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THE TITANIUM-VANADIUM SYSTEM

by

Richard Mather Powers

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Head of Major Department

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Dean of Graduate College

Iowa State College
1952

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I. PURPOSE OF STUDY

Since both titanium and vanadium have been considered as desirable materials for use in certain reactors, it was thought that a study of alloys between these two might lead to materials with even more desirable properties than either metal alone. Consequently, a systematic investigation of the alloys of the titanium-vanadium system was undertaken.

II. LITERATURE SURVEY

Before initiating experimental work on the titanium-vanadium alloy system, a literature survey was made. What studies had been carried out were of a limited nature only, no systematic overall investigation of this binary system was found.

The earliest work reported on an alloy of these metals was that of Kroll (1) who employed powder metallurgy techniques on mixtures of titanium with a number of alloying elements. The briquets were formed by pressing at 15 tons per square inch into 3/4 inch diameter coins, 1/4 inch in height. These compacts were presintered in a vacuum; then sintered at a high temperature under 50 millimeters of argon. Following this treatment, they were covered with a salt layer and hot-rolled into one millimeter strips. The single vanadium alloy of Kroll's investigation that was prepared in this manner contained 4.77 per cent vanadium and was reported to possess good rollability. The alloy had a Brinell hardness of 477 and exhibited a microstructure showing a titanium matrix with a grain boundary constituent.

More recently E. I. Larsen, E. F. Swazy and others (2) investigated a number of titanium alloys, including those of vanadium. The alloys were fabricated by powder metallurgy techniques, using Bureau of Mines titanium powder. The size analysis of this material was the following: 8 per cent through 200 mesh, 20 per cent through 100 mesh, 41.6 per cent through 60 mesh, and 99.9 per cent through 30 mesh. The principal impurities in the titanium were the following: Mg 0.27 per cent; Fe 0.06 per cent; Al 0.01 per cent; Si 0.01 per cent; Cl 0.23 per cent; H 0.095 per cent to .111 per cent; O 0.058 per cent to 0.072 per cent; and N 0.024 per cent to 0.035 per cent.

Powder mixtures were compacted at a pressure of 30 tons per square inch. These compacts were sintered for one hour at 2200° F in a vacuum of less than one micron. The sintered specimens were cold-rolled with intermittent vacuum anneals, or sheath rolled at 1475° F. For the titanium-vanadium alloys, the above titanium powder was combined with 95 per cent lump grade vanadium that had been crushed to pass the 30 mesh screen. Alloys containing 0.5 per cent, 5 per cent, and 15 per cent vanadium were pressed into bars and sintered for one hour at 2200° F. No depression of the melting point was observed. The 15 per cent vanadium bar did not cold-roll appreciably. However, the 0.5 per cent and the 5 per cent vanadium alloys were cold-rolled to reductions of between 25 per cent and 58 per cent without serious edge cracking. The results of alloying may best be summarized in the following table.

Further work was reported by Larsen and others (3) on a 5.74 per cent vanadium alloy. This alloy was prepared from 95 per cent lump vanadium and du Pont titanium sponge. The melting stock was prepared by compacting the mixture of metals in a 1.938 inch die. Melting and casting took place in graphite under an atmosphere of argon that had been purified by passage over titanium sponge at 900° C before entering the furnace. The charge was heated by a split-graphite resistance furnace using currents up to

Table 1

Properties of Several Titanium-Vanadium Alloys
(Larsen, _et_ _al_. (3) p 239)

Per cent vanadium	Resistivity (microhm-cm.)	Hardness (Rockwell "A")	Tensile strength (p.s.i.)	Per cent elongation
0.5% (C.R.77%)	73	66	130,500	3% (2")
0.5% (C.R.77% Ann. at 1850° F)		61	98,700	12.5% (2")
5%	87	68	153,000	0
15% (could not be cold-rolled				

3400 amperes at 10 volts. The alloy generally absorbed from 0.03 to 0.06 per cent carbon from the crucible. In one alloy that contained 5.74 per cent vanadium, a superficial tenacious oxidation product formed on annealing in a gas-fired furnace, but did not interfere with the properties or impair forging. They reported that this titanium-vanadium alloy hardened appreciably on quenching.

Considerable work has recently been published on the binary, ternary, and quaternary alloys of titanium by Craighead and others (4). They report that the transition temperature of titanium is progressively lowered by additions of vanadium up to 5 per cent.

The tensile properties of several titanium-vanadium alloys with 5 per cent vanadium were studied by Busch and Dickenson (5a). They obtained considerable variation in physical properties of the 5 per cent vanadium alloy samples.

Recently, a phase diagram of the titanium-vanadium system has been reported by Adenstedt and others (5b). Using both crystal bar and commercial sponge titanium, together with commercial grade vanadium, these investigators found that the beta to alpha plus beta phase boundary was lowered by additions of vanadium to titanium. The single phase alpha field was found to extend to the 3.5 per cent vanadium composition at 650° C for the crystal bar titanium. At this temperature, the beta to alpha plus beta boundary was located at about the 20 per cent vanadium composition. In addition to the phase diagram, resistivities at 0° C, coefficients of expansion from room temperature to 1200° F, and lattice parameters and hardnesses as a function of composition were determined. The age hardening properties of a 15 per cent vanadium alloy were also investigated.

A still more recent partial phase diagram of the titanium-vanadium system has been published by Pietrokowsky and Duwez (5c). As the result of metallographic studies and lattice parameter determinations, the beta to alpha plus beta transition boundary was determined as being near the 18.5 per cent vanadium composition at 650° C. The solubility of vanadium in alpha titanium was reported as about 1.5 per cent at that temperature.

III. PREPARATION OF STARTING MATERIALS

In connection with the work reported here, an effort was made to start with quite pure metals in order to obtain a reasonably accurate phase diagram of the titanium-vanadium system. Fortunately, titanium of good quality was obtainable on the market. Vanadium, on the other hand, had to be prepared in the laboratory since metal of sufficient purity was not readily available commercially at the time.

A. Electrolytic Method

At the beginning of the investigation, serious consideration was given to preparation of the alloys by powder metallurgical methods. Because of earlier success in the preparation of powdered zirconium by fused salt electrolysis (6), it was decided to extend the electrolytic method to the preparation of titanium and vanadium powders.

Titanium was prepared by electrolysis of K_2TiF_6 dissolved in a bath composed of NaCl and KCl (7) at temperatures between 700° C and 800° C. The resulting powder, freed from salt, was comparable in properties to commercial titanium. Not much success, however, was had in the preparation of vanadium (8) by electrolysis of K_2VF_5, the powder obtained in this process being coated with a green film. Because of the difficulty encountered with vanadium, attempts to prepare the pure metals by electrolysis of fused salts were discontinued.

B. Vanadium

A series of reductions was made in order to prepare enough vanadium for a study of the titanium-vanadium system. The two methods employed in production of the vanadium used in the alloy studies differed mainly in the material that served as the thermal booster in the bomb reductions.

1. Calcium reduction of vanadium pentoxide using a sulfur booster

The method used for the production of pure vanadium metal was essentially that devised by J. R. Long (9), who prepared high quality metal from commercial grade vanadium pentoxide. He employed a mixture of vanadium pentoxide, calcium, and sulfur in a bomb reaction to obtain massive vanadium. Vanadium pentoxide may be reduced to the metal by calcium according to the equation

$$V_2O_5 + 5\ Ca \rightarrow 2V + 5\ CaO \quad \Delta H = -321.5\ kcal\ (10).$$

Unless additional heat is supplied to the reaction, the metal is obtained largely in the form of unconsolidated powder (11). In order to obtain more massive metal, heat must be supplied by a concurrent reaction such as

$$Ca + S \rightarrow CaS \quad \Delta H = -113.4\ kcal\ (10).$$

A proper adjustment of the proportions of the vanadium pentoxide, the calcium, and the sulfur can be made to give a good yield of compact, high purity vanadium metal.

The preparation of vanadium used for this study was carried out in an iron bomb 13 inches in length, made from 2.5 inch standard iron pipe. A 1/4 inch iron plate was welded in one end of the pipe, thus closing off that end, and a threaded-on screw cap on the other end completed the bomb. To heat the bomb, in order to initiate the reaction, a gas-fired barrel-type furnace was used (9). The bomb was suspended in it by means of an iron hook and the bomb temperature followed by a thermocouple placed in a protection tube that had been welded to the side of the bomb. The furnace temperature was regulated with a thermocouple and Wheelco Capacitrol regulator, which actuated a solenoid gas valve in the line to the furnace. In these reductions, a jolt-packed electrically fused dolomitic oxide liner was used. Approximately 1.5 inches of the oxide were first jolted into the bottom of the bomb. A tapered graphite mandrel (1/8 inch taper per 15 inches of length) provided with a removable center rod to permit its withdrawal, was carefully centered on the oxide covered bottom. More liner material was continuously added with jolting to the annular space around the mandrel until the annulus was full. The bomb was then held upright in a vise while the mandrel was carefully twisted out, leaving behind a smooth-walled liner. The entire operation required about 15 minutes. Once made, the lined bomb was argon flushed and capped until ready for filling.

The following ingredients went into the charge:

Vanadium pentoxide (Vanadium Corporation of America)
Analysis: SiO_2 0.01% Cl 0.003% Fe 0.005%
Alkalies trace

Calcium (Ames redistilled)
Analysis: Fe 14 p.p.m. Mn 13 p.p.m. N 110 p.p.m.

