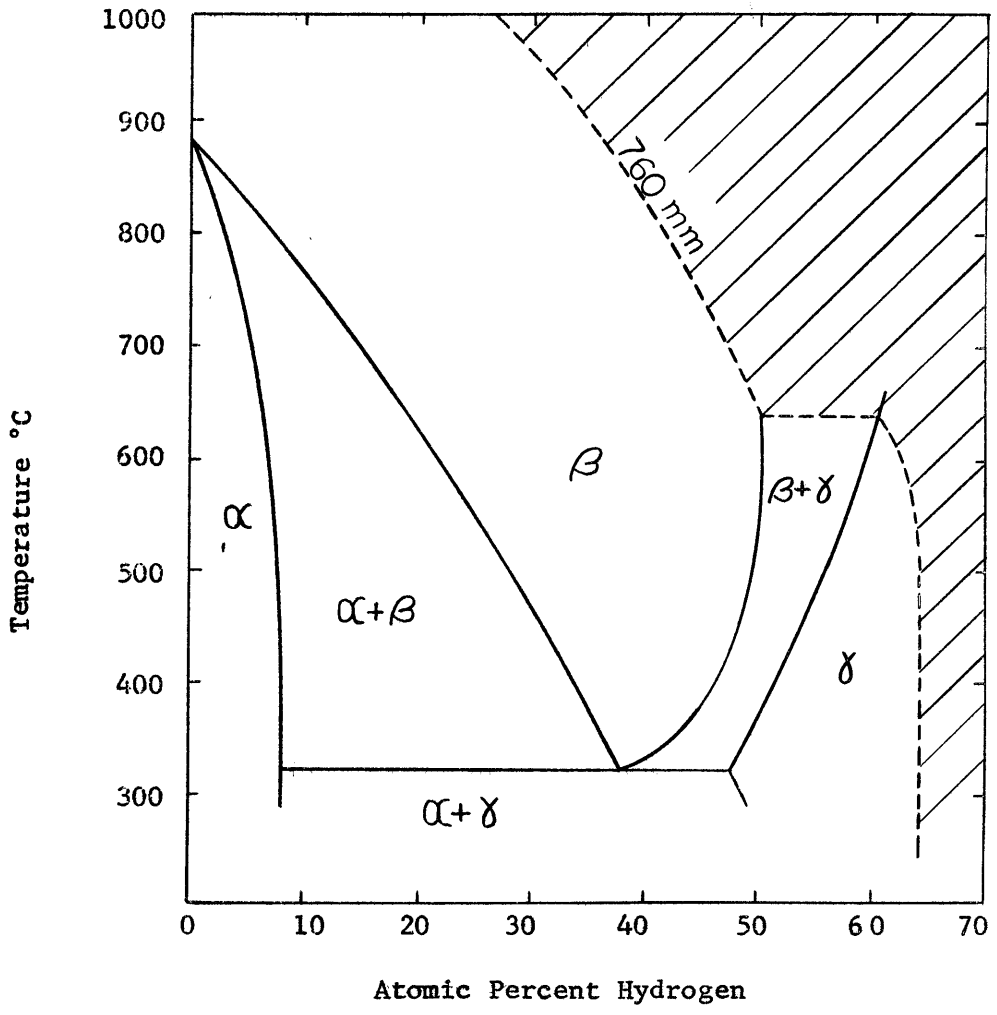


Figure 9 Titanium-hydrogen equilibrium diagram as reproduced from McQuillan (3).

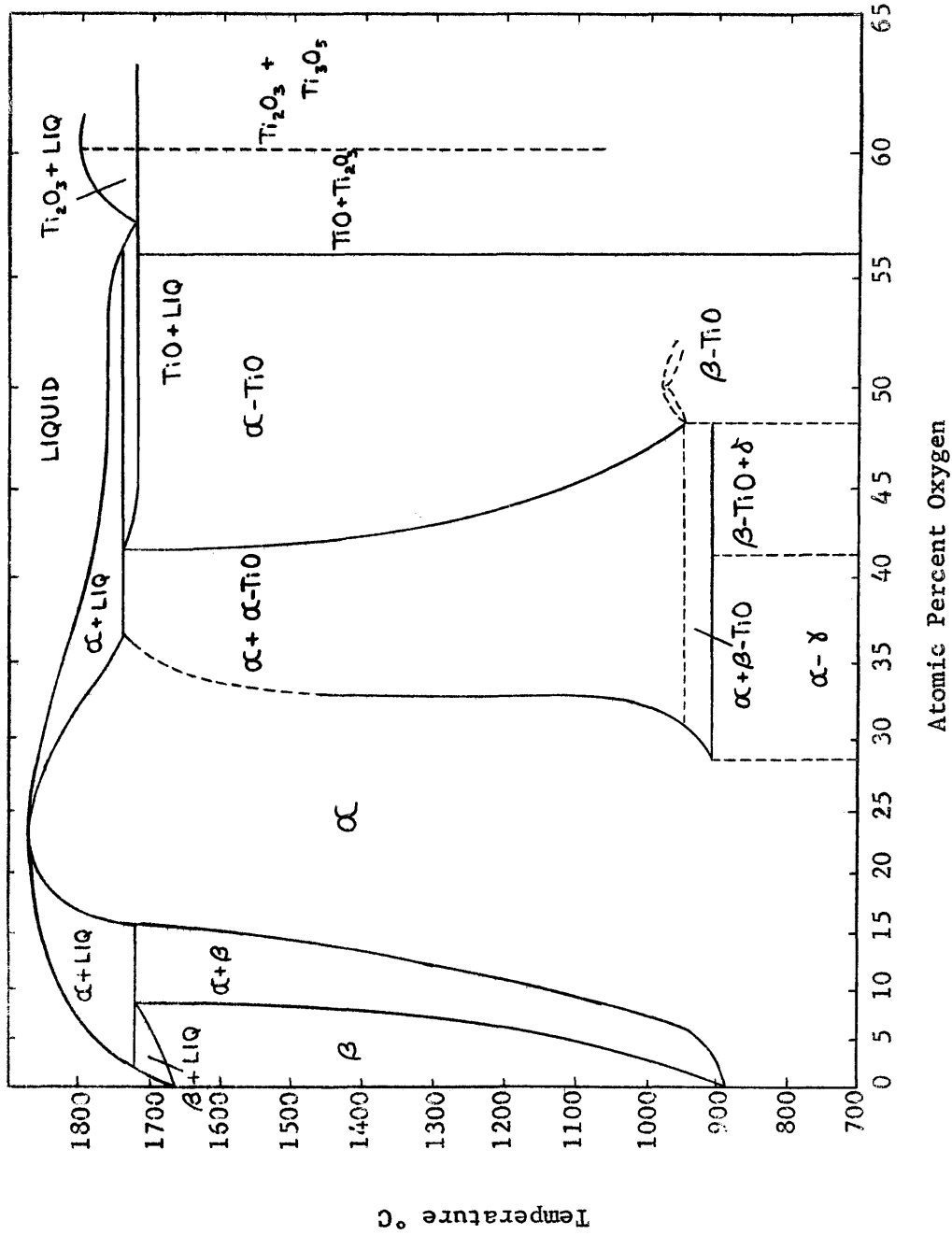


Figure 10 Titanium-oxygen equilibrium diagram from Bacon and Schofield, Jour. Inst. Metals, vol. 84, 1955, p. 47.

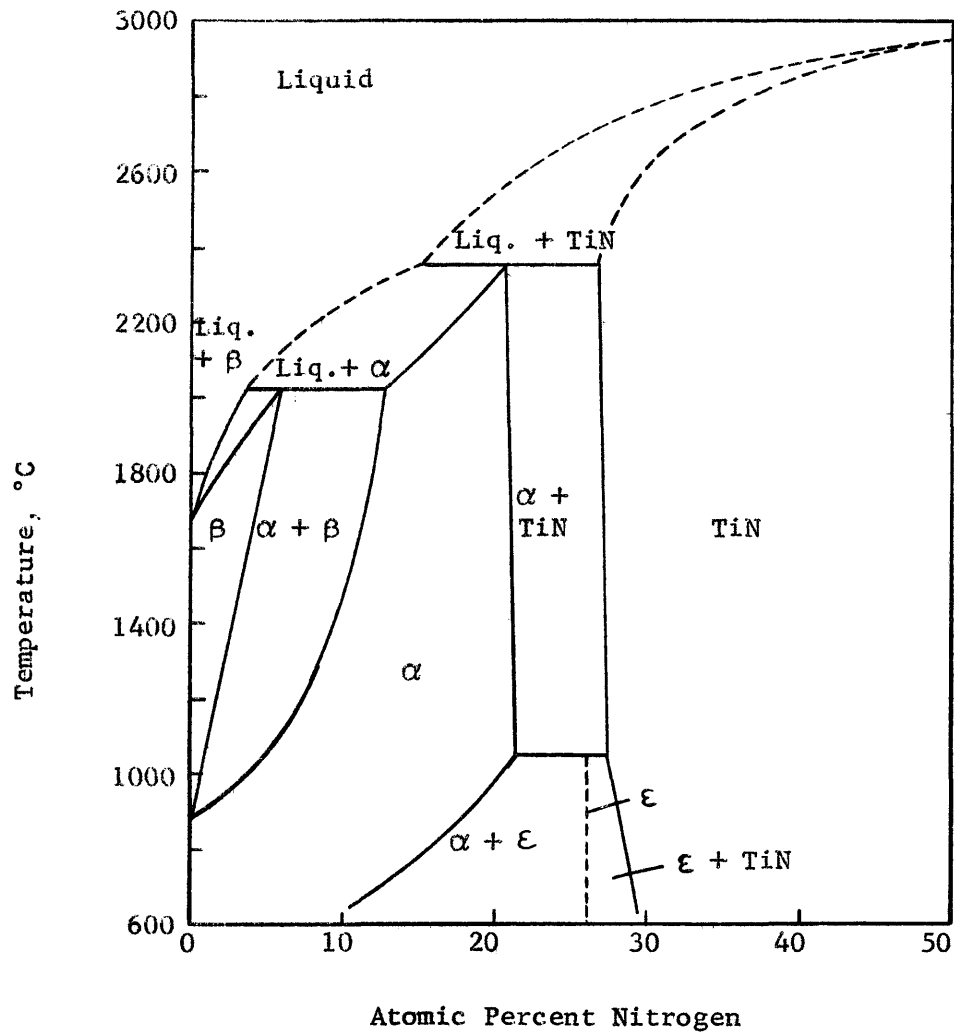


Figure 11: Titanium-nitrogen equilibrium diagram as reproduced from McQuillan (2).

of these alloying agents. Hydrogen has the effect of lowering the transformation temperature; both oxygen and nitrogen have the effect of raising it. Oxygen and nitrogen are, for this reason, known as α -stabilizing agents in their respective binary systems with titanium. The phase transition does not occur abruptly, when brought about by alloying agents, as it does in a pure substance. An α to β phase transition, brought about isothermally by alloying additions, begins with the first appearance of β phase when the α phase becomes saturated with the alloying agent. Further alloying additions increase the proportion of β phase present, until the transformation is complete. The discontinuity in physical properties, which occurs abruptly at 882.5°C when a specimen of pure titanium is heated, takes place over a range of compositions under these circumstances, as the specimen passes through the region of two condensed phases. In a binary system, any given physical property in this region will vary linearly, as the proportion of α to β phase, between its magnitude in the α phase at the temperature of the run to its magnitude in the β phase at the same temperature. As predicted by the Phase Rule, such a linear variation could not be expected in a ternary system, although it would be approached as an end result as the concentration of any component of the system approached zero.

The process of absorption of hydrogen by titanium differs from that of oxygen and nitrogen in that hydrogen, once absorbed, can be removed by vacuum annealing. The equilibrium hydrogen content of a

titanium specimen, at constant temperature, is a function only of the surrounding hydrogen pressure. An infinitesimal pressure change will be accompanied by a corresponding infinitesimal change in hydrogen content of the specimen. To be more precise, the absorption process is thermodynamically reversible. The most important result of this fact is that hydrogen concentration may be expressed as a function of the independent variables, pressure and temperature. The absorption of oxygen and nitrogen by titanium is not reversible because, at ordinary temperatures, the equilibrium pressures are unattainably low.

Sieverts' Law

Sieverts (1), in his investigation of gases in metals, has demonstrated that gases such as oxygen, nitrogen and hydrogen, which exist as diatomic molecules in gaseous form, are largely dissociated and exist in monatomic form when occupying interstitial positions in solid solution. By assuming complete dissociation of the solute molecules and conformance of the solid solution to Henry's Law, the expression $N = k\sqrt{p}$ is easily derived. This linear relationship between the square root of the partial pressure, p , of the gas over the solution and the solute concentration, N , is known as Sieverts' Law. k is a unique property of each phase, and is therefore subject to the remarks of the previous section concerning linear variation of physical properties in two phase regions.

Sieverts' Law is particularly adaptable to the analysis, for phase boundaries, of data obtained in making a series of isothermal additions

of hydrogen to a reversibly absorbing metal. A plot of the square root of the equilibrium pressures against their corresponding mole fractions of hydrogen in the solution is linear in a one-phase region, in accordance with Sieverts' Law. The slope of this linear plot is equal in magnitude to k , a property of the single phase, and an abrupt change in the slope, therefore, may be expected to mark the appearance or disappearance of a phase. Figure 1 is an example of this type of plot. The curvature which appears in these plots at higher concentrations of interstitial hydrogen indicates a deviation from Sieverts' Law.

Appendix 2

Procedure for Arc-Casting Dilatometric Specimens

An arc-melting furnace previously in operation in the Metallurgy Department was used to prepare the dilatometric specimens. Each specimen required a series of four melting operations -- two operations in a standard copper hearth and two in a specially prepared copper chill mold. Figure 12 is a drawing of this mold. Prior to each melt the system was evacuated until a leak-rate of 1 micron Hg per minute was attained, and an atmosphere of 14 cm Hg of argon was admitted to the system. Melting under an argon atmosphere was necessary for proper arc stability.

Alloying with oxygen was accomplished in the first two melting operations. A piece of iodide-process titanium crystal bar weighing approximately 50 grams, and a quantity of titanium dioxide calculated to produce an alloy of the desired composition, were placed together in the cup of a standard copper hearth. They were melted by a 20-volt arc, passing 200 amperes, applied for 3 minutes. The resulting button was turned over in the cup and remelted under the same conditions

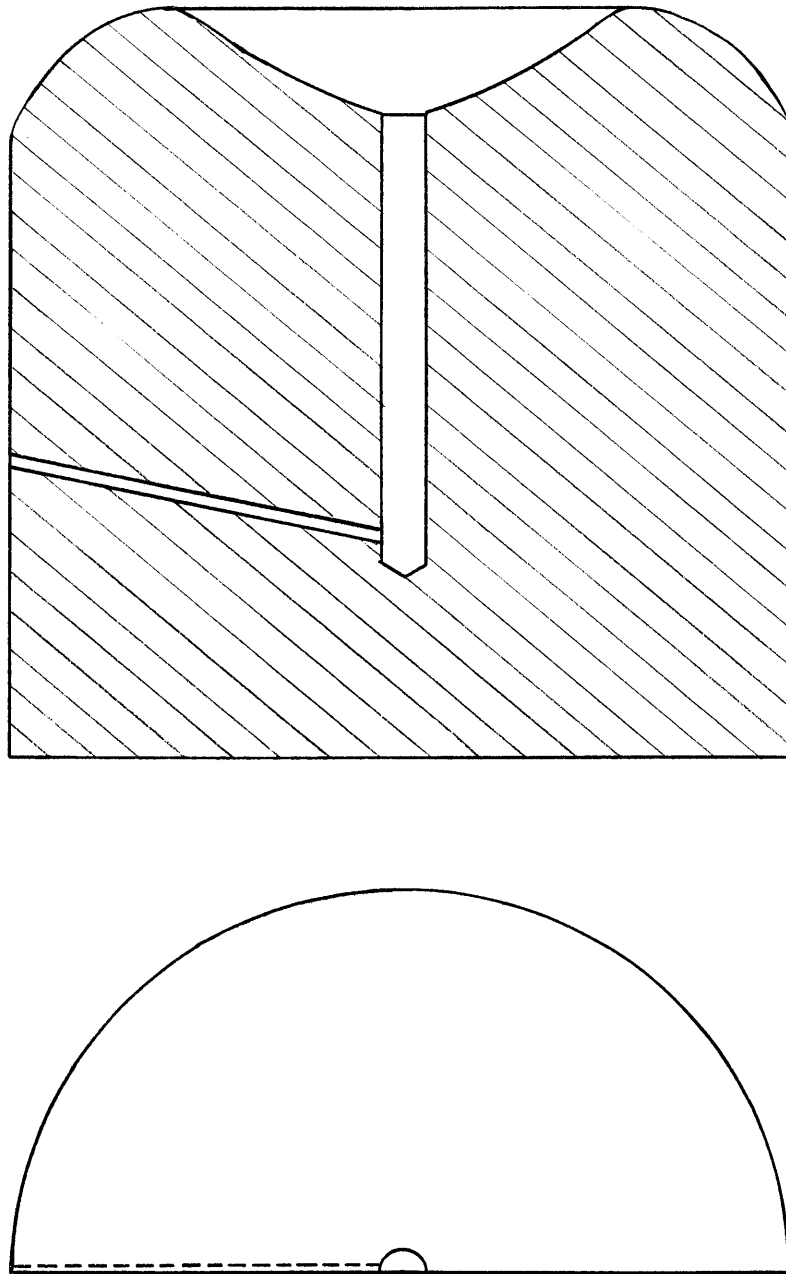


Figure 12 Drawing of one half of the copper chill mold used in preparing the dilatometric specimens.

except that an arc-current of 400 amperes was used.

The casting operation was carried out in the third and fourth melting operations. The titanium-oxygen alloy button prepared in the first two meltings was placed in the cup of the copper chill-mold and the entire assembly was placed on the standard copper hearth, with the button centered under the electrode. An initial melt for 1 1/2 minutes at 20 volts and 400 amperes was carried out to form the alloy button to the mold cup for better thermal conductivity between the two. The button did not attain sufficient fluidity during this melt to run completely into the mold, but did sag slightly in the center, forming a small nipple on the bottom of the formed button. Several unsuccessful casting attempts showed that this nipple prevented the melt from running into the mold during the final melting. When it was ground off after the forming melt, casting was accomplished using a 20-volt arc and a current of 1200 amperes for 1 1/2 minutes.

The resulting casting was a rod, attached to the remaining metal which solidified in the cup, and was completely sound and apparently homogeneous.

Appendix 3

Analyses of Materials

Iodide-Process Titanium

Two 1-lb batches of iodide-process titanium were obtained from the Foote Mineral Company, however an analysis was supplied only with the first batch received. Foote Mineral Company did not have available an analysis of the second batch supplied. The analysis which was received follows:

Lot No. 907-4	%Si	0.001
	%Mg	0.003
	%Cr	0.002
	%Mn	0.002
	%Al	0.002
	%Fe	0.003
	%Ni	Not Detected
	%Ca	0.005
	%Cu	0.0005
	%Mo	Not Detected
	%Zr	0.05

Titanium Dioxide

The TiO_2 used was a J.T. Baker reagent and its analysis, as recorded on the label is as follows:

Lot No. 91841	% Water-soluble Salts	0.050
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%As	0.0001
%Fe	0.002
%Pb	0.002
%Zn	0.002

Titanium Hydride

Analysis was not supplied by Metal Hydrides, Inc. with the titanium hydride or on subsequent request.

Appendix 4
Sample Calculations

I Definitions of symbols to be used:

- P_1 = H_2 reservoir pressure reading before H_2 addition (cm Hg)
- P_1' = H_2 reservoir pressure reading before H_2 addition, corrected to $0^\circ C$ (cm Hg)
- V_1 = volume of H_2 reservoir before H_2 addition (cc)
- T = room temperature at the time of the addition ($^\circ C$)
- n_1 = moles H_2 in reservoir before H_2 addition
- P_2 = H_2 reservoir pressure reading after H_2 addition (cm Hg)
- P_2' = H_2 reservoir pressure reading after H_2 addition, corrected to $0^\circ C$ (cm Hg)
- V_2 = volume of H_2 reservoir after H_2 addition (cc)
- n_2 = moles H_2 in reservoir after H_2 addition
- Δn = moles H_2 admitted to the specimen chamber in a particular increment
- n_T = total moles H_2 admitted to the specimen chamber
- P_3 = equilibrium H_2 pressure in the specimen chamber (cm Hg)

- P_3' = equilibrium H_2 pressure in the specimen chamber corrected to 25°C. (As determined experimentally, heating the furnace from 25 to 800°C increases the specimen chamber pressure by a factor of 1.052. Correction of specimen chamber pressure to 0°C was found to be negligible for all but the highest equilibrium pressures attained.)(cm Hg)
- V_3 = specimen chamber volume after equilibrium has been attained following H_2 addition. (cc)
- n_3 = moles gaseous H_2 in the specimen chamber at equilibrium
- n_H = moles interstitial hydrogen in the test specimen
- n_O = moles interstitial oxygen in the test specimen
- n_N = moles interstitial nitrogen in the test specimen
- n_{Ti} = moles titanium in the test specimen
- N_H = mole fraction hydrogen in the test specimen
- ΔX = cumulative light spot motion
- Δl = cumulative change in specimen length
- l = specimen length as prepared (1.6 in.)

II Volume functions as determined by the volumetric calibrations.

$$V_1 = 260.81 + 0.291 P_1$$

$$V_2 = 260.81 + 0.291 P_2$$

$$V_3 = 233.17 + 0.092 P_3$$

III Calculation of total moles H_2 admitted to the specimen chamber

A. Data:

$$P_1 = 61.85$$

$$P_2 = 52.24$$

$$T = 26.2$$

$$\alpha = .000182 = \text{mean cubical coefficient of expansion} \\ \text{of mercury between 0 and } 35^\circ\text{C}$$

$$\beta = 10.5 \times 10^{-6} = \text{linear coefficient of expansion of} \\ \text{steel}$$

$$t_s = 20^\circ\text{C (scale assumed to have been calibrated at } 20^\circ\text{C)}$$

B. Calculations:

$$P_1' = P_1 - P_1 \frac{\alpha T - \beta(T - t_s)}{1 + \alpha T}$$

$$= 61.85 - 61.85 \frac{(.000182)(26.2) - (10.5 \times 10^{-6})(26.2 - 20.0)}{1 + (.000182)(26.2)}$$

$$= \underline{61.57 \text{ cm Hg}}$$

$$V_1 = 260.81 + 0.291 (61.85)$$

$$= \underline{278.81 \text{ cc}}$$

$$n_1 = \frac{P_1' V_1}{R(273 + T)} = \frac{\frac{61.57}{76} \frac{278.81}{1000}}{(0.082)(273 + 26.2)}$$

$$= \underline{0.00921 \text{ moles } H_2}$$

By a similar calculation:

$$n_2 = \underline{0.00770 \text{ moles H}_2}$$

$$\Delta n = n_1 - n_2$$

$$= 0.00921 - 0.00770$$

$$= \underline{0.00151 \text{ moles H}_2}$$

$$n_T = \Delta n + \text{moles H}_2 \text{ admitted in previous additions}$$

$$= 0.00151 + 0.00894$$

$$\underline{\underline{n_T = 0.01045 \text{ moles H}_2}}$$

IV. Calculation of the hydrogen concentration in the test specimen

A. Data:

$$\text{Specimen weight} = 5.037 \text{ g}$$

$$\text{Oxygen concentration} = 615 \text{ ppm by weight}$$

$$\text{Nitrogen concentration} = 137 \text{ ppm by weight}$$

$$P_3 = 2.84 \text{ cm Hg}$$

$$\text{Furnace temperature} = 800^\circ\text{C}$$

B. Calculations:

$$P_3' = \frac{P_3}{1.052} \quad (\text{factor determined experimentally})$$

$$= \frac{2.84}{1.052}$$

$$= \underline{2.70 \text{ cm Hg}}$$

$$V_3 = 233.17 + 0.092 P_3$$

$$= 233.17 + 0.092 (2.84)$$

$$= \underline{233.43 \text{ cc}}$$

$$\begin{aligned}
 n_3 &= \frac{P_3 V_3}{R (T + 273)} \\
 &= \frac{2.70}{76} \frac{233.43}{1000} \\
 &= \frac{(0.082)(26.2 + 273)}{(0.082)(26.2 + 273)} \\
 &= \underline{0.00035 \text{ moles H}_2}
 \end{aligned}$$

(Note that the temperature at the time of the equilibrium pressure reading is approximated in this calculation by the temperature at the time of the H₂ addition. This approximation was made in order to expedite the calculations.)

$$\begin{aligned}
 n_H &= 2(n_T - n_3) \\
 &= 2(0.01045 - 0.00035) \\
 &= \underline{0.02017 \text{ moles H}}
 \end{aligned}$$

$$\begin{aligned}
 n_O &= \frac{(10^{-6} \times \text{ppm oxygen}) (\text{specimen weight})}{\text{atomic wt. oxygen}} \\
 &= \frac{(0.000615)(5.037)}{16} \\
 &= \underline{0.00019 \text{ moles O}}
 \end{aligned}$$

By similar calculation:

$$n_N = \underline{0.00005}$$

$$\begin{aligned}
 n_{Ti} &= \frac{(1.000 - 0.0615 - 0.0137)(5.037)}{47.90} \\
 &= \underline{0.10507 \text{ moles Ti}}
 \end{aligned}$$

$$\begin{aligned}
 N_H &= \frac{n_H}{n_H + n_O + n_N + n_{Ti}} \\
 &= \frac{0.02017}{0.02017 + 0.00019 + 0.00005 + 0.10507} \\
 &= \underline{\underline{0.16077}}
 \end{aligned}$$

V. Calculation of $\Delta l/l$:

A. Data:

$$\begin{aligned}\Delta X &= 3.438 \\ \text{dilatometer} \\ \text{magnification factor} &= 318.9 \\ &= 1.6 \text{ in.}\end{aligned}$$

B. Calculation:

$$\begin{aligned}\Delta l/l &= \frac{\Delta X}{318.9 \times l} \\ &= \frac{3.438}{318.9 \times 1.6}\end{aligned}$$

$$\underline{\underline{\Delta l/l = 0.00674}}$$

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