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Effect of Interstitial Elements on Phase Relationships in the Titanium-Aluminum System

R. M. Waterstrat

U.S. DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
(Formerly National Bureau of Standards) American Dental Association Health
Foundation
Paffenbarger Research Center
Gaithersburg, MD 20899

May 1988

Issued October 1988

Final Technical Report for Period November 1981 to September 1987.
Contracts N00014-82-C-0061 and N00014-86-K-0470

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An apparatus has been designed and constructed for neutron diffraction studies on polycrystalline samples in a high vacuum at temperatures up to approximately 1500 °C or higher. Neutron diffraction data have been obtained from titanium-aluminum alloys containing 12 to 45 atomic percent aluminum at temperatures ranging from 900 °C to over 1300 °C. Unusually high background intensities were observed in single-phase α -Ti alloys containing 14 and 16 atomic percent aluminum between 900 °C and 1000 °C. This suggests the existence of atomic short-range order as reported by previous investigators. Addition of 1 atomic percent oxygen to such alloys was found to eliminate the short-range ordering behavior and replace it with an extended α -Ti plus α_2 -Ti₃Al two-phase region.

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19. The α -Ti solid solution region of the Ti-Al phase diagram was found to terminate in a peritectoid transformation at about 1150°C, but with increasing aluminum content, it apparently reappears at higher temperatures. At 1200°C or higher, a single diffraction line is observed in alloys containing approximately 40 atomic percent aluminum. The line was tentatively identified as that of a disordered hexagonal close-packed phase (i.e., α -Ti), and this phase has since been reported by other investigators. The presence of this new phase, which was not anticipated in previous studies of the phase diagram, implies that the β -Ti phase may possess a more limited solubility for aluminum than was previously reported, and this will require that the existing phase diagram be modified significantly.

Addition of up to 6 atomic percent oxygen to Ti-Al alloys has been found to elevate both the α -solvus and α -transus temperatures, in agreement with some previous studies, and it appears that oxygen stabilizes both the α -Ti and α_2 -Ti₃Al phases.

The use of high-temperature neutron diffraction in combination with other experimental measurements, such as differential thermal analysis, seems to promise more reliable Ti-Al phase diagrams.

EFFECT OF INTERSTITIAL ELEMENTS ON PHASE RELATIONSHIPS
IN THE TITANIUM-ALUMINUM SYSTEM

Final Technical Report
ONR Contracts N00014-82-C-0061 and N00014-86-K-0470
November 1, 1981 - September 30, 1987

Submitted by
American Dental Association Health Foundation
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National Institute of Standards and Technology
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FOREWORD

This Final Technical Report is presented by the American Dental Association Health Foundation, Paffenbarger Research Center at the National Bureau of Standards, Gaithersburg, Maryland under ONR Contracts N00014-82-C-0061 and N00014-86-K-0470. The work was sponsored by the Office of Naval Research, Arlington, Virginia. Dr. B. A. MacDonald was the Program Manager.

This report covers the entire project period from Nov. 1, 1981 to Sept. 30, 1987. The project was initiated to explore the use of neutron diffraction as a method for discovering the influence of interstitial solutes on phase boundaries in the titanium-aluminum system.

Dr. R. M. Waterstrat, the Principal Investigator, was associated with Dr. E. Prince of the Reactor Division at the National Bureau of Standards in obtaining all of the neutron diffraction data. Mr. A. Giuseppetti assisted with sample preparation, x-ray diffraction and optical metallography. We wish to express our appreciation to Mr. W. Jones and technical staff of the Vacuum Furnace Systems Corporation, Souderton, Pennsylvania for designing and constructing the special vacuum furnace used in this study. We are also especially grateful to Mr. Bill Lugmayer, P.E. of Lugmayer Associates Inc., Clinton, Maryland for expert advice and technical assistance in electron-beam welding and to Mr. F. A. Schmidt at the Materials Preparation Center, Ames Laboratory, Ames, Iowa for fabricating the critical neutron "window" from special high purity vanadium metal.

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I. INTRODUCTION

The objective of this research was to determine the effects of interstitial solute elements, such as oxygen, nitrogen and carbon on the $\alpha/\alpha + \alpha_2/\alpha_2$ phase boundaries in the Ti-Al system. These effects must be adequately defined since the interstitial elements are ubiquitous contaminants in titanium alloys beginning with the initial starting material (titanium sponge) and accumulating through the various stages of fabrication of the alloys. Once present, they cannot be easily removed, and there is justifiable concern that they may produce adverse effects on the mechanical behavior of these alloys.

The interstitial elements of this investigation are abundant in the ambient atmosphere during hot forming or thermal welding and are difficult to exclude. Some contamination of titanium alloys is, therefore, virtually unavoidable since hot titanium is capable of scavenging the interstitial elements in an ultra-high vacuum (pressures $< 10^{-6}$ Torr) or from the highest purity inert gases (impurity contents < 5 ppm). The only practical solution to these problems is to set maximum allowable limits for interstitial contamination and then impose effective controls on it. This requires a knowledge of its effect on alloy properties and behavior.

It is already well established that excessive amounts of oxygen, for example, can embrittle titanium and its alloys. In pure

titanium the embrittlement mechanism probably involves an interaction between dissolved oxygen atoms and dislocations which produces a ductile/brittle transition (Ref. 1). In titanium-aluminum alloys, however, oxygen also promotes the formation of the brittle α_2 phase (Ti_3Al), an atomically ordered version of the more ductile α phase structure (see Fig. 1). However, there is a lack of precise information about the effect of oxygen on the stability of the α_2 phase. Phase relationships in the Ti-Al-O system, for example, have not been well defined.

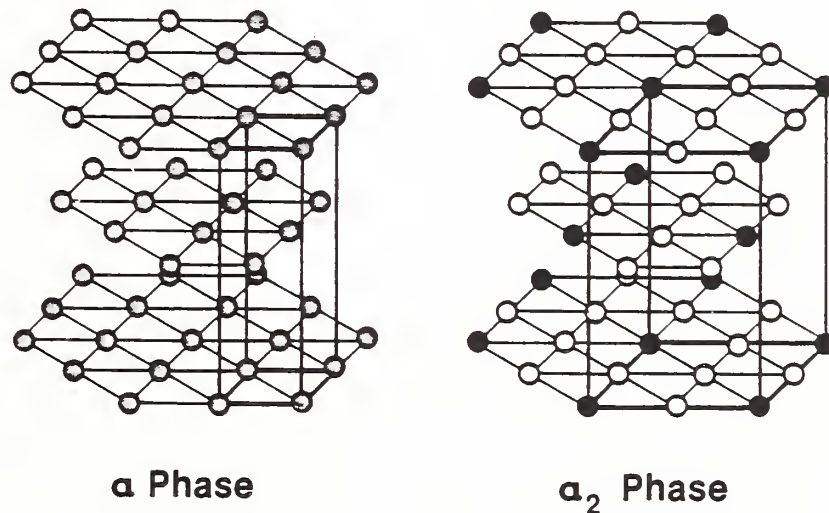


Fig. 1. Schematic representation of the (αTi) structure and the α_2 (Ti_3Al) structure. Open circles represent Ti atoms, dark circles represent Al atoms and shaded (grey) circles represent a statistically random occupancy by both Ti and Al atoms in the ratio called for by the phase composition. Thick lines outline the respective unit cell for each structure. The structure of the α_2 phase actually involves slight displacements of the Ti atoms from these "ideal positions" (ref. 10).

II. CRITICAL EVALUATION OF PREVIOUS STUDIES

The influence of interstitial elements on phase relationships in the Ti-Al system has received only limited prior study, and this was mostly concerned with the effects of dissolved oxygen. The earliest studies were directed mainly to the influence of interstitials on the $\alpha/\alpha + \beta/\beta$ phase boundaries. Van Thyne and Kessler (Ref. 2) reported that additions of up to 1% oxygen or nitrogen raise the temperature of the $\beta/\alpha + \beta$ phase transformation and widen the $\alpha + \beta$ field. They also reported that carbon is increasingly soluble (up to about 1%) in the α Ti terminal solid solution as the aluminum content increases to about 10%, and this increased solubility occurs at progressively higher temperatures since the peritectoid reaction ($\alpha \rightarrow \alpha + \beta + \text{TiC}$) temperatures are also raised significantly.

Schofield and Bacon (Ref. 3) essentially confirmed the results of Van Thyne and Kessler (Ref. 2) and extended them to higher aluminum contents. They also presented ternary isothermal sections at 950°, 1000° and 1050°C for the Ti-Al-O system.

Nikitenko (Ref. 4) made the observation that surface oxidation of titanium alloys at 350 to 500° promotes embrittlement through α_2 phase formation. Subsequent studies by other authors pursued this topic in greater detail.

Glazova (Ref. 5) presented isothermal sections for the titanium-aluminum-oxygen system at 800°C and 1000°C, but it is difficult to reconcile or compare his results with those of other workers because he claims to have observed several new phases.

Crossley (Ref. 6) has reported that 0.1% oxygen decreases the solubility of aluminum in primary α Ti by about 0.6% (~ 1.0 At. %) at 700° and thus promotes the formation of the Ti_3Al (α_2) phase. However, his annealing method raises questions about contamination, questions which are not fully discussed in his paper.

Kornilov et al. (Ref. 7) studied the joint solubilities of aluminum and oxygen in α -Ti at 600°C, and their data suggest that the solubility of aluminum in α Ti is less than 2% (4 at. %) at an oxygen content of 5 at.%.

Vavilova et al. (Ref. 8) have determined the solubility of aluminum in titanium to be 6% (by wt.) at 800°C and have compared this with the solubility value of 4.5% Al in an alloy containing .35% oxygen at the same temperature. They report that the two-phase region ($\alpha + \alpha_2$), which they say extends from 6 to 15% Al in the binary Ti-Al system, is somewhat smaller in the oxygen-containing alloys and that the homogeneity range of the α_2 phase (reported as 15 to 22% Al) is also smaller for oxygen-containing

alloys. They propose, therefore, that oxygen contamination of the titanium-aluminum alloys is linked with decreases in ductility.

Lim et al. (Ref. 9) studied the formation of coherent α_2 phase in titanium alloys containing 8% Al at 695°C. They report that increasing the oxygen content from ~ 500 to 1000 ppm produces a marked decrease in ductility which then remains essentially unchanged at higher oxygen levels. This decrease in ductility is accompanied by a substantial increase in the volume fraction of the α_2 phase. They suggest that increasing the oxygen content raises the temperature of the $\alpha/\alpha + \alpha_2$ transition for a constant Al concentration. They also present evidence that oxygen strongly partitions to the α_2 phase and acts as an α_2 stabilizer.

Obviously, more data is needed at various temperatures in order to define the influence of oxygen on the $\alpha/\alpha + \alpha_2$ phase boundaries more accurately. Nevertheless, there is general agreement among these studies that oxygen promotes the stability of the brittle α_2 phase (Ti_3Al) by shifting the $\alpha/\alpha + \alpha_2$ (α solvus) phase boundary to lower aluminum concentrations.

The picture of oxygen as an α_2 stabilizer (Ref. 9) is supported by crystallographic observations. Gehlen (Ref. 10) has shown that the crystal structure of α_2 is basically the same as that of the α phase if one ignores the identities of the atoms (See Fig.

1). However, in the α_2 phase, the Ti atoms are slightly displaced from the sites that they occupy in the α Ti structure. The displacement results in larger octahedral interstices which are more suitable for oxygen atoms. Gehlen (Ref. 10) also suggests a tendency toward "covalency" as a stabilizing factor for the α_2 phase.

Kornilov et al. (Ref. 11) employed neutron diffraction methods to locate the preferred sites of oxygen atoms in the α phase (α titanium) structure. They reported that the oxygen atoms enter octahedral interstices in the α phase structure and, in doing so, displace titanium atoms from their usual positions. Three different ordering arrangements exist, depending on the oxygen content. It may be possible to determine the site preference for oxygen atoms in the α_2 phase (Ti_3Al) structure in a similar study. A detailed comparison of the structural relationships in these two oxygen-dissolving phases is needed to develop a better understanding of the oxygen partitioning and the influence of oxygen on the stability. According to Kornilov et al. (Ref. 11), the "bonding" strengths in these phases may vary significantly as a function of the oxygen content.

The general impression that one obtains after surveying all of this literature is that the influence of interstitial impurities, such as oxygen, on phase boundaries in the Ti-Al system is inadequately defined. This should not be surprising since the

binary Ti-Al phase boundaries themselves were not well defined at the time when these studies were done. Each investigator was apparently forced to establish his own binary "reference standards" and then determine "shifts" in the location of these boundaries which were, presumably, produced by a third element. Unfortunately, the "reference standards" were never adequately characterized for essentially the same reasons that apply in the case of the binary alloys. These are discussed in Section III. As a result, one can seldom be certain whether the observed "shifts" in phase boundaries are real or simply due to errors in establishing the true equilibrium reference state in the binary system.

It should be obvious, of course, that defining the influence of a third element is much easier if one first obtains an accurate binary phase diagram. However, impatience to obtain "practical" results can cause one to place excessive reliance on existing binary phase diagrams without seriously questioning their validity. The reliability of binary Ti-Al phase diagrams is, however, a factor of critical importance in several large industries, and the binary system should be re-evaluated before beginning any study of third-element effects.

III. ASSESSMENT OF THE BINARY TI-AL PHASE DIAGRAM

There is an extensive literature on the Ti-Al alloy system mainly because of its practical relevance in almost every aspect of

commercial titanium applications. The literature, however, is often contradictory and somewhat controversial. There are now some excellent critical reviews (Refs. 12-14) of this system. An "assessed" Ti-Al phase diagram has been compiled recently by J. L. Murray (Ref. 14) based on her extensive evaluation of about 100 references dating back as far as 1923. Despite the vast amount of time and effort which have been expended on Ti-Al phase relationships over the years and the great practical significance of this system, it is surprising that the details of the phase diagram are still not adequately established.

The experimental difficulties that one encounters when attempting to determine phase equilibria in titanium alloys are, for the most part, widely recognized. Advancing technology has evolved methods for dealing with these problems, however, and many reliable titanium phase diagrams currently exist. But the Ti-Al system, being more difficult to study, is not one of them. The reason why the Ti-Al phase equilibria are especially difficult is that certain Ti-Al high-temperature structures cannot be retained by quenching. When these samples are studied at room temperature, severely decomposed structures are not always easily interpreted. The samples should be studied at the requisite high-temperatures where critical information is most needed. Unfortunately, many investigators do not have access to experimental apparatus which is capable of high-temperature

studies on reactive metals. High-temperature methods can also be tedious and time-consuming, and this too inhibits their use.

Another reason why Ti-Al phase equilibria are poorly understood is that most of the previous research effort was narrowly focused on what was believed to be the region of greatest "practical" relevance, i.e., temperatures below 1200°C and aluminum contents of less than 10 at. % where one sees the initial slopes of the β transus and α solvus boundaries. The rest of the diagram has, to a large extent, been considered to be somewhat irrelevant for "practical" purposes and not given much attention. However, this narrowly-focused effort has obviously not produced the desired result. We still do not possess a thorough understanding of the α solvus boundary or a complete picture of the α Ti solid solution region. Phase boundaries of the α_2 phase are also rather uncertain, even though their locations have an important bearing on how much of the α_2 phase will form when the alloy composition enters the two-phase ($\alpha + \alpha_2$) region. Murray's review (Ref. 14) concludes that more work is needed to define coherent vs. incoherent phase boundaries and to elucidate the effect of impurities such as oxygen. Our own work will show that there are important questions to be answered concerning the existence and extent of short-range atomic ordering in the α Ti solid solution. It will also show that the solubility of Al in the β phase has been seriously overestimated and that a high-temperature phase

region at about 40 at. % Al has probably been missed completely in the previous studies.

In any case, it seemed obvious to us that before one can understand the behavior of a third element, it is necessary to have a better understanding of the binary Ti-Al system. Therefore, this is where we directed our initial studies.

IV. EXPERIMENTAL PROCEDURES

A. Sample Purity

Commercial titanium alloys have an interstitial element content of roughly 1000 ppm. It is important to know whether contamination at this level is having a significant effect on the microstructure and mechanical properties of these alloys. It seems desirable, therefore, that a comparison should be made between samples containing about 1000 ppm of oxygen, for example, and samples containing lower oxygen contents (< 200 ppm) as well as with samples having higher oxygen contents (~ 1 at. % O). This means that the oxygen content of the samples must be carefully controlled at each step in the experimental procedures. It also means that no other impurities should be introduced and that the aluminum contents of the samples should be constant and well established if one is to have a valid comparison. Therefore, throughout this investigation, we placed a special emphasis on the prevention of sample contamination since impurities, once introduced, are virtually impossible to remove. Of course, when conducting experiments on titanium alloys at high

temperatures, some contamination is unavoidable because of the exceptional reactivity of these alloys. Every effort was made to limit this contamination, and we have conducted numerous chemical analyses to determine whether it had attained serious levels as a result of any of our experimental procedures. We believe that the effort required to accomplish this is justified by the confidence which we can place in our final results.

Our first task was to obtain high-purity starting materials having particularly low levels of interstitial contaminants (<300 ppm). This is not a difficult task for metals such as aluminum, which is readily available in the requisite state of high purity. However, the elimination of interstitials from pure titanium is quite difficult, and there are few reliable sources for such material. The purest titanium ever produced commercially was probably the so-called "iodide" titanium sold by the Foote Mineral Co., the New Jersey Zinc Co. and other manufacturers in the 1950's. According to a Foote Mineral Co., "Products List" dated June 1, 1959, this material typically contained 50 ppm total interstitials (C, N and O). However, the production of this material was apparently discontinued some years ago. We contacted the Foote Mineral Company and were told that the company no longer makes or sells this product and would not do so even on special order. Our inquiries to other American manufacturers brought forth similar responses as did our inquiries to European manufacturers. Having concluded that it

was not available in Western countries, we turned to the "Eastern bloc." A letter to the Soviet trade mission brought no response, but we subsequently learned that the People's Republic of China has recently been exporting "iodide" titanium to the United States where it was being sold by an American importer. We, therefore, purchased two bars of this material and submitted some of this material to vacuum fusion analysis. Metallographic studies revealed no evidence of particulate matter either in the grain boundaries or within the grains, and the bars had an excellent appearance (Fig. 2). Our vacuum fusion analysis of this bar revealed a total interstitial content (C, N, and O) of 150 ppm (see Table 1). The only material now being produced in the United States having a comparably low interstitial content is probably the TIMET Corporation's "El 60" product which, unfortunately, contains about 3% residual salt left over from the electrolytic refining process. This is enough salt to produce a "sputtering" of the electric arc during "melt-down" operations and users of the product generally conduct a preliminary melting in order to eliminate it. It is commonly assumed that, since the "sputtering" is eliminated by this pre-melting, the residual salt has also been eliminated by simply being vaporized at these high temperatures. This assumption, however, may be incorrect. We deliberately added 0.685 grams of dehydrated salt to 13.079 grams of pure (salt-free) iodide titanium and then melted this (5% salt + 95% Ti) mixture four times while monitoring the weight losses

Table 1 MANUFACTURERS' "TYPICAL" ANALYSES FOR "HIGH-PURITY TITANIUM (IN PPM BY WEIGHT).

Element	1982 Electrolytic TIMET El 60 ⁽¹⁾	1959 Foote ⁽²⁾ Iodide Process	1982 Chinese Iodide Process (Nominal)	1982 Chinese Iodide Process (Analyzed)	1982 MRC ⁽³⁾ MARZ Grade
Si	20	50	40		4
Al	10	50	100		5
Mg	10	30	N.D.		<.1
Pb	N.A. ⁽⁴⁾	N.D. ⁽⁵⁾	10		<.1
Mn	10	30	N.A.		5
Cr	10	20	N.A.		3
Sn	200	10	N.A.		<.1
Fe	10	20	100		22
Ni	10	10	N.A.		10
Mo	10	N.D.	N.A.		<.1
Ca	N.A.	30	N.A.		1
Cu	10	3	N.A.		8
V	200	N.A.	N.A.		5
W	N.A.	N.D.	N.A.		<.1
Zr	10	500	10		3
C	90	10	100	40	35
O	100	20	210	100	140
N	20	20	50	10	5
Cl	800	N.A.	30		3
Stated Purity	99.85+	99.92	99.90+		99.97
Prices	\$88/lb	\$125/lb	\$57/lb		(3)
Year	(1982)	(1959)	(1982)		

Sources: El 60 Titanium Metals Corp.
P.O. Box 2128
Henderson, Nev. 89015
Phone: 702-564-2544

Chinese Iodide Continental Metals Corp.
820 Second Ave.
New York, N.Y. 10017
Phone: 212-421-9811

MARZ Materials Research Corp.
Orangeburg, N.Y.
Phone: 914-359-4200

(1) Somewhat higher purities are also available on special order.

(2) This material is no longer available.

(3) This is a premium product for which prices are quoted on an individual basis.

(4) N.A. - not analyzed.

(5) N.D. - not detected.

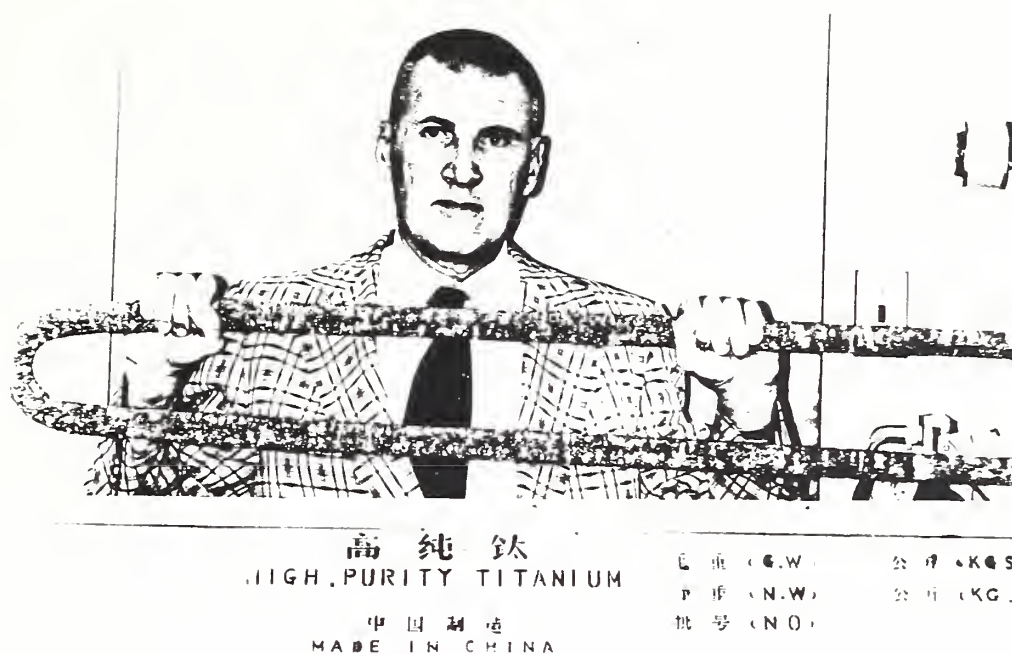


Fig. 2. High-purity "iodide" Ti crystal bar imported from the People's Republic of China; used as the starting material of this investigation.

Weight Losses During Arc-Melting

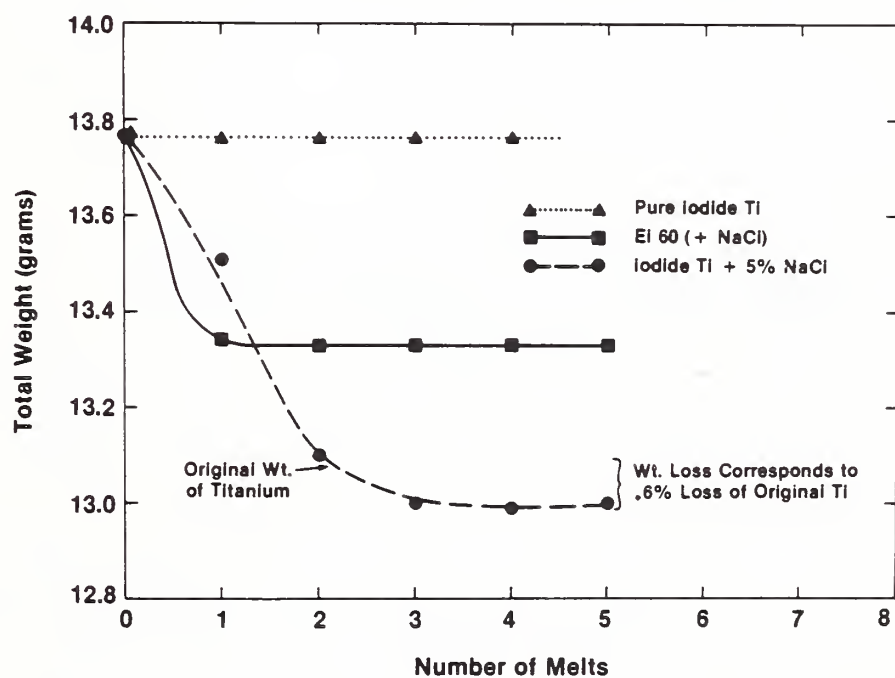


Fig. 3. Weight losses produced by repeated arc-melting for pure iodide Ti, El 60 Ti and synthetic Ti + 5% dehydrated NaCl mixture.

after each melt. The total observed weight loss after the melting was 5.6%, which significantly exceeds the 5.0% salt in the original mixture (see Fig. 3). It seems obvious, therefore, that these losses are not due to simple evaporations of salt. They probably involve the Ti also. In further support of this conclusion, we melted some pure iodide titanium (salt-free) four times under the same conditions and observed a total weight loss of less than 0.1%. We, therefore, concluded that our use of the "El 60" material would not only impose the added burden of pre-melting but would introduce uncertainties in regard to the salt content and thus pose an unnecessary risk to the accuracy of our data. Furthermore, the cost of the "El 60" product was significantly higher than that of the Chinese "iodide" titanium. A summary of the various available source materials is given in Table 1.

B. Sample Preparation

Before melting our samples, we undertook an evaluation of several alternate melting procedures to determine which procedure would best maintain the purity of our starting materials. Trial samples of our "iodide" titanium were melted (four times each) using these three separate procedures:

Procedure #1 - Evacuate the melting chamber, using only a roughing pump, to a pressure of $\sim 10^{-6}$ Torr and then introduce special high-purity argon gas before arc-melting.

Procedure #2 - Evacuate the melting chamber using an oil-diffusion pump (backed by the roughing pump) to a pressure of $\sim 10^{-6}$ Torr and then introduce the special high purity argon gas before arc-melting.

Procedure #3 - Evacuate the melting chamber as in Procedure #2 and backfill with the special high-purity argon gas. Purify the argon in situ by electrical heating of an interior 1" x 6" zirconium strip (0.004" thick) followed by arc-melting.

The samples prepared by each of these procedures were then submitted to a vacuum-fusion analysis with the results shown in Table 2.

Table 2

Effects of Various Furnace Atmospheres on Arc-Melted Titanium

	Gas Content (ppm)		
	O	N	C
Pure Iodide Ti	100	10	40
Roughing Pump (10^{-4} mmHg)	120	10	40
Diffusion Pump (10^{-6} mmHg)	90	10	80
Zr-Gettered Argon	140	10	1260

Procedure #1 is quite satisfactory for our purposes. The use of the oil-diffusion pump in procedure #2 did not provide much additional lowering of the oxygen content and seems to have increased the carbon content, perhaps by back-streaming of the oil in the diffusion pump. All subsequent sample preparations were, therefore, carried out using procedure #1. Each 20 gram sample was melted four to six times and inverted between melts. Melting losses were always < 1%. Chemical analysis of samples containing substantial amounts of Al, O, N or C (see Table 3) showed compositions corresponding closely to those expected based on the nominal amount of each element that had been added. Oxygen was added as TiO_2 , nitrogen as chemically analyzed TiN and carbon as TiC. High-purity metallic aluminum was also used.

Samples were homogenized using a procedure developed by Shull et al. (Ref. 15) who showed that homogenization in the α phase region avoids the chemical segregation which would occur if the sample were cooled from the β region. All homogenization annealing treatments were done in a tungsten resistance furnace in a vacuum corresponding to pressures of $< 10^{-8}$ Torr. Homogenization times were one week at 1000°C and two weeks at 900°C . The samples were then furnace cooled to room temperature before being removed from the furnace.

C. Preparation for Neutron Diffraction Experiments.

Each 20 g button was sectioned with an abrasive wheel using plentiful water-cooling to prevent overheating. Small ($3/32$ " dia.) holes were drilled in the ends of each half button using electrical discharge machining (EDM) techniques, and the two 10 gram sections of each sample were then suspended, one above the other, in the high-temperature neutron diffraction apparatus with vanadium wire. The vacuum lines and connections in the apparatus were all metal with copper gaskets so that no organic material was exposed to the vacuum. The high vacuum was achieved using a turbo-molecular pump which maintained pressures of at least 10^{-5} Torr even when the chamber was heated to high temperatures. This seemed to be adequate since all samples had bright, clean surfaces when removed from the chamber, even after having been heated to high temperatures in prolonged (overnight) experiments. Special interlock systems were incorporated to prevent damage to the apparatus in the event of loss of vacuum, water-cooling or electric power. A continual check was provided against possible short-circuiting by the sample against the heating elements by connecting a resistance meter between them.

Although some preferred crystalline orientation no doubt existed in our samples, it was not a serious problem for our experiments. Because the grain size ranged from one to four mm, about ~ 100 grains were immersed in the neutron beam. The samples were, therefore, not rotated during the experiments.

The initial experiment on each sample involved heating it in the high-temperature apparatus to a temperature corresponding to that of its prior homogenization and holding for about 1 hour to permit temperatures to equilibrate and to disperse any nonequilibrium structures which may have formed when the sample was cooled to room temperature after its homogenization treatment. A complete pattern was then recorded in the angular region $2\theta = 14$ to 42 degrees. Thus, equilibrium data was obtained for most samples first at 1000°C and then, after re-homogenizing, at 900°C . In addition, data was taken on selected samples by temperature scanning. This involved raising the temperature in small (5° to 10°C) increments while scanning for the strongest diffraction lines of existing or anticipated phases. One could thereby observe a phase transition by following the disappearance of one line and the appearance of another. We found that about 10 to 15 minutes time was sufficient to re-establish phase equilibrium in our samples at temperatures above 1000°C when the temperature was raised by about 10°C . Thus, phase transformation temperatures could be established to about $\pm 5^{\circ}\text{C}$ if sufficient time was allotted following each temperature increment. Phase boundaries determined in this manner agreed well with those determined using DTA methods within our experimental accuracy ($\pm 10^{\circ}\text{C}$).

Vaporization of aluminum from our samples did not pose a significant problem at temperatures up to 1300°C . None of our

samples has yet been studied above 1350°C. We estimate that our apparatus is capable of operation up to at least 1500°C. The maximum temperature is set by the melting temperature of the vanadium furnace elements (approximately 1930°C). We have chemically analyzed several of our samples after prolonged study in our apparatus at the higher temperatures, and it appears that there is minimal, and probably insignificant, contamination (see Table 3).

TABLE 3 ANALYSES OF BINARY TI-AL SAMPLES AFTER COMPLETION OF ALL EXPERIMENTS INCLUDING HOMOGENIZATION AND HIGH-TEMPERATURE NEUTRON DIFFRACTION EXPERIMENTS.

Sample #	At. % Al (Intended)	At. % Al (Analyzed)	O (ppm)	N (ppm)	C (ppm)
1	14.00	14.05	380	4	158
2	16.00	16.03	296	5	142
3	18.00	17.80	212	10	143
4	20.00	19.76	302	4	122
5	22.00	21.87	334	20	278

No attempt was made to evaluate the peak intensities quantitatively although future studies might include such refinements. This study was intended to simply locate various phase boundaries and identify the phases. Obviously, however, phase transformation temperatures can be located more precisely and at a significantly lower cost using DTA methods (Refs. 13,15,16). The primary advantage of using high-temperature

diffraction methods lies in its identification of the high-temperature phases which participate in these transformations and in its unique sensitivity for detecting ordered structures in this alloy system.

V. COMPARATIVE EVALUATION OF X-RAY

AND NEUTRON DIFFRACTION METHODS

The basic principles of X-ray and neutron diffraction are quite similar, and both of these methods can be used to identify the structure of polycrystalline samples. However, there are some fundamental differences between the two methods in regard to such things as sample dimensions, absorption characteristics, atomic scattering behavior, availability of suitable radiation sources and, last but not least, there is a significant cost differential. All of these factors must be considered when one chooses which of these methods should be used in specific instances.

X-ray sources are less expensive than neutron sources and are readily available in most laboratories, whereas neutron beams having the desired wavelength and intensity are obtained from atomic reactors. Once having located a suitable neutron source (most often from an atomic reactor), it is necessary to obtain the collaboration of the reactor group's staff who will coordinate and supervise the experiments in accordance with the normal operating schedule of the reactor which includes

alternating "start ups" and "shut downs" for reactor maintenance or modification. One must schedule experiments well in advance so that they do not conflict or interfere with other experiments being done at the reactor.

Experimental apparatus to be used at the reactor face must be safe and reliable for continuous operation, unattended, over many hours. It is also desirable that the apparatus can be quickly placed in operation at the reactor at a pre-scheduled time and removed promptly when the experiment is finished to make way for others. Reactor time is a valuable commodity, and prolonged delays in using one's allotted time are not welcome. There is also a lively competition for "reactor time" which generates pressure to use it efficiently.

VI. DESIGN AND CONSTRUCTION OF A HIGH-TEMPERATURE NEUTRON DIFFRACTION APPARATUS

Our choice of neutron diffraction for investigating the constitution of Ti-Al alloys was predicated on several factors. First of all, it offers an especially sensitive means for discriminating between the α -phase terminal solid solution and its ordered counterpart, the α_2 phase (see Fig. 1 and Fig. 4).

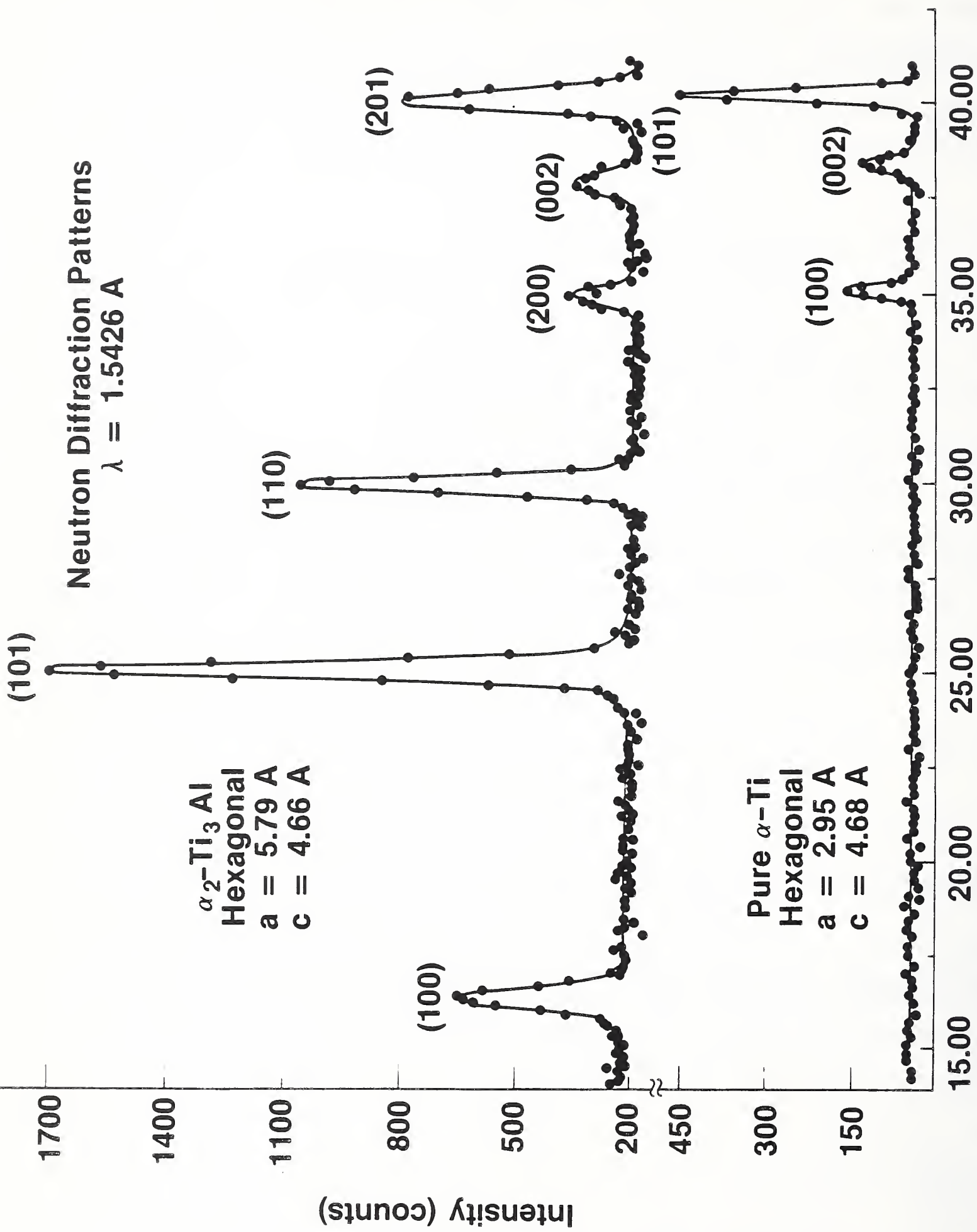


Fig. 4. Neutron diffraction patterns for (αTi) phase (annealed Ti powder) and $\alpha_2(\text{Ti}_3\text{Al})$ phase (annealed Ti_3Al). Peaks are identified by the Miller indices of their respective unit cells. The patterns were obtained at room temperature using unrotated samples.

Secondly, it permits the use of massive samples (~ 20 g.) with low surface-to-volume ratios and irregular shapes. Sample contamination is, therefore, minimized when the sample is heated in a vacuum or inert gas atmosphere. Thirdly, the relatively large sample size insures that a larger number of grains will intercept the incident radiation beam than is the case with X-rays. This permits a more random sampling of the crystal orientations. Finally, neutron diffraction offers a wider latitude in designing associated high-temperature apparatus. One can surround the sample with furnace components and vacuum chambers while still maintaining an adequate beam intensity at the sample. Furthermore, if these components are fabricated from vanadium, there will be essentially no diffraction peaks from them and one will see only the diffraction lines from the sample itself. Pure vanadium is a natural "null matrix" material for neutrons which contributes no significant coherent diffraction peaks and has a minimal neutron absorption coefficient.

We, therefore, set out to design and construct an apparatus having the unique feature that all portions of the apparatus which intercept the neutron beam would be constructed of pure vanadium (see Fig. 5). This includes heating elements, heat shields and vacuum chamber walls. The heating element and heat shields are located inside the vacuum chamber, along with the sample, to protect them from oxidation. The neutron beam is transmitted efficiently into and out of the vacuum chamber by a

Furnace for High Temperature Neutron Diffraction Studies

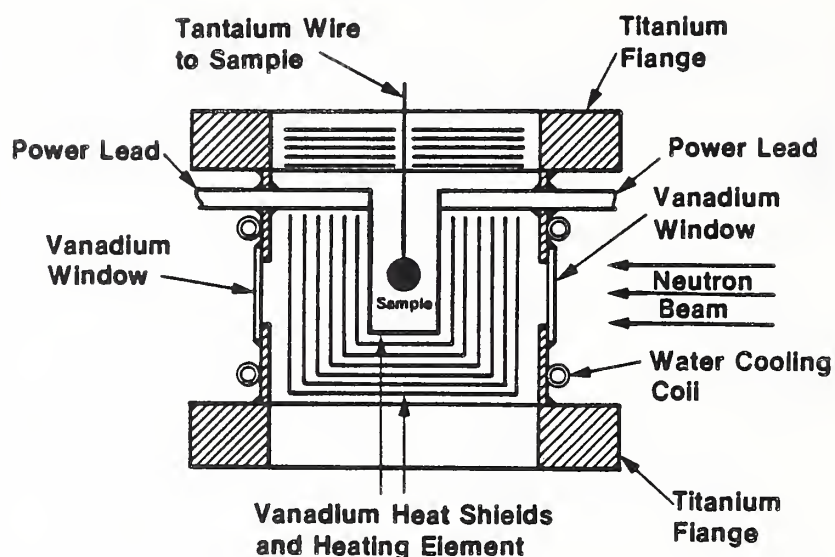


Fig. 5. Schematic representation of high-temperature neutron diffraction apparatus operable to about 1500°C under a high vacuum.

vanadium "window" ($1/8$ " thick x 2" wide) incorporated directly in the wall of the vacuum chamber (Figs. 5 and 6). In order to insure that the window will maintain a high vacuum ($\sim 10^{-6}$ Torr), it is welded to the chamber wall. This means that the wall itself must be constructed from a material which has a thermal expansion coefficient and thermal conduction characteristics close to those of vanadium. Titanium was chosen for these reasons. The entire apparatus (except the window, etc.) was, therefore, constructed of commercial-purity titanium using electron-beam welding. After preliminary experiments indicated that vanadium and titanium could be welded with this method, the vanadium window itself was welded successfully to the chamber wall without cracking. A helium leak test indicated that the completed chamber was leak-tight at pressures down to 10^{-9} Torr.

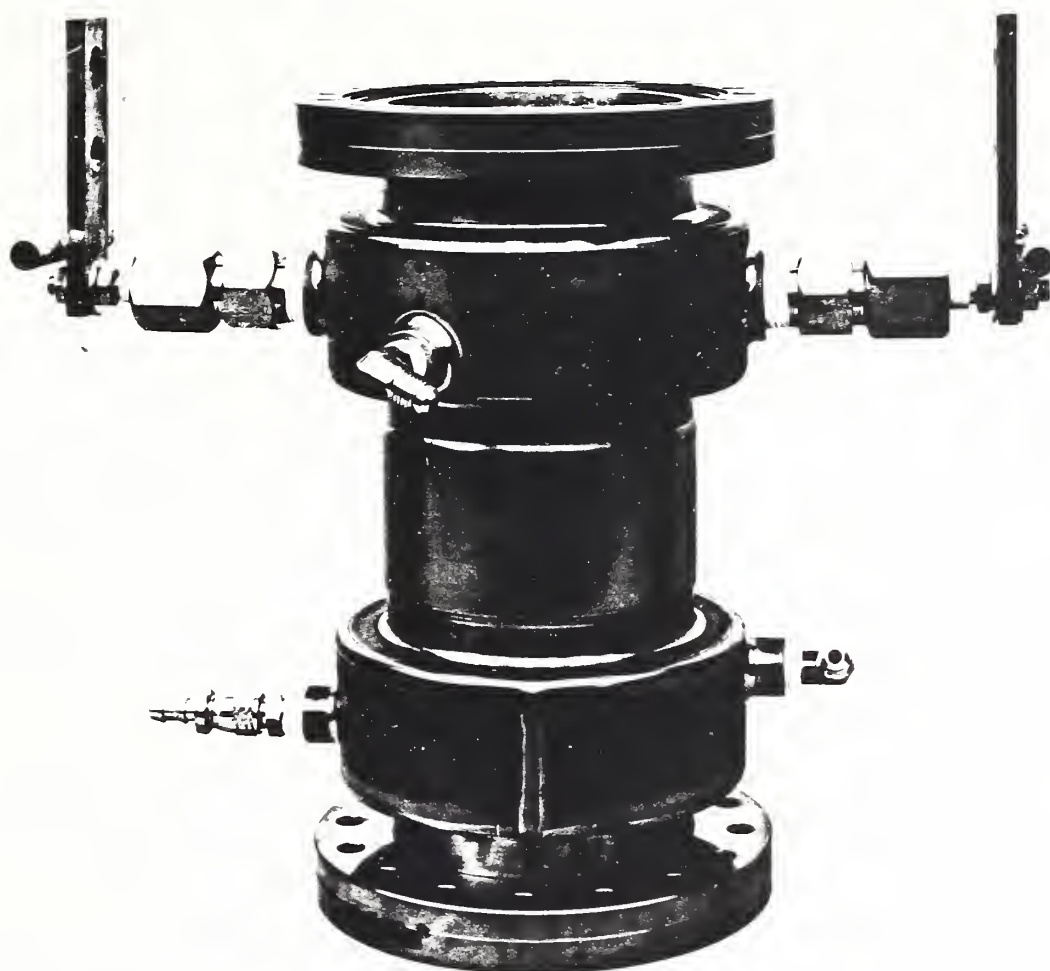


Fig. 6. Photograph of the completely assembled high-temperature neutron diffraction apparatus ready for attachment to the vacuum system.

The temperature of the sample was regulated by means of a control thermocouple which was placed at the base of the hot zone so that it would not be in the path of the neutron beam. The control thermocouple was then calibrated against a standard thermocouple that was placed at the exact position to be occupied by the sample. These thermocouples were also calibrated against the electrical current in the furnace heating elements. Later experiments showed that the temperature at the sample position remained constant ($\pm 1^\circ\text{C}$) during experiments of several hours

duration and that the sensitivity of the temperature controller permitted us to regulate the temperature in increments as small as 1°C or less. The actual temperature of the sample, however, seemed to be 30° to 40° higher than indicated by the calibration, based on a comparison of observed α/β transitions with those reported in the literature. The accuracy could, of course, be greatly improved if the thermocouple were placed near the hot sample, but then it would be exposed to intercontamination with the sample and might also contribute, undesirably, to the diffraction pattern. We felt, moreover, that these additional risks were unnecessary for our studies since we were primarily interested in the variation of the transition temperatures from one sample to another rather than in the absolute values. Furthermore, the absolute values of many transitions are obtainable, for a given composition, from previous studies already published (Ref. 14).

We have not yet determined the maximum temperature at which this apparatus can be operated effectively. It is certainly somewhere below the melting point of the vanadium heating elements (~1900°C), but we have so far operated it only up to about 1350°C. We observed some heating of the chamber walls, but this can probably be eliminated by design changes and more effective water-cooling. In principle, there is no reason why a similar apparatus could not be operated at temperatures up to 3000°C, but then one would have to construct the heating elements and heat

shields of tantalum or tungsten with a resultant contribution to the diffraction pattern. A photograph of the apparatus is shown in Fig. 6.

VII. EXPERIMENTAL RESULTS

A. The Binary Titanium-Aluminum System

Neutron diffraction patterns obtained at room temperature for pure α Ti phase and for α_2 phase (Ti_3Al) are shown in Fig. 4. Both of these phases have essentially the same hexagonal structure geometry with similar atom positions (Fig. 1). However, the atom sites are occupied by titanium and aluminum in a statistically random manner for the α Ti phase, whereas in the α_2 phase the atom distribution is highly ordered. This ordering of the Ti and Al atoms doubles the "a" parameter while the "c" parameter remains virtually unchanged (see Fig. 4). The effect of the atomic ordering is to produce strong "superlattice lines" (100, 101, and 110) in addition to the so-called "fundamental lines" (200, 002, 201) which remain essentially unchanged. The neutron diffraction pattern of the α_2 phase, shown in Fig. 4, did not change significantly between room temperature and 1000°C, and this suggests that there are no significant structural changes occurring in this temperature range. One can, therefore, detect very small amounts of the α_2 phase (~ 2-3%) in an α phase matrix, but the converse (α in α_2 phase) is rather difficult to detect due to the overlapping lines.

We then proceeded to examine Ti-Al alloys containing 14, 16, 18, 20 and 22 at. % Al, first at 1000°C and then, after further homogenization, at 900°C. The structures which we observed in each case (α and α_2 phases) and the relative proportions were essentially in agreement with those indicated in the recent phase diagram by Shull et al. (Ref. 13) as well as with the assessed Ti-Al phase diagram by Murray (Ref. 14). Our data points are superimposed on the newly-proposed phase diagram in Fig. 7.

B. Short-range Atomic-Ordering in the α Ti Phase

It is noteworthy that the samples containing 18 and 20 at. % Al contained major quantities of the α_2 phase at 900°C. These essentially disappeared when the sample was heated at 1000°C. The sample containing 18 at. % Al produced only the lines of the α Ti phase, but all of the observed lines were immersed in an unusually high background intensity. A similar high background was also observed in the α Ti pattern of the 16 At. % Al sample at both 1000°C and 900°C, but α Ti patterns from other samples had a normal background. Previous workers (Refs. 17,18) have reported evidence of short-range atomic ordering in this region of the phase diagram, but the results were somewhat ambiguous.

We believe that the high background intensities are direct evidence of short-range atomic ordering. Neutron diffraction methods should be particularly sensitive to short-range ordering in this case because the atomic scattering factors of Ti and

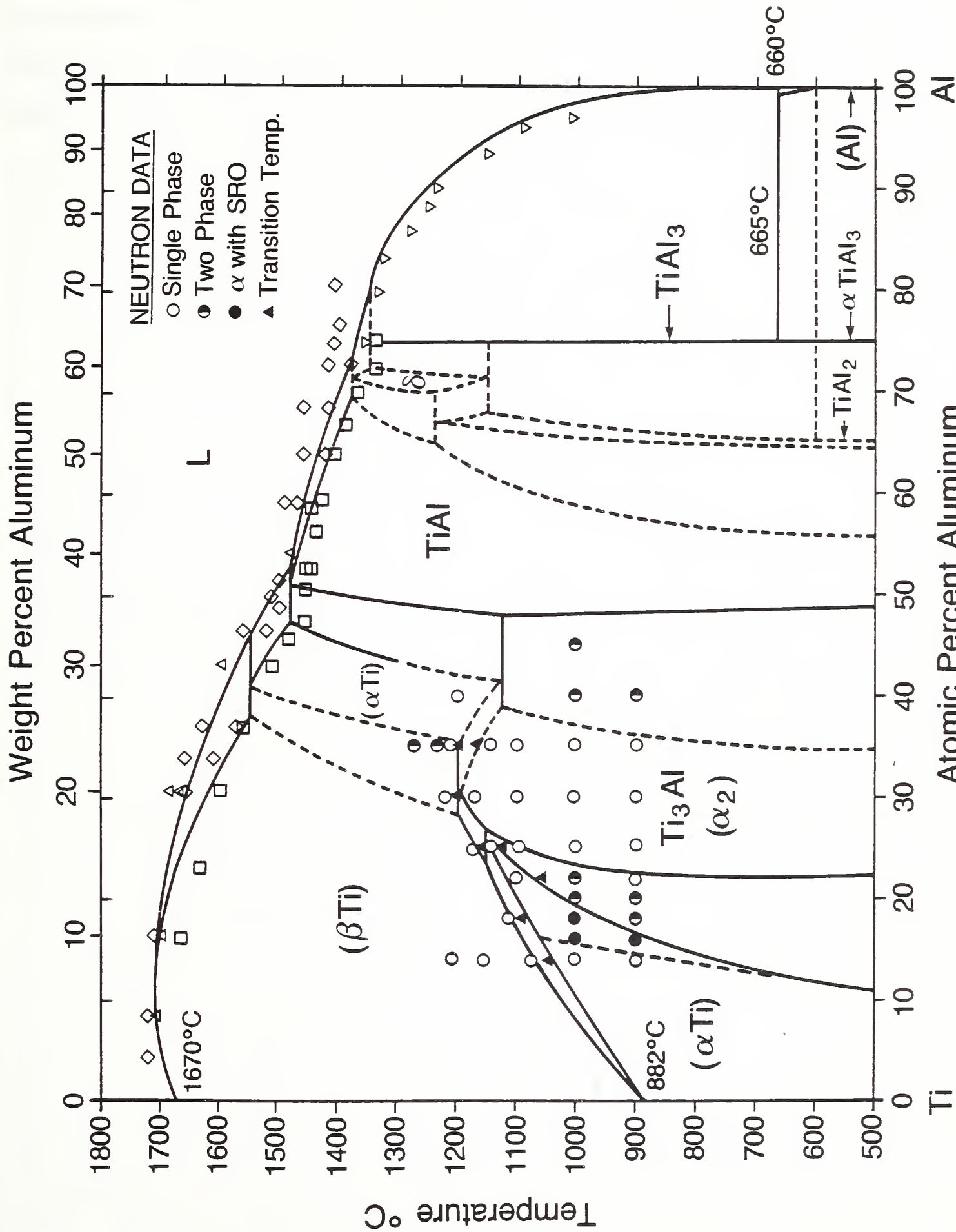


Fig. 7. Tentative revised phase diagram of the TiAl system. This is essentially the assessed diagram of J.L. Murray (Refs. 14,20) modified so as to be compatible with our observed high-temperature neutron diffraction data. The new high-temperature phase at ~ 40 at. % Al is tentatively identified as (αTi). The region of SRO is also shown.

Al atoms are of nearly equal magnitude but opposite sign ($b = -0.38$ and $+ 0.35$ respectively). This combination would be expected to produce a large apparent "temperature factor" in neutron diffraction data, i.e., high diffuse background intensity.

The presence of short-range atomic order can have a significant influence on the mechanical and physical properties of these alloys. In this context, our subsequent results for alloys containing about 1 at. % oxygen may be very significant. We have observed that this small amount of oxygen essentially eliminates the short-range order and replaces it with a two-phase mixture of α and α_2 phases. One can expect this effect to be critically dependent on the aluminum and oxygen contents in localized regions of the alloy, and this may explain Shull's observation of small α_2 phase clusters (Ref. 13).

Our direct evidence of short-range ordering in binary Ti-Al alloys having a low interstitial content also supports Shull's contention that discrepancies between various versions of the $\alpha + \alpha_2$ region in the Ti-Al phase diagram can be produced by differences in short-range ordering (Ref. 13). Shull pointed out that certain types of measurement such as magnetic susceptibility (Ref. 19) would be quite sensitive to short-range ordering while other methods such as optical microscopy (Refs. 13,10) would be unable to detect it at all. Thus, the position of phase

boundaries may differ significantly in these two types of experiments.

In Fig. 7 we have drawn a dashed line to separate the regions of the α Ti solid solution that are with and without short-range ordering. This line corresponds rather well to the α solvus boundary of Swartzendruber et al. (Ref. 19) who used magnetic susceptibility as a primary experimental method.

C. The Ti-Al Phase Diagram up to 50 at. % Al and above 1200°C

Ti-Al phase relationships above 1200°C are not well understood because most previous investigators have worked with "quenched" samples which yield ambiguous interpretations. It appears, however, that this region of the phase diagram is ideally suited for our high-temperature neutron diffraction methods. We have used our new high-temperature facility to explore this region directly for the first time. This rather preliminary study was conducted by examining critical diffraction peaks of various phases as the temperature was gradually raised. For example, we looked at the strong (101) peak for the α_2 phase and the (101) peak of α Ti. (Note that these are two separate lines occurring with a wide angular separation.) We also monitored the (110) peak of the β phase. By carefully increasing the temperature in small increments (~ 5 to 10°C) and waiting 10 to 15 minutes for the sample to equilibrate between each increment, we were able to follow phase transitions well enough to reproduce known

transitions in the Ti-Al system at temperatures above 1000°C. Our high-temperature data essentially confirmed the location of the β transus and α solvus boundaries as determined in the previous studies (Refs. 13,14,16) and are compatible with the previously defined α_2 phase boundaries.

However, above 1200°C there were serious discrepancies. The previous work had indicated that the β phase region extended to over 40 at. % Al (Ref. 14), but we failed to see any β phase lines at 35 or 40 at. % Al. Instead, the pattern obtained at about $1200 \pm 10^\circ\text{C}$ consisted of only one line at $2\theta = 40.6^\circ$ ($d = 2.22\text{\AA}$). This line was obviously not a β phase line nor was it a line of the equiatomic γ phase. The absence of the strong (101) superlattice line ruled out the α_2 phase.

The unidentified line had a moderate intensity and seemed to correspond roughly to the strongest line of the disordered hexagonal αTi solid solution. This had to be a tentative identification, however, since none of the other lines of the αTi pattern were observed. The failure to see other lines might be expected, however, since the α phase would produce a relatively weak pattern at such high Al contents. This is caused by the positive and negative atomic scattering potentials of Al and Ti atoms cancelling each other and presumably leading to zero intensity at approximately 50 At. % Al in a disordered Ti-Al phase. In order to confirm our tentative identification of the

α Ti structure, we would probably need to conduct high-temperature x-ray diffraction studies on these samples. Such facilities were not available to us at this time, however, so we decided to examine a 40 at. % Al sample that had been rapidly quenched (cooling rate of 10^6 °C/sec) using an arc furnace equipped with a piston and anvil device. X-ray diffraction patterns see (Fig. 8) obtained at room temperature from quenched foils having the nominal composition 40 at. % Al showed only the lines of a hexagonal (α Ti) structure together with weak lines of TiAl γ phase. No "superlattice" lines of the α_2 phase were detected. The strongest line in the pattern occurred at $d = 2.195 \pm 0.01$ Å. The quenched foil was subsequently annealed for a few minutes in a high vacuum at 1100°C and its x-ray pattern was then that of the ordered hexagonal α_2 phase, complete with "superlattice" lines. This suggests a re-establishment of equilibrium in the annealed sample which is compatible with the existing phase diagram.

It appears, therefore, that the existing phase diagrams (Refs. 13,14,20) must, once more, be modified. The diagram must apparently include a disordered hexagonal phase stable above 1150°C whose existence had not been previously detected. One might regard this new phase region as an extension of the α Ti terminal solid solution, but the two-phase regions are apparently not connected in the binary Ti-Al system. We established this by carefully heating our sample containing 30 at. % Al in

temperature increments of about 3°C while monitoring its neutron diffraction pattern for signs of the α Ti phase. We found no sign of this phase at any temperature. The strong (101) super-lattice line of the α_2 phase remained until about 1202°C. At 1205°C the α_2 phase line disappeared and was replaced by the strong (110) line of the β phase. Thus, we conclude that the two disordered hexagonal Ti-Al phases are separate phase regions rather than a single continuous phase in the binary system.

We have not yet acquired sufficient data to fully define the phase boundaries in this system, but we have plotted the data points provided by our neutron diffraction study and constructed tentative phase boundaries (using dashed lines) that are compatible with the data (Fig. 7). The new phase boundaries are also compatible with previous solidus and liquidus points taken from reference 14. Obviously, the solubility of Al in β Ti is significantly less than had been previously reported, and this reduced solubility is apparently caused by the presence of the newly-discovered high-temperature (α Ti) phase.

D. The Influence of Oxygen on the Phase Boundaries in the Ti-Al System

Having established the binary Ti-Al phase boundaries in the region of interest, we turned our attention to the influence of oxygen on these boundaries. The time remaining did not permit us

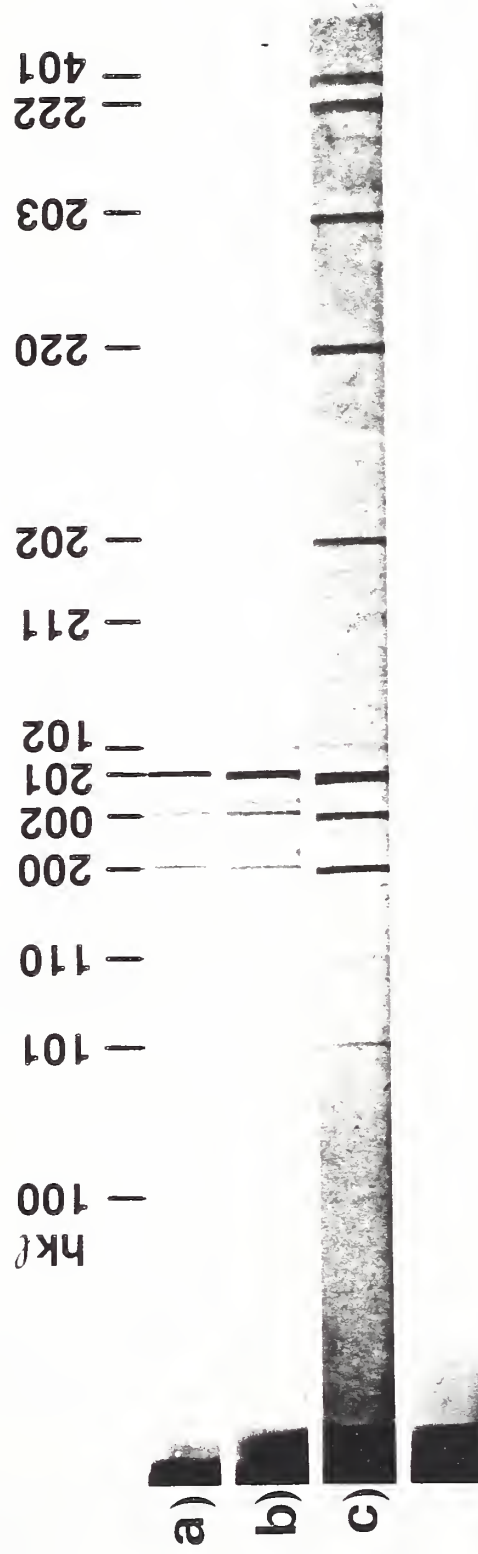


Fig. 8. X-ray diffraction patterns from $Ti_{60}Al_{40}$ alloys which were quenched from the liquid ("splat"-cooled) compared with pattern of Ti_3Al . Miller indices (hkl) are for Ti_3Al . Top to bottom are: (a) $Ti_{60}Al_{40}$ quenched and then annealed at $1100^{\circ}C$, (b) $Ti_{60}Al_{40}$ as-quenched, (c) Ti_3Al .

to completely evaluate these influences, but we were able to examine four alloys containing 1 at. % and 6 at. % oxygen. The data, obtained by temperature scanning focused on the strong (101) line of the α_2 phase, are plotted in Fig. 9 together with tentative phase boundaries that are compatible with this data. It appears that dissolved oxygen raises the β transus and α solvus temperatures and increases the stability of the α Ti phase, in agreement with previous work. The solubility of Al in α Ti is apparently reduced by the presence of oxygen, in agreement with previous results.

The most interesting effect produced by dissolved oxygen in α Ti, however, is its ability to eliminate the short-range order (SRO) that we observed in some of our binary alloys. For example, no SRO was seen in our alloys $\text{Ti}_{83}\text{Al}_{16}\text{O}$ and $\text{Ti}_{81}\text{Al}_{18}\text{O}$ at 1000°C, whereas binary Ti-Al alloys having the same nominal Al contents (16 and 18 at. %) both contained prominent SRO. Similarly, at 900°C we saw no SRO in our alloy $\text{Ti}_{83}\text{Al}_{16}\text{O}$ although the binary $\text{Ti}_{84}\text{Al}_{16}$ alloy showed pronounced SRO. In each case, the former region of SRO was replaced by a region containing the two phases, $\alpha + \alpha_2$. Such behavior may produce significant changes in the mechanical properties of these alloys. In general, our preliminary results on the oxygen-containing alloys support the previous studies which established oxygen as a strong stabilizer of the α phase with respect to the β phase. More data are needed, however, to develop a truly quantitative picture.

Weight % Aluminum

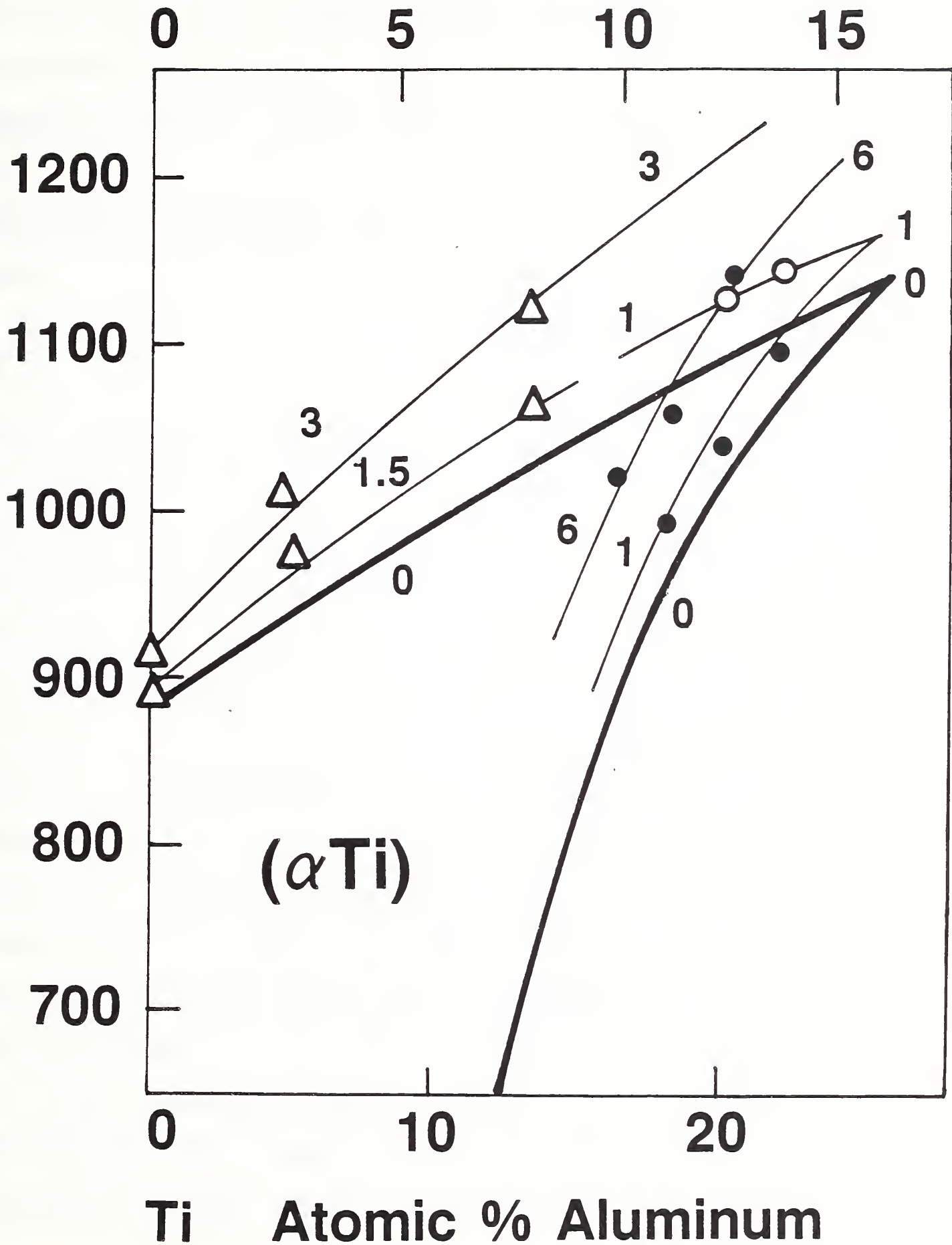


Fig. 9. Influence of oxygen on the αTi phase region in the Ti-Al system. Numbers adjacent to the phase boundaries signify oxygen content (At. %). Data for alloys containing < 17 at. % Al (unfilled triangles) are from Refs. 2 and 3. All other data points are from this study. Unfilled circles are transus points. Filled circles are solvus points. The location of the β transus boundary for alloys containing 6 at. % Al was not determined.

VIII. CONCLUSIONS

In order to determine the influence of interstitial elements on the phase relationships in the Ti-Al system, one must obviously begin with reliable information about the binary Ti-Al system itself. We have found that the recently "assessed" phase diagram (Refs. 14,20), based on an extensive literature dating back many years, is still fundamentally inadequate.

The exact location of the α solvus boundary, for example, which has been the focus of so much previous work, is still uncertain. This is partly due to an inadequate knowledge of "coherency" effects and partly to a lack of information about the effects of short-range ordering in the α Ti solid solution. We have found that neutron diffraction methods can be very useful for detecting and measuring the amount of short-range order in Ti-Al alloys. We have also observed that the short-range ordering in these alloys is strongly influenced by the presence of dissolved oxygen in the amount of < 1 atomic percent. Oxygen apparently destabilized the short-range order and replaced these single-phase regions with two-phases; disordered α Ti and the long-range ordered α_2 phase. The extent to which this "destabilization" occurs depends sensitively on the Al and O contents, and it may have a profound influence on the strength and ductility of commercial titanium-aluminum alloys. More work is obviously needed in this area.

Our high-temperature data at about 1200°C revealed a new binary Ti-Al phase at about 40 at. % Al which seems to have escaped detection in most of the previous studies because it cannot be easily retained by quenching. The neutron diffraction pattern of this phase contained only one peak, however, and this is insufficient for positive identification of the crystal structure. Rapid quenching of this alloy from the liquid state produces a disordered hexagonal α Ti structure. This identification is compatible with the observed single neutron diffraction peak at 1200°C if one assumes that the observed peak is indeed the strongest peak of the α Ti phase and that the weaker peaks do not have intensities comparable to the background scattering. The diffraction angle of the observed peak ($2\theta = 40.6^\circ$) corresponds to a d-value of 2.22Å, and this clearly rules out a β Ti or γ TiAl structure but is compatible with an α Ti structure. The α_2 phase is ruled out by the absence of the strong (101) superlattice peak.

The existence of a new Ti-Al phase at ~ 40 at. % Al implies that the solubility of Al in β Ti has been greatly overestimated in the previous studies of this binary system (see Refs. 14,20). More work is clearly needed, particularly high-temperature measurements, in order to adequately define the phase relationships in this region.

We have thus far obtained only a limited amount of data from alloys containing oxygen. It seems to indicate that oxygen has the effect that was anticipated. The α/β transition temperatures (β transus) and α/α_2 boundary (α solvus) are displaced to significantly higher temperatures by as little as 1 at. % oxygen. More data is needed, however, to define the location of the α solvus and α_2 phase boundaries. We had hoped to complete this portion of our work in the allotted time period, but we have encountered repeated and prolonged delays in obtaining permission to purchase some critical equipment. This, combined with unavoidable reactor "shut-downs" for maintenance and modification, has inordinately delayed the work. Greater flexibility in procurement procedures is needed to permit more efficient coordination with the operating schedule of the reactor.

If such problems can be eliminated, one can obtain extremely useful data from high-temperature neutron diffraction measurements. The ability to detect short-range order and to discriminate sensitively between the αTi and $\alpha_2(\text{Ti}_3\text{Al})$ phases are significant advantages of this method. Another advantage is the ability to identify high-temperature phases that cannot be retained by quenching, particularly if the structure involves atomic ordering.

However, the use of neutron diffraction for simply determining transition temperatures is inappropriate since such determinations can be accomplished more quickly, more accurately and less expensively with differential thermal analyses (DTA). Perhaps the best method for determining a phase diagram, such as Ti-Al, would be a combination of DTA, for determining transition temperatures, and high-temperature neutron diffraction for phase identification. The technology for conducting DTA studies on levitated samples under high pressure of inert gases to suppress vaporization has already existed for several years (Ref. 21) and has been used successfully in determining the closely-related Nb-Al phase diagram (Ref. 22). It is time to apply these techniques to the Ti-Al system.

We wish to conclude this study by offering our samples to other investigators. We have prepared numerous samples of Ti-Al ternary alloys containing small amounts of oxygen, nitrogen and carbon in anticipation of further work. These samples have been annealed in a very high vacuum (10^{-8} Torr) for homogenization and could be used for DTA studies as well as for neutron diffraction. The samples should now be made available to other investigators so that work may proceed as rapidly as possible on these vitally important alloy systems.

Acknowledgments

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We wish to thank the Vacuum Furnace Systems Corporation for undertaking to construct the special vacuum furnace apparatus for heating the samples during the neutron diffraction measurements. The apparatus was subsequently found to be highly reliable and capable of providing accurate data while protecting the samples from contamination. We wish to thank Mr. Bill Lugmayer, P.E., for his enthusiastic advice and assistance with electron-beam welding and Mr. F. A. Schmidt of the Materials Preparation Center, Ames Laboratory, for offering the use of their facilities to fabricate the pure vanadium window for our vacuum furnace apparatus. Finally, we would like to thank Mr. A. Giuseppetti for assisting us through the many phases of sample preparation and metallographic study.

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