Sulfur U.S.P. pure sublimed (J. T. Baker Chemical Company)

The charge was weighed out on a pan balance to the nearest tenth of a gram and then transferred to a fruit jar and thoroughly mixed. Before addition of the mixture to the bomb, a layer of calcium (30 grams) was placed in the bottom of the bomb. This appeared to decrease the tendency toward the formation on the bottom of the metal of a thin black skin which gave evidence of being a lower oxide of vanadium. In filling the bomb with reaction mixture, care was taken to prevent the liner material from falling into the charge. Additions of from one sixth to one tenth of the charge were made at one time, then the mixture would be carefully pressed down with an iron rod and the next addition made. The remaining space at the top of the charge was filled with the finely divided dolomitic oxide, which was added after first covering the charge with a thin calcium layer of approximately 8 grams. During the reaction, a thin impervious layer formed in this region and prevented the more loosely packed dolomitic oxide at the top from falling into the reaction mixture. The bomb cap, jolted nearly full of the dolomitic oxide, was screwed onto the threaded bomb with pipe-dope as a thread seal. After the bomb had been sealed, it was placed in the furnace which was maintained at a temperature of about 850° C. The bomb wall temperature climbed steadily as the bomb picked up heat from the furnace. After five or six minutes in the furnace, a sudden increase in the rate of climb of this temperature occurred, indicating that the bomb was firing. The wall temperature rose to a maximum in the neighborhood of 900° C and then started back again. At this point, the bomb was lifted from the furnace and allowed to cool in air.

When the bomb had cooled to room temperature, the cap was screwed off with a large pipe wrench and the charge knocked out by banging on the bomb sides with a weighted mallet. The slag formed a porous plug, often golden in color, that sometimes dropped out as a unit, followed by the shiny metal button on the bottom. When it was necessary to recover some of the metal beads, the slag was merely placed in water, where it disintegrated with bubbling and evolution of hydrogen sulfide. Following a preliminary cleaning, the metal button resulting from the reduction was usually soaked overnight in distilled water. To remove the last traces of superficial calcium oxide or calcium sulfide, the button was allowed to stand in dilute hydrochloric acid; then given several distilled water rinses and a final acetone dip and drying.

A number of preliminary runs were made in which the amount of sulfur was varied with respect to the vanadium pentoxide. Twenty grams of sulfur to 180 grams of vanadium pentoxide was the least amount of sulfur tested. In general, with the lower amounts of sulfur, the resulting yields and buttons were unsatisfactory. A typical charge that produced a satisfactory metal for alloy studies was composed of 180 grams of vanadium pentoxide, 372.8 grams of calcium in 50 per cent excess, and 40 grams of sulfur. Several runs were then made under these conditions to produce sufficient metal for study of the titanium-vanadium alloy system, with no attempt being made to maximize the yields or to otherwise improve the product. The resulting metal was comparable to that produced by Marden and Rich or by J. R. Long as judged by the criteria of chemical purity, malleability and of electrical resistivity (12).

2. Calcium reduction of vanadium pentoxide using an iodine booster

In addition to vanadium prepared by the previous process, a final series of alloys was made using vanadium prepared by J. R. Long. The same general process was followed as before, the only exception being the use of iodine (13) instead of sulfur as a booster. The heat supplying reaction thus became

$$Ca + I_2 \rightarrow CaI_2 \qquad \Delta H = -257 \text{ kcal } (10).$$

Considerably more iodine by weight is required than sulfur to supply a given amount of additional heat. In determining a satisfactory charge to yield good metal, the iodine content of the charge was increased until reasonable yields and hardnesses were obtained. Then a number of runs was made to build up a stockpile of metal for the alloy studies. The same experimental details were used as when sulfur was employed as the booster. Typical results for a few runs are shown in Table 2. The yields given in the table are for the largest piece obtained on reduction. Total yields, which included smaller pieces and small recoverable beads, would be higher.

Table 2

Vanadium Reductions Using an Iodine Booster

Run No.	Weight of V_2O_5 (g)	Weight of Ca in 65% xs (g)	Weight of I_2 (g)	% Yield of massive metal
RJL2-238	160	314	80	68.7
RJL2-237	160	318	95	75.5
RJL2-236	160	314	80	80.0

C. Titanium

1. National Lead Company titanium sponge

The titanium metal used in the first series of titanium-vanadium alloys was obtained in the form of sponge and was assumed to have been produced by the well known process that employs the reaction between titanium-tetrachloride and magnesium metal at an elevated temperature. In order to reduce sputtering caused by residual magnesium or chloride in the titanium on arc melting, these volatile impurities were removed by heating the sponge under vacuum. Two different systems were used to "degunk" the sponge. In the first, the titanium sponge was placed in a molybdenum boat inside of an evacuated silica furnace tube of 1.375 inches inner diameter. The silica tube, closed at one end, was attached through a large ground glass standard taper joint to a large diameter pyrex glass manifold that led to the pumping system. The glass joint was sealed with pyseal and cooled on the outside by a tightly-wound 1/4 inch copper coil through which water flowed. A large glass cold trap formed an integral part of the glass manifold. The pumping system consisted of a small water cooled Distillation Products diffusion pump (V.M.B. 10) backed by a Welch Duo-Seal mechanical pump. During a run, the trap was surrounded by liquid air. Pressure in the system was measured by a Phillips gauge that was inserted into the side-arm of the manifold with a pyseal joint.

The silica tube was heated by a Hoskin's resistance furnace, which was placed on a carriage that could be wheeled over the furnace tube and backed off after a run. The furnace operated from a 220 volt stepped transformer and its temperature was controlled by means of a Brown potentiometric recorder-controller. The Brown instrument operated an on-off switch which was in series with the furnace. To reduce the fluctuation of the furnace temperature that would occur if current to the furnace were cut entirely off by the controller, a 4 ohm resistor was placed in parallel with the switch. The step transformer was set to give a current through the furnace large enough to carry it above the desired operating temperature when the switch in the Brown controller was closed. When the switch opened, the 4 ohm resistor, which had been shorted out by the closed switch, was thrown in series with the furnace, reducing the current and lowering the furnace temperature to a value below the desired operating temperature. In this way, fluctuations in furnace temperature were minimized.

In a typical run employing the above apparatus, 66.3 grams of titanium sponge was charged to the furnace in a molybdenum boat. The system was closed and pumped down to 0.1 micron after which the furnace tube was heated in steps to 1055° C over an 8.5 hour period. The maximum pressure reached during the preheat was 0.36 micron at 605° C, whereupon it dropped to 0.01 micron at 1055° C. Heating was continued for 7.5 hours at this elevated temperature and with a vacuum of less than 0.01 micron. At the end of this time, the resistance furnace surrounding the silica furnace tube was pulled away and the temperature of the charge in it dropped rapidly. When cool, the charge was removed from the furnace and stored under argon until ready for arc melting. A dark deposit on the walls of the silica furnace tube indicated that some material was subliming from the titanium sponge. Several runs were carried out in a similar manner to prepare 99.6 per cent titanium for Series I alloy.

A second apparatus used to clean up the titanium sponge was that of Dr. O. N. Carlson. The heating was carried out in a graphite crucible. This was heated by a split-graphite resistor. Power was taken from a large, high-current, low-voltage transformer. The entire furnace was enclosed in a large, water-cooled tank having inner shields of molybdenum and alumina to reduce radiation losses. In spite of the increased size of the furnace, not much larger changes could be accomodated than in the previous apparatus, though the temperatures reached were considerably higher. Titanium sponge (82.8 grams) was placed in the graphite crucible and charged to the furnace. The system was evacuated to 6 microns and the power was turned on. Over a one-half hour period, the temperature rose to 1610° C. The pressure at that temperature reached 150 microns, but dropped down to 5 microns after 15 minutes in the 1600° C to 1650° C temperature range, when the power was shut off and the furnace allowed to cool for several hours. On removal from the furnace the crucible was found to be filmed with a shiny layer, probably titanium carbide, and the charge volume had shrunk. The apparent weight loss was 0.6 grams. During the run, with each increase of power to the heater, the pressure rose, then settled back to approximately 5 microns. The current would again be raised. A second run was made using this same crucible, it being stored under argon in the mean time. This second run differed from the first in that no appreciable rise in pressure occurred. Thus the previous pressure rise must have been caused by degassing of the graphite crucible.

A quantitative spectroscopic analysis of untreated titanium sponge from National Lead Company's Titanium Manufacturing Division showed the following results:

Cu	very weak	Ni	very faint trace	V	very weak
Mg	moderate	Pb	faint trace		
Mn	weak	Si	trace		

The only impurity element present in any appreciable quantity, magnesium, was presumably removed by the subsequent vacuum annealing treatment.

2. duPont titanium sponge

High grade duPont titanium sponge was used in an untreated state for preparation of alloys with vanadium. This metal analyzed 98.2 per cent titanium.

IV. ALLOY PREPARATION

A. Electrolytic Co-deposition of Alloys

Electrolytic co-deposition of both vanadium and titanium metals to form an alloy directly was attempted by electrolysis of fused salts. The mixtures consisted of K_2TiF_6 and K_2VF_5 dissolved in NaCl and KCl. The results of this limited investigation were not sufficiently promising to warrant further study at the time. It was hoped that the deposit would be of such purity and character that powder metallurgy techniques might then be successfully employed. The resulting alloy powder produced by this electrolysis, however, was considerably enriched in vanadium, indicating that vanadium was being preferentially deposited from the bath.

B. Co-reduction of Alloys

Several alloys were prepared by co-reduction. The method was a modification of the one used for vanadium production. Oxides of the two metals were mixed in the desired proportions and reduced by calcium, using a sulfur booster.

Two preliminary runs were carried out by calculating the charge from one found to be satisfactory for vanadium by R. J. Long, i.e. 160 grams of vanadium pentoxide, 300 grams of calcium metal, and 20 grams of sulfur. The vanadium pentoxide employed by J. R. Long, as well as these preliminary experiments was contained in a commercial grade of vanadia analyzing 89 per cent V_2O_5. This charge almost filled the 2.5 inch inner diameter bomb used to carry out the reductions. In making up the 90 per cent (atomic) vanadium alloy with titanium for example, 131 grams of vanadium pentoxide added as the 89 per cent commercial grade, 12.5 grams of pure titania, 300 grams of calcium, and 24.2 grams of sulfur were used. The charge was arrived at by a rough consideration of the heats of reaction at room temperature, and neglect of other quantities such as the change in heat capacities and heats of fusion. Since a rough indication of the total heat requirements for a satisfactory metal was known from previous work on vanadium by J. R. Long to be about 350 kilocalories for the 2.5 inch bomb, the additional heat necessary to arrive at this value was supplied by the reaction of calcium and sulfur.

A second charge was also determined for the 80 per cent (atomic) vanadium alloy on the basis of the first co-reduction. This charge consisted of 120 grams of vanadium pentoxide added as the 89 per cent grade, 23.5 grams of titania, 306 grams of calcium and 30 grams of sulfur. Calcium in 60 per cent excess of the theoretical requirements was used in both of these tests on co-reduction.

When the bomb was suspended in the furnace set at 850° C, the first charge fired in about three minutes, the outside thermocouple reaching a maximum temperature of 903° C before dropping back again. After the temperature had decreased slightly, the cherry-red bomb was withdrawn from the furnace and set aside to cool in air. As a matter of caution, the second run which was designed to give an 80 per cent vanadium alloy contained only 30 grams of sulfur which was less than the calculated amount. It took eight minutes for this bomb to fire and the maximum temperature to be reached was only 835° C. In these preliminary runs, the following yields of massive metal were obtained: for the 90 per cent vanadium alloy, 44.25 grams or 54.8 per cent yield; and for the 80 per cent vanadium alloy, 38 grams or 47 per cent yield.

The biscuits of metal produced in these two runs were somewhat porous, indicating that more sulfur might be used in any succeeding runs. While the titania used in these reductions was of analytical grade, the vanadia was the commercial inexpensive material used extensively by J. R. Long in the development of a less expensive process for preparing the metal. On the basis of these exploratory tests, plans were made to extend the co-reduction experiments with the purest available starting materials.

Reductions employing pure starting materials were carried out after making up charges that were modifications of a satisfactory vanadium charge. Approximately the same temperature rise was desired in the alloy charge as for vanadium in order to insure fusion of the products of the reaction. This was estimated in a rough manner by developing the same total heats in each case. Temperature rise was indicated very approximately by the thermocouple in the outer bomb wall. A satisfactory bomb charge arrived at empirically for pure vanadium was the following: 180 grams of pure vanadium pentoxide, 372.8 grams of calcium, and 40 grams of sulfur. This charge almost filled the 2.5 inch bomb and contained two mols of metal.

As a first approximation of the reactions involved during a reduction, the following are considered probable:

$5\ Ca + V_2O_5 \rightarrow 5\ CaO + 2V$ ΔH -321.5 kcal (10),

$Ca + S \rightarrow CaS$ ΔH -113.4 kcal (10) and

$TiO_2 + 2\ Ca \rightarrow 2\ CaO + Ti$ ΔH -85.4 kcal (10).

Any heats of a slag forming reaction, heat capacities and heats of fusion were neglected. The total heat liberated by a bomb full of the above charge (2 mols of metal) was thus taken to be 321.5 + (40/32)(113.4) for a total of about 460 kilocalories.

To prepare an 80 per cent vanadium (atomic per cent) alloy, for example, a charge containing two mols of total metal was used since it should almost fill the 2.5 inch experimental bomb. The following amounts of oxide were required; (.8)(1 mol V_2O_5/2 mols V)(181.9 g V_2O_5/ mol V_2O_5) or 145.5 grams of vanadium pentoxide, (.2)(2 mols TiO_2/ 2 mols Ti)(79.9 g TiO_2/mol TiO_2) or 32 grams of titanium dioxide per 2 mols of metal. The calcium requirements for vanadia are (.8 mol V_2O_5)(5 mol Ca/mol V_2O_5)(40 g Ca/mol Ca) or 160 grams of calcium. For titania, the calcium requirements are (.2)(2 mols TiO_2/2 mols Ti)(2 mols Ca/mol TiO_2) (40 g Ca/mol Ca) or 32 grams of calcium. The heat evolved from the vanadia reduction amounts to (.8)(321.5 kcal) or 267.5 kilocalories, while that from titania is (.2)(2) (85.4 kcal) or 34.2 kilocalories.

The total heat from this oxide metal reaction was about 300 kilocalories. The difference between this heat and that determined empyrically for a good reduction of 460 kcal, i.e., about 160 kcal, must be made up by action of calcium upon sulfur. This requires (161.7 kcal/113.4 kcal/mol)(32 g S/mol S) or 45.6 grams of sulfur. The calcium to react with this sulfur is 57.1 grams. Total calcium theoretically required is thus 249.1 grams. When an additional 50 per cent excess calcium, which had been found empyrically to yield a satisfactory product, was added, the final charge for the 80 per cent vanadium alloy with titanium was

V_2O_5	145.5 g	Ca	344 g
TiO_2	32 g	S	45.6 g

When this was thoroughly mixed and reacted, 70 grams of alloy product were obtained. The slag above the button was dark and porous, not the partly golden color of vanadium reductions with 50 per cent excess calcium. The alloy button was placed in a beaker of water and heated to remove most of the slag. It was then given a ten minute treatment in dilute (1:15) hydrochloric acid to clean up the rest of the slag, washed several times in distilled water, acetone rinsed and dried. The recovery of metal fines that are trapped in the slag is usually a somewhat time and reagent consuming process on a small scale. Most of the fines and pellets thus entrapped were salvaged by repeated leaching with hot water and decantation of the lighter calcium hydroxide and unhydrolyzed calcium sulfide. When most of the slag had been poured off, treatment with hydrochloric acid left only the metal beads behind. The beads were then washed with distilled water, acetone rinsed, and dried. The total yield of metal included beads as well as the larger buttons.

As in the vanadium reductions, about 30 grams of calcium were withheld from the mixed charge, to be placed on the bottom of the liner to prevent oxide formation on the surface of the metal button. In addition to the calculated amount of calcium, about 8 grams more were used to cap the charge and to prevent the dolomitic oxide at the top from mixing with the charge. After a co-reduction, the alloy was cleaned in the usual manner and arc melted under argon that had been purified by a zirconium getter. Arc melted buttons were then sectioned and densities measured on all alloys to get some indication of the composition. A plot of density against composition had been obtained by co-melting the metals as described later in this report.

A summary of the charge compositions and the yields is given in Table 3. Note the difference between the anticipated and the actual alloy compositions. It is seen from this table that vanadium is more readily reduced than titanium. Although too much reliability should not be attached to alloy compositions in the titanium-rich end of the system, it is obvious from the density determinations that pure titanium was not obtained under the conditions of 30 per cent excess calcium and the use of sulfur as booster. All other runs except that of titanium were carried out using a 50 per cent excess of calcium. Poor results for titanium under these conditions cast considerable doubt on the purity of co-reduced alloys in the high titanium region of this system, although by increasing the per cent of excess calcium or by changing to an iodine booster, more satisfactory alloys might have been prepared. No runs other than those tabulated were carried out by co-reduction. It was felt that more reliable results could be obtained in studying the titanium-vanadium system by starting with the pure metals and melting them together. Microstructures of several co-reduced alloys are shown in Figures 1 through 4.

Table 3

Coreduction of Titanium-Vanadium Alloys

Atomic % V Charged	Composition of Charge (g)				Density (g/cc)	Alloy Comp. Atomic % V	Arc Melted Hardness (R_A)	% Yield Massive Alloy	Total % Yield
	V_2O_5	TiO_2	Ca	S					
100	180.0	0	373.0	40.0	6.104	----	50.0	88.0	97.0
80	145.5	32.0	343.0	45.6	5.995	94.0	54.6	69.6	78.4
70	127.3	47.9	390.6	57.8	5.908	89.0	53.9	62.4	76.0
60	109.2	64.0	392.5	62.0	5.756	80.0	58.1	61.7	71.4
40	72.7	96.0	395.5	70.4	5.413	60.0	64.1	45.4	71.4
40	72.7	96.0	405.0	75.4	5.545	68.0	63.5	48.6	71.3
20	34.6	121.6	368.0	84.4	5.134	43.0	67.0	46.3	73.2
20	35.0	123.1	384.4	75.8	4.944	31.5	69.0	49.0	71.0
10	14.9	118.0	343.0	87.7	4.528	----	73.0	54.4	79.8
0	0	150.8	394.0	82.5	----	----	74.4	47.3	72.0
0	0	127.8	336.0	90.0	----	----	----	55.8	81.3
0	0	139.0	316.0*	97.9	4.058	----	77.4	53.5	67.6

*Calcium employed in 30% excess for this reduction. In all the rest, 50% excess calcium used.

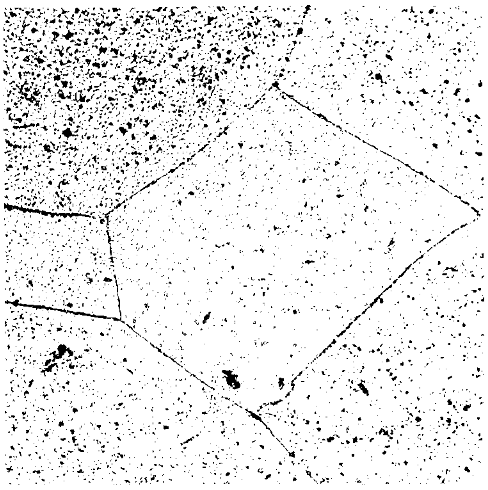


Figure 1. Vanadium (Series I) as-arc-melted from bomb reduced metal using sulfur as booster. Etchant HNO_3 (conc). 1 HF (48%), 3 glycerol by volume. X 250

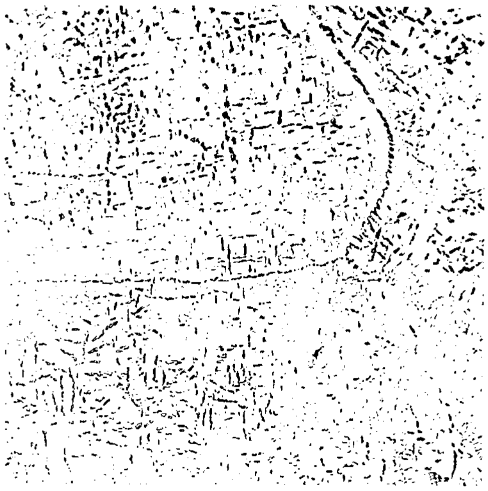


Figure 2. 89% vanadium as arc-melted from coreduced alloy. Second phase possibly impurity seen in single phase alloy matrix. Etchant 2 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

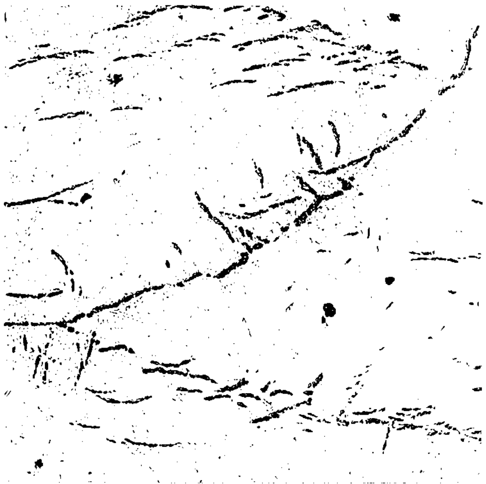


Figure 3. Approximately 68% vanadium as-arc-melted from coreduced alloy. Second phase (probably alpha) in single phase alloy matrix. Etchant 2 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

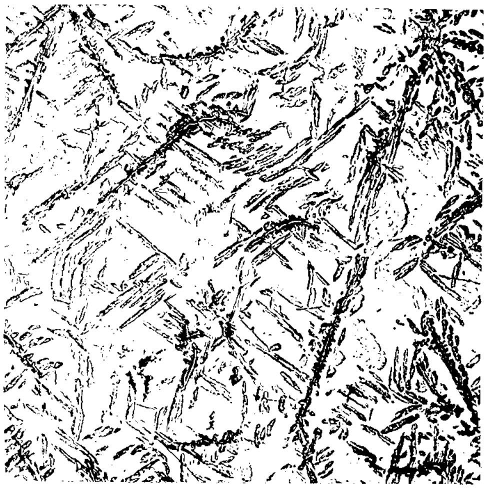


Figure 4. Approximately 20% vanadium alloy as-arc-melted from coreduced alloy. Probably primary alpha in a beta matrix. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

C. Arc Melting

1. Arc melting of sulfur boosted vanadium with National Lead Company titanium sponge

Arc melted alloys were used for most of the studies of the titanium-vanadium system. As a rule, alloys prepared by arc melting procedures were void-free. Two series of alloys were prepared in this manner; the first, Series I, was made in connection with work of an exploratory nature. This series was prepared from vanadium metal that had been reduced from the pentoxide using calcium as the reductant and sulfur as the booster. This was combined with National Lead Company titanium sponge that had been "degunked" according to either of the procedures mentioned in the previous section.

Small chunks of titanium, up to 3/4 inch size, were selected for the co-melting. The dense vanadium buttons were cut to approximately pea size on a carborundum cut-off wheel. Component metals in the desired proportions were weighed on an analytical balance. The metals were mixed and transferred to a one inch diameter die and pressed at approximately 30 tons. In some cases, the die was flushed with tank argon before, during, and after addition of the metal in order to reduce the entrapment of air in pressing. Compacts of approximately one-half inch in thickness were produced in this manner when the total weight of metal was approximately 75 grams. These compacts were stored under tank argon until arc melted, sometimes after several weeks had elapsed. The compacts before arc melting were quite fragile, so that care had to be taken to prevent loss of components during the handling before melting.

A small arc melting furnace of conventional design was used to prepare these alloys. The alloy compact was placed in a depression in the copper hearth and the furnace closed and evacuated. After several flushes with argon, the furnace was filled with this gas at atmospheric pressure. Before melting the charge, the arc was struck to a small zirconium getter button that rested in another depression in the hearth, and residual gasses were cleaned up by this melted metal. Each alloy of this series was subjected to two meltings, the buttons being flipped over between meltings. In this way, fairly homogeneous alloys were usually obtained. In the higher vanadium range where larger pieces of vanadium were used, this treatment was insufficient. Discrete chunks of soft vanadium were sometimes plainly visible in the sectioned alloy and confirmed as being vanadium by hardness measurements. In several such cases, alloys in this state were returned to the arc furnace for remelting.

2. Arc melting of iodine boosted vanadium with du Pont titanium sponge

A second series of alloys, Series II, was prepared in order to cover the more interesting portions of the titanium-vanadium system more thoroughly. This series was prepared from vanadium that had been reduced from the pentoxide by calcium, using iodine as the booster. This was combined with the best grade of du Pont titanium sponge available. This sponge was untreated in contrast to that employed for Series I alloys. The metals of this series were processed in a similar manner to that of the first series, but were arc melted four times instead of two, with the button being turned over between meltings.

Metal losses as the result of arc melting were caused principally by crumbling of the titanium sponge from the pressed alloy compacts. The mixture of metals was weighed following both pressing and arc melting. The difference in weight between these two measurements ranged from 0.15 per cent to a maximum of 3.2 per cent, with most of the losses ranging about 0.5 per cent. The larger losses were attributed to mechanical losses in transferring the compact to the arc furnace rather than to sputtering losses during melting.

V. ALLOY ANALYSIS

The analysis of titanium-vanadium alloys proved to be somewhat of a research problem in itself. After several months of work, however, the analytical section of the Ames Laboratory developed a satisfactory method for the determination of the vanadium in these alloys. The determination of titanium in the presence of vanadium, however, was not entirely satisfactory. Therefore, the alloys were analyzed for vanadium, and the titanium was determined by difference. Since all of the alloys that were analyzed chemically contained at least 2.5 per cent titanium, this method of determining the major constituents was considered adequate. The compositions of a few alloys which were not chemically analyzed were estimated by measuring their densities and referring to a plot of density against composition that had been prepared using chemically analyzed alloys.

The analytical procedure that was developed for vanadium in the titanium-vanadium alloys was based on the following reaction in a solution of the alloy titrated with ferrous ion:

$$Fe^{+2} + V^{+5} \qquad Fe^{+3} + V^{+4}$$

After several modifications, the following procedure was evolved (14). One to four grams of the alloy contained in a platinum dish were first slowly dissolved in hydrofluoric acid, with the addition of several drops of nitric acid to initiate the reaction. Between 5 and 10 ml. of concentrated sulfuric acid were then added and the solution evaporated to fuming in order to remove the hydrofluoric and nitric acids. The concentrated solution was then diluted to from 100 to 500 ml. with distilled water. An aliquot was made 10 molar in sulfuric acid and about 0.5 grams of sodium bismuthate added. The solution was then heated to the boiling point giving a yellow solution. The sides of the flask were rinsed down with water, the solution cooled, and 3 ml. of phosphoric acid and 2 to 3 drops of ferroin were added. This solution was diluted to about 5 molar in sulfuric acid and titrated with standard ferrous ammonium sulfate to an end-point that changed from bright blue to olive green. The ferrous ammonium sulfate was standardized against $Ce(HSO_4)_4$ immediately before titrating the vanadium, using ferroin as indicator. Per cent vanadium was calculated by the following formula:

$$\% \text{ V} = (\text{ml.} \times \text{N})_{FeSO_4} \times 0.05095 \times 100/\text{sample weight} \times \text{aliquot}$$

Titration of duplicate aliquots checked within the normal limits of error for the burette readings. Duplicate samples of an alloy checked well within one per cent of total vanadium in most cases.

The above procedure was employed in analyzing the vanadium metal used to make the alloys. The titanium metal used in making the alloys was first analyzed by the cupferron procedure (15) which was not applicable in the presence of vanadium.

For analysis of titanium in the titanium-vanadium alloys, the procedure of Simpson and Chandlee (16) was tested. In this method, the titanium is precipitated from an acid solution by parahydroxyphenylarsonic acid, then ignited to the oxide for weighing. Results of a limited number of determinations of titanium in the vanadium alloys were not very reproducible. An indication of the variation of these results is seen in the determination of titanium in the 48.3 per cent titanium alloy based on the vanadium determinations. Values of 55.7 per cent titanium and 51.7 per cent titanium were found using this procedure. Even in the high titanium range, an alloy containing 92.9 per cent titanium showed 94.0 and 98.0 per cent titanium. The high results obtained, as well as the discoloration of the precipitate indicated co-precipitation. In isolated cases, alteration of the valance states of vanadium, either boosting it entirely to the + 5 state or reducing it to the + 3 state gave results for titanium that approached the values calculated from the vanadium analyses. When it became evident that more modification of this method would be necessary before consistently satisfactory analyses could be obtained, work on this method for titanium was suspended.

VI. DETERMINATION OF THE PHASE DIAGRAM

The phase diagram of the titanium-vanadium system is shown in Figure 5. It was arrived at principally by a combination of melting point determinations, heat treatments, metallographic examinations, and x-ray studies of alloys made by co-melting titanium and vanadium. Evidence for this diagram is considered in the following sections.

A. Melting Temperature Determinations

The method of Pirani and Althertum (17) was employed in the measurement of the melting temperatures of the titanium-vanadium alloys. This method consists essentially of heating a specimen by slowly increasing a high electrical current that is passing through it and observing the melting temperature by means of an optical pyrometer focused on a small hole drilled in the specimen. The highest temperature attained before the small hole starts to fill with melt is taken as the melting point of the pure metal. A variation of this technique can be employed

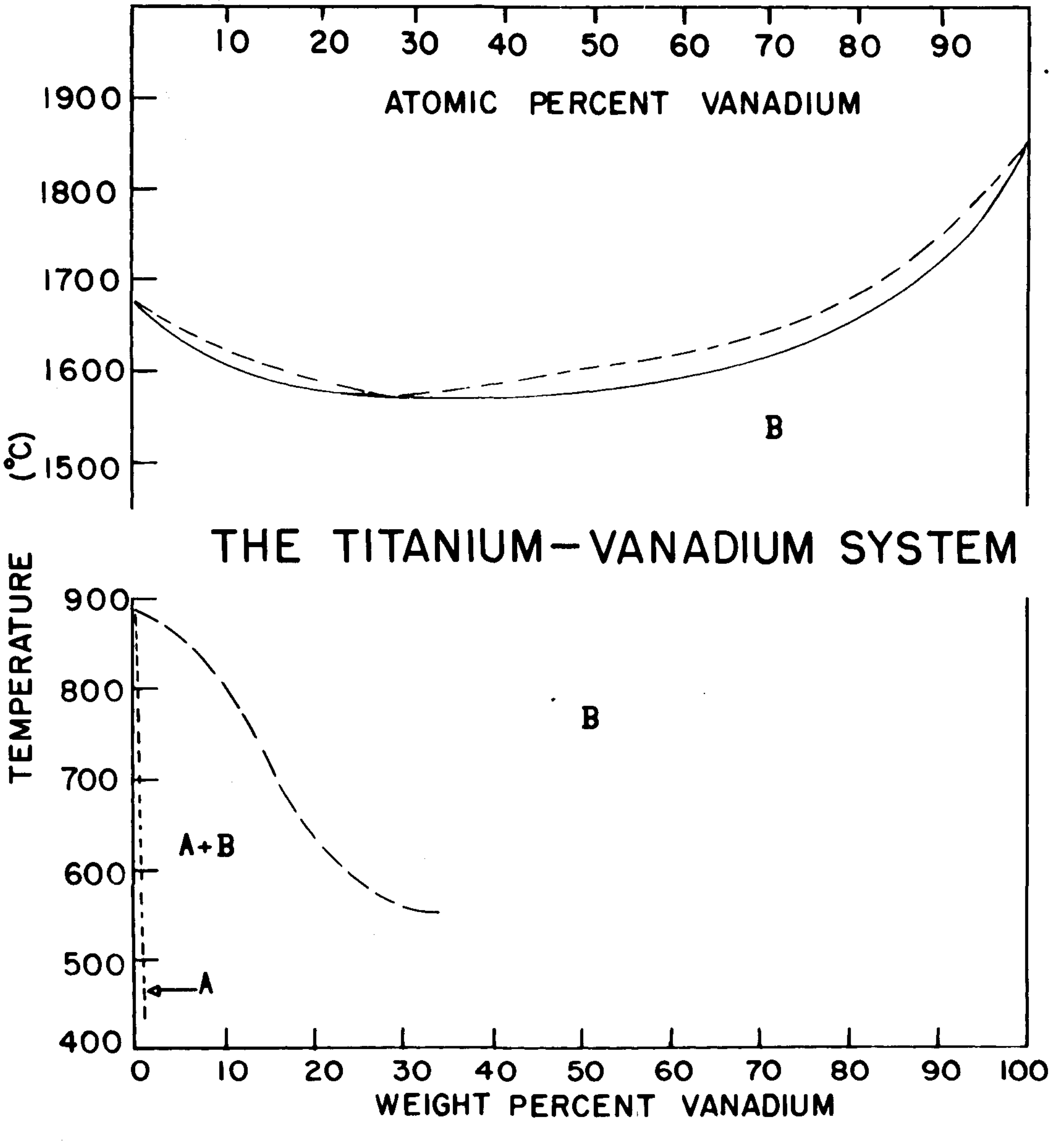


Figure 5. Phase Diagram of Titanium-Vanadium System.

to determine the solidus, and estimate the liquidus for alloys.

1. Preparation of specimens

In this investigation, specimens were cut directly from arc melted buttons by taking parallel cuts across the center section. The specimens, approximately 1.5 to 2 inches in length, and 0.25 inch by 0.5 inch in cross-section, were narrowed at the center by grinding on an abrasive wheel or cutting on a cut-off wheel. A 0.04 inch diameter hole was then drilled at the narrowest portion of the specimen. The hole was drilled to a depth of at least three times the diameter to insure black-body conditions in the hole. Because it was located at the narrowest part of the specimen, melting usually occurred at the hole. Considerable care had to be taken to prevent the small drill from breaking. A cutting oil and slow drilling speeds were used in most cases. Even with frequent re-sharpening, the drill would occasionally break in the specimen, which consequently had to be discarded. Following the drilling, the hole was washed free from oil with benzene, then filled with detergent powder (Dreft), which was subsequently washed out with a high velocity water stream. After flushing the hole with distilled water, it was filled with acetone several times, then blown out and dried. In order to determine whether or not appreciable iron was being introduced by the drill, a titanium sample was cut up and analyzed after a melting point determination. A section of the titanium containing the hole was found to contain 100 p.p.m. of iron. Another section, some distance removed from the hole, showed 104 p.p.m. of iron. These results indicate that no appreciable amounts of iron were introduced by this drilling.

2. Melting point furnace

The details of the furnace used for melting temperature determinations are shown in Figure 6. A large water-cooled jacket provided with a circular pyrex window or sight glass for viewing the specimen, rests on a recessed rubber gasket in the base plate. Two water-cooled copper electrodes pass through this base plate, one being brazed to it, the other insulated from it by a tightly fitting rubber seal. Copper clamps attached to water-cooled electrodes are used to hold the specimen vertically in the furnace. Details of one of these clamps is shown on the lower right of Figure 6. The furnace is evacuated through an outlet in the base plate by a Distillation Products MB-200 booster pump which is backed by a Welch

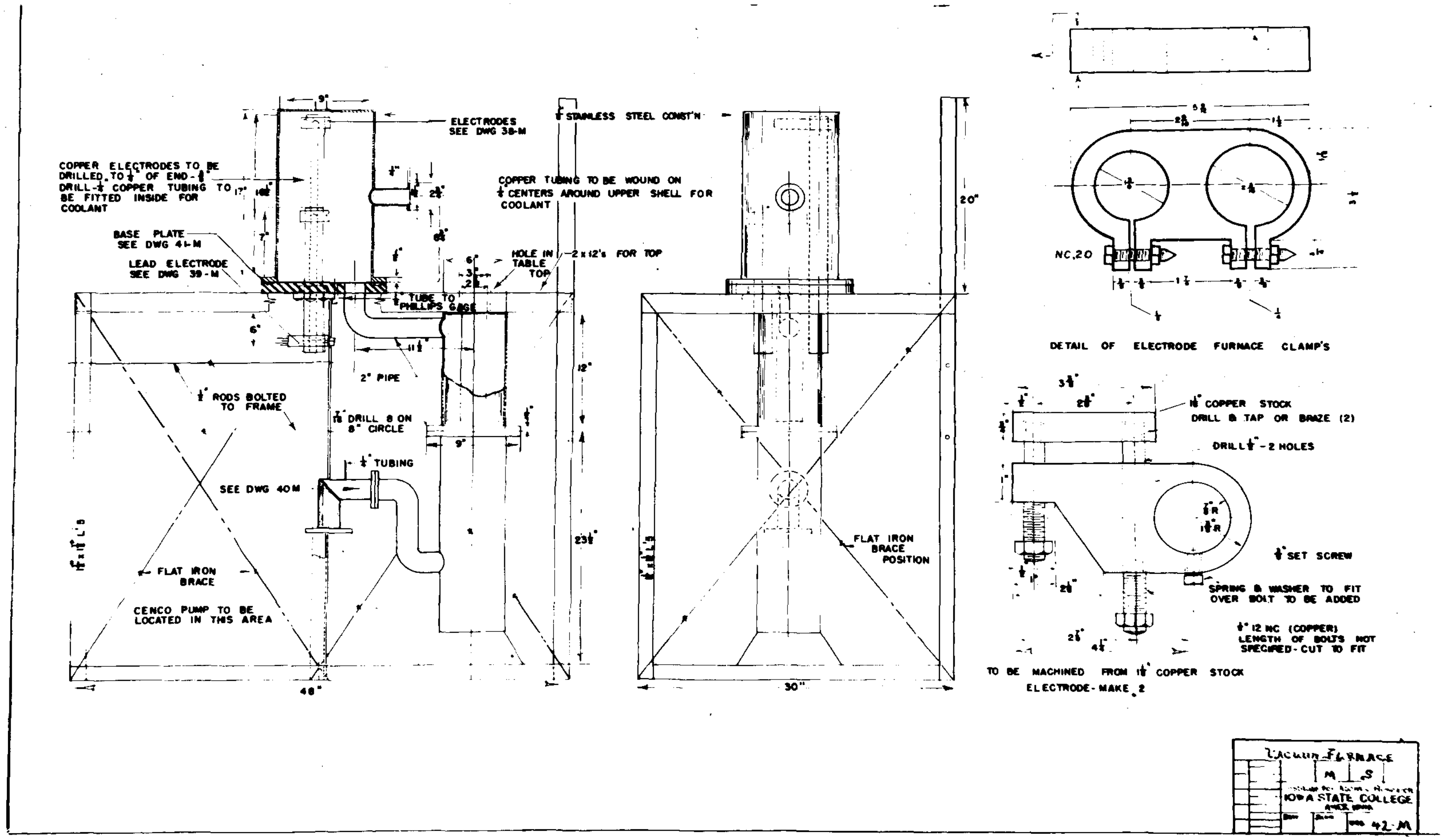


Figure 6. Melting Point Furnace.

Duo-Seal mechanical pump. The pressure in the system is measured by a Phillips' cold-cathode ionization gauge, connected to the system through the base plate.

Power for heating the specimens by the passage of high current was obtained from a step-down transformer having a capacity of 10 KVA. This transformer, supplied by the Banner Manufacturing Company (Model S.P.E.), was water-cooled and operated from three ganged heavy-duty Variacs connected to a 440 volt A.C. supply.

3. Temperature measurement

Two different Leeds and Northrup disappearing-filament optical pyrometers were used in following the melting of the metals and alloys. Each of these was calibrated against a Bureau of Standards calibrated tungsten-ribbon lamp in the usual manner, and the resulting graph of true temperature against apparent temperature used to correct the pyrometer readings.

In addition to the pyrometer corrections, a further correction was applied for the transmission of the pyrex window in the furnace jacket. The transmission of this window was measured on a Beckmann spectrophotometer in the wavelength region of 6500 A. A piece of black cardboard containing a 1/4 inch diameter hole to restrict the light beam was inserted in place of the usual absorption cell. With the card in place, the instrument was balanced at 100 per cent transmission. The card was of such a length that removal and replacement of it in the instrument did not appreciably change the balance point. The pyrex window was then placed in front of the hole in this card and the per cent transmission was read directly from the scale. The average of several readings, used in conjunction with the tables of Forsythe (18), enabled temperature corrections for the window to be determined by interpolation. To simplify this interpolation, graphs were made of the Forsythe tables. In the course of this investigation, it became evident that fogging of the window occurred during melting point determinations. Therefore, the window was removed after each determination and its transmission measured so that proper temperature corrections could be made.

4. Procedure

In carrying out a melting temperature determination, the following procedure was usually employed. The specimen, prepared in the manner previously described, was clamped in the furnace with about 1.25 to 1.75 inches of the specimen extending between the clamps. The furnace was then closed and evacuated until the pressure had dropped to about 0.04 micron. Current through the specimen was increased stepwise and the temperature allowed to level off at each setting in order to reduce any tendency for a rapid rise in pressure due to degassing of the furnace. As the melting range was approached, the rate of heating was reduced to prevent overshooting the melting temperature, and the temperature was followed continuously with an optical pyrometer sighted on the black-body hole in the specimen. Runs usually required about one hour, with the pressure in the furnace maintained at approximately .1 micron. Specimens mounted for melting determinations were always in a vertical position, which gave a horizontal position to the black-body hole. Specimens melted suddenly whereas alloys generally exhibited incipient melting, followed by gradual filling of the hole as the liquidus temperature was approached. The temperature at which liquid first appeared in the hole was taken to be the solidus temperature. As the hole filled, the temperature readings at the wall-liquid junction would continue to rise and then fall, due to increasing deviation from black-body conditions in the hole. The highest temperature observed was employed in estimating the liquidus temperature.

5. Standardization of the method

The validity of the melting point method as employed under the above conditions was checked by determining the melting point of nickel. Electrolytic nickel powder was pressed into 1/4 inch x 3/8 inch x 4 inch compacts at about 25 tons per square inch pressure and sintered by passage of current through the compact clamped in the melting point furnace. Each specimen was heated for approximately 15 minutes in the temperature range between 1150° and 1215° C. The resulting bars of nickel were cut in two, so as to approximate the length of the titanium-vanadium alloys used in this investigation. The specimens were then prepared in the manner described above for melting point measurements. Hole depths were measured to determine what variation, if any, might be introduced by changes in this parameter. No appreciable difference in melting point was found when the depth to diameter ratio was varied from 3.14 to 4.41 in the case of nickel.

The mean value of seven determinations for the melting point of nickel was 1453 ± 7° C. Maximum deviation from the mean value was 10° C. The mean melting temperature is in fair agreement with that determined by Wensel and Roeser (19) of 1455° C. or the handbook value of 1452° C (20). The method having been checked for the known metal, considerably more confidence was felt towards its extension to the measurements on vanadium, titanium, and their alloys.

6. Window correction

In connection with some early melting point determinations on vanadium a variation of from 1746° to 1863° C in the melting point was observed after correcting for the glass of the window. It was suspected that fogging of the sight window was invalidating some of the results. On investigation, it was found that fogging sometimes reduced the transmission of this sight glass from its starting value of 92.5 per cent to as low as 23 per cent. In order to eliminate this source of error in the melting point determinations of the series II alloys, the sight glass transmission was determined after each melting run as indicated earlier in this report.

In general, the higher the vanadium content of the alloy, the more intense the fogging became. As might have been expected, the amount of vapor condensed on the sight glass was also dependent on the pressure in the system and the length of time the specimen was heated at temperatures near the melting range. In order to reduce the amount of fogging, the time at the elevated temperatures was reduced somewhat and the melting specimen was surrounded by a molybdenum shield which cut down the area of the heated specimen visible to the sight glass. A frontal opening in the shield of 1/8 inch was found to be fairly satisfactory for most of the determinations. The effect of shielding may be shown by two analagous runs carried out over approximately the same time interval on pure vanadium, which had been previously melted under a 0.05 to 0.09 micron vacuum. For the specimen surrounded by a shield with a 1/8 inch frontal opening, the transmission after a run was 87.1 per cent, while for an almost identical sample with three times the frontal opening, the measured transmission was 73.1 per cent. Runs in which excessive amounts of fogging had occurred were rejected for melting temperature determinations, since too much uncertainty was introduced in selecting the proper value of transmission to correspond to the highest temperature observed before hole closure. An arbitrary limit of about 70 per cent was set on the amount of fogging.

As an example of the error that one can encounter with excessive fogging, a reading on pure vanadium gave a maximum temperature of 1749° C for the melting point, uncorrected. The sight glass transmission was then measured and found to be only 30 per cent which led to a sight glass correction of 322° C. The resulting corrected melting point temperature was 2071° C, a value decidedly in error. As an indication of the difference in the observed melting point of vanadium that would be introduced by failure to correct for fogging, the following data are given. For a final sight glass transmission of 89.6 per cent, the difference between the fully corrected temperature and a temperature only corrected for the transmission of pyrex (92.5 per cent), was 11° C. The corrections for 84.4 and 72.9 per cent transmissions were 25° and 64° C, respectively, above that for pyrex alone.

Fog continued to be evolved from vanadium samples, even after two or three repeated melting point determinations on the same sample, so that vanadium, and not a volatile impurity in it was probably responsible for the fogging. It was also found that if the fogged sight glass were allowed to stand in air, especially in moist air, for any length of time, the transmission was very apt to change. This was noticeable particularly in the high-vanadium range. For example, after heating an 84.5 per cent vanadium alloy, a fogged sight glass with an initial transmission of 82.5 per cent was changed after 10 minutes to 85.2 per cent. Moisture from the breath accelerated the change. Alloys with greater than 80 per cent titanium did not yield films that changed appreciably on standing.

The effect of total pressure in the system on fogging was found to be very great. When vanadium was melted under a pressure of 1.1 microns instead of 0.1 micron, fogging became negligible and the sight glass had its initial transmission of 92.5 per cent. The data obtained at 1.1 microns are in agreement with that of Marden and Rich (11, p 788) who considered vanadium to be " * * * one of the least volatile metals at its melting point. A sample may be held in the molten condition in high vacuum for a considerable time without appreciably blackening of a glass container." However, the observations at 0.1 micron indicate some volatility of vanadium at its melting point.

7. Gas pickup

Some contamination by oxygen and nitrogen in the course of the melting temperature determinations was expected. In the present experiments, hardness measurements were used as an index of the extent of contamination of the pure metals by these gases. The hardness at the center of a pure vanadium specimen that had been once melted under a 0.04 to 0.14 micron vacuum was 40.1 on the Rockwell "A" scale. Reference to a graph of oxygen content against hardness (21) indicates that this hardness corresponds with that for vanadium containing 0.04 weight per cent oxygen. Although the hardness of the above sample is probably due to the combined effect of oxygen and nitrogen, it may be concluded that the amount introduced is small.

On the other hand, vanadium that had been melted in a 1.1 micron vacuum to test the effect of additional gas on the metal, was found to have a melting point in excess of 1880° C and a hardness of R_A 72.5. The oxygen content was estimated to have increased to 1.4 per cent (21). The observed increase in melting point and hardness of vanadium is probably due to an increase of oxygen or nitrogen or both in the metal. The surface of the pure vanadium in these present experiments was slightly golden after melting in the 1.1 micron vacuum and the properties had changed considerably. Also, melting temperatures of the 51.67, and 69.5 per cent vanadium alloys determined in the 1.1 micron vacuum were 85° and 40° C higher, respectively, than the melting temperatures of the same alloys when determined in the 0.1 micron vacuum. The alloys on removal from the furnace were covered with a blue-gold film. In the case of the 51.67 per cent alloy, the hardness had risen from R_A 63 for the annealed alloy before melting, to R_A 74.9 after melting. Even smaller amounts of gas introduced by melting alloys in the 0.1 micron vacuum, appeared to be accompanied by an increase in melting temperature in the high vanadium range. This is illustrated by the 84.5 per cent vanadium alloy in which the initial melting temperature was 1692° C. Second and third meltings of this specimen at the same pressure gave values of 1697° and 1728° C, respectively. This increase in melting temperature on remelting appeared to be fairly general for alloys with greater than 20 per cent vanadium. This behavior was apparently reversed for alloys containing less than 20 per cent vanadium. A 14.77 per cent vanadium alloy, for example, showed an initial melting temperature of 1605° C which on remelting in a 0.1 micron vacuum dropped to 1590° C. Even more illustrative are the melting points of a crystal bar titanium specimen, which in successive meltings under a 0.03 to 0.095 micron vacuum gave the melting points of 1677°, 1663°, 1636°, and 1631° C respectively. The hardness after the fourth melting had changed from the original R_A of 45, to 51. This corresponded to a change in oxygen content from 0.03 to 0.08 weight per cent (22). These results seem to indicate that very small amounts of dissolved oxygen or nitrogen lower the melting point of titanium.

8. Summary of melting temperature determinations

Results of the melting determinations on the titanium-vanadium alloys are shown graphically for Series I alloys in Figure 7. Results of Series II alloy melting experiments are shown both in Table 4 and graphically in Figure 8.

As a result of these determinations on vanadium prepared by calcium reduction of the pentoxide and the use of either sulfur or iodine as the booster, the best melting point is considered to be 1860° ± 20° C. This value is believed to be close to the true temperature for pure vanadium. The metal analyzed 99.1 to 99.55 per cent vanadium, gave a fairly clean microstructure, and had a room temperature resistivity of about 29 microhm-centimeters. The most probable value for this melting point reported by van Arkel (10, p 224) is 1700° ± 10° C (23). A value of 1900° ± 25° C has recently been reported by Adenstedt and others (5b).

The best value obtained for titanium in this series of experiments is 1677° C for the crystal bar metal. The next best value is taken to be 1673° C for the first melting of du Pont titanium. This compares to a value of 1727 ± 10° C reported by Fast (25) or to one of 1700° ± 15° C recently reported (5b).

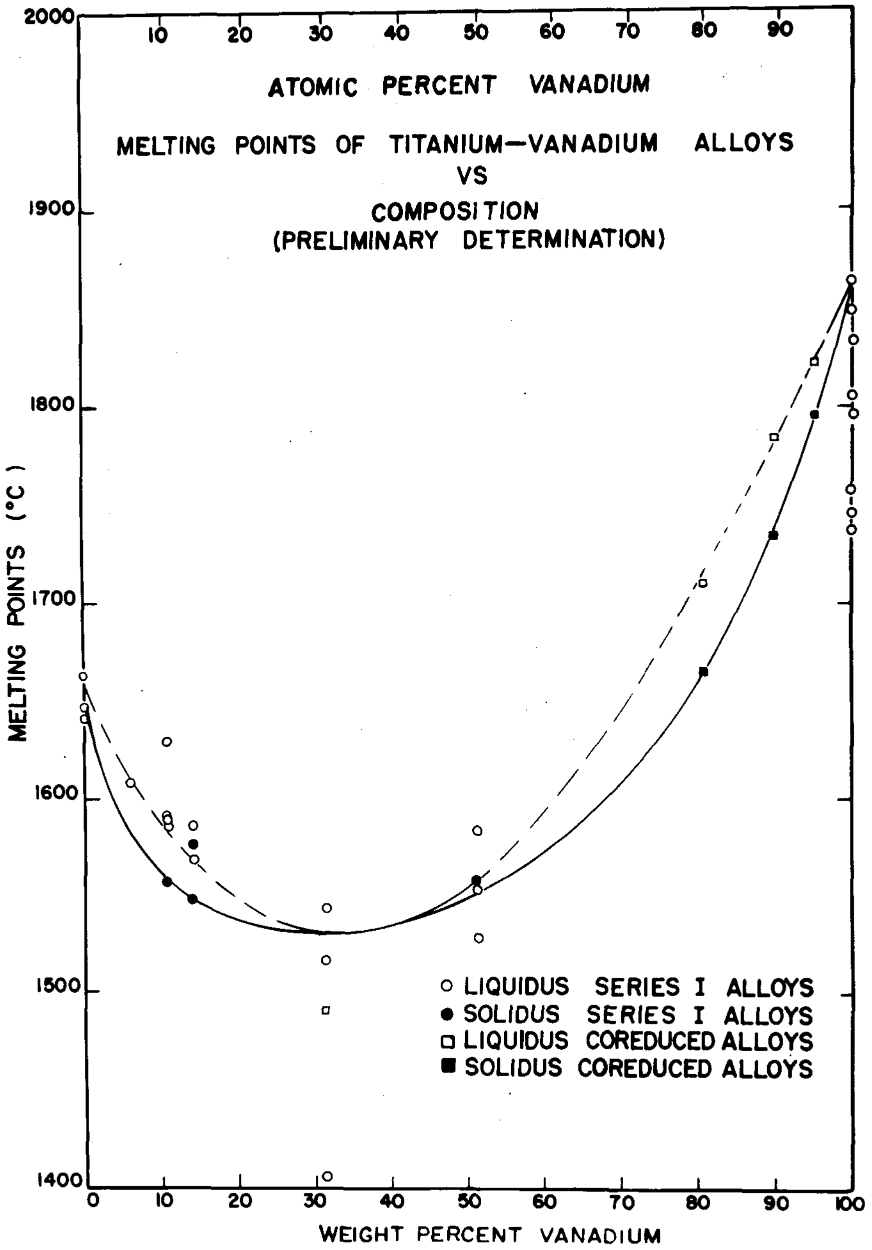


Figure 7. Melting Points of the Titanium-Vanadium System. Series I Alloys.

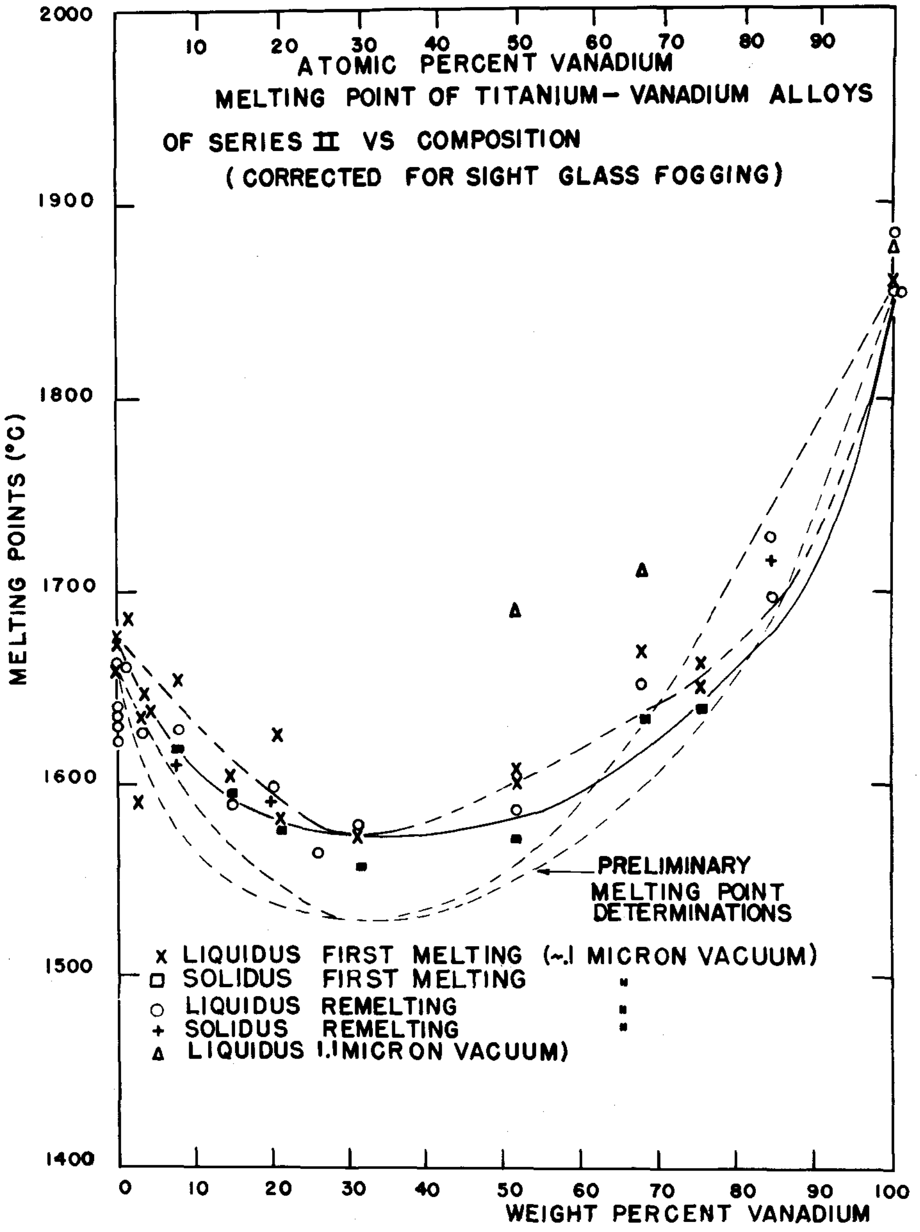


Figure 8. Final Melting Points of Titanium-Vanadium System.

Table 4

Melting Data on Series II Titanium-Vanadium Alloys

Composition (weight per cent)	Pressure (microns)	Sight glass transmission per cent	Pyrometer corrected temp. (^{o}C)	Temperature after sight glass corr.
duPont, Ti	.04	88.6	1635	1658
	.06 -.04	89.4	1602	1622 (R)
	.04 -.07	89.6	1620	1640
	.06	92.6	1658	1673
Crystal Bar Ti	.03 -.08	89.6	1655	1677
	.03 -.04	88.5	1639	1663 (R1)
	.055-.2	87.0	1610	1636 (R2)
	.095	88.8	1609	1631 (R3)
1.20 % V	.18 -.12	88.4	1660	1685
	.05	88.6	1638	1661 (R)
2.475 % V	.1 -.09	89.9	1572	1590
3.14 % V	.08 -.09	89.5	1610	1630
	.04 -.05	90.5	1608	1626 (R)
		87.9	1609	1633
	.25 -.2	90.0	1625	1645
4.22 % V	.05 -.04	89.8	1618	1638
7.55 % V		90.4	1632	1651
			(S)1599	(S)1617
	.18	90.0	1609	1628 (R)
			(S)1591	(S)1609
14.77 % V	.13 -.2	87.9	1583	1605
			(S)1573	(S)1595
	.1 -.075	88.8	1570	1590 (R)
20 % V	.1 -.09	89.9	1572	1590
			(S)1567	(S)1585
	.06	90.5	1580	1598 (R)
			(S)1572	(S)1590

Table 4 (Cont'd)

Composition (weight per cent)	Pressure (microns)	Sight glass transmission per cent	Pyrometer corrected temp.(°C)	Temperature after sight glass corr.
21.0 % V	.1 -.12	87.5	1558	1580
			(S)1554	(S)1576
	.13 -.12	89.9	1561	1579 (R)
	.06	89.7	1604	1624
			(S)1564	(S)1582
26.1 % V	.095	88.0	1547	1567
			(S)1545	(S)1565
	.085	86.6	1555	1579 (R)
31.27 % V	.1 -.09	90.5	1559	1575
			(S)1542	(S)1558
	.06 -.07	91.2	1564	1579 (R)
51.67 % V	.085	90.8	1588	1605
	.06	88.6	1580	1601
			(S)1560	(S)1570
	1.1	93.3	1672	1687 (R)
69.5 % V	.09 -.07	87.1	1642	1669
			(S)1612	(S)1633
	.07	85.4	1621	1651 (R)
	1.1	92.6	1694	1710 (R)
75.48 % V	.09	85.4	1621	1651
	.08	88.0	1637	1662 (R)
			(S)1615	(S)1639
84.50 % V	.07 -.06	87.8	1665	1692
	.07 -.06	83.7	1661	1697 (R1)
			(S)1657	(S)1693
	.06	85.5	1694	1728 (R2)
			(S)1682	(S)1715

Table 4 (Cont'd)

Composition (weight per cent)	Pressure (microns)	Sight glass transmission per cent	Pyrometer corrected temp.(°C)	Temperature after sight glass corr.
V (I_2 boosted)	.13 -.12	89.6	1830	1859
	.03 -.08	84.4	1811	1854 (R)
	.1 -.08	72.9	1773	1854 (R)
	.13 -.09	87.1	1851	1884 (R)
	1.1	92.9	1859	1877 (R)

(R) Repeated melting determinations.

(S) Observed solidus temperature.

The higher melting point determined here for vanadium reverses the order of titanium and vanadium found in the earlier literature. This new melting point of vanadium appears reasonable when viewed from a semi-theoretical standpoint (26). The interatomic distances are seen to decrease from 2.93 Å to 2.64 Å in passing from titanium to vanadium. At the same time, the number of cohesion electrons per atom increases from 4 to 5. Thus the electron charge density is greater about the vanadium atom than the titanium atom and the resulting increased binding energy is consequently reflected in the higher observed melting point for the vanadium.

In drawing the solidus and approximate liquidus curves of this system, the tendency for the melting temperatures to be raised by remelting at 0.1 micron in the high vanadium alloys, and lowered for the low-vanadium alloys, was kept in mind. After drawing the solidus curve through representative experimental points that had been determined on alloys least contaminated by oxygen, the liquidus curve was dotted in slightly above the average experimental values obtained for the temperature of hole closure. Results are shown in Figures 7 and 8.

The minimum in the liquidus curve is in agreement with predictions based on considerations of atom size differences and other factors (27). When the atom sizes differ by 8 per cent or more but are still within the favorable 15 per cent for solid solution, there is usually, other conditions being favorable for a continuous series of solid solutions, a minimum occurring in the liquidus curve. In the case of the titanium-vanadium system, the atomic size difference as calculated from the tabulated distance of closest atomic approach (28) is about 10 per cent and therefore would come within the province of the above statement.

B. Thermal Analysis

Cooling curves were run at several compositions in an attempt to establish the boundaries of the alpha plus beta field in the titanium-vanadium system.

Due to some difficulty encountered in drilling the metal specimens used in these experiments, they were each cut into two pieces by means of a carborundum wheel. Opposing faces were then grooved to accommodate a chromel-alumel thermocouple junction. The two pieces were wired together so that the thermocouple junction lay directly in the center of the specimen. This assembly was then heated in a 1.25 inch diameter quartz tube under a vacuum of 0.002 to .02 microns. Each specimen was held at approximately 950° C for two hours, then the furnace was shut off and the cooling curves were recorded on a Brown recorder. The results obtained on several Series 1 alloys are shown in Table 5.

The thermal arrest values given were derived from the first detectable change in slope of the cooling curves. Cooling rates before the arrest varied from 25° per minute for titanium to 10° per minute for the 14.1 per cent vanadium alloy. It is evident from these data that the

Table 5

Thermal Analyses of Titanium-Vanadium Alloys

Composition (weight per cent)	Beginning of thermal arrest on cooling from 950° C
National Lead Co. Ti	895° C
5.96 % V	770° C
10.7 % V	635° C
14.1 % V	558° C
33.9 % V	none observed to room temperature
51.4 % V	none observed to room temperature

beta to alpha transformation is rapidly lowered with increasing vanadium content.

In order to obtain a better indication of the temperature at which transformation begins on cooling, differential thermal analyses were conducted using nickel as a reference body. The cooling rates in these experiments varied from approximately 20° per minute for pure titanium to 4° per minute for the 10.7 per cent vanadium alloy. The results are given in Table 6.

Attempts to obtain reliable thermal arrests on heating with the apparatus used were unsuccessful. The differential cooling curves were felt to be of somewhat greater reliability than the regular cooling curves. The beginning of the halt at 887° for duPont titanium corresponded fairly well with values for high purity metal of from 882.5 to

Table 6

Differential Thermal Analyses of the Titanium-Vanadium Alloys

Composition (weight per cent)	Beginning of thermal arrest on cooling from 950° C	
duPont titanium	887°	
5.96 % V	800° 804° 815°	(806° Avg.)
10.7	719° 744°	(732° Avg.)

885° C (29) (30). A higher value than for pure metal might be expected, owing to the possible presence of oxygen which is known to raise the transition point. The beginning of the transition as determined by the cooling methods is no doubt below the theoretical line because of possible hysterisis. These results give only an indication that a transition is occurring and do not locate it with any precision. Metallographic data was considered more reliable in determining the boundary lines for the alpha plus beta field shown in the figure.

C. Microstructures of the Titanium-Vanadium Alloys

1. Preparation of metallographic specimens

Metallographic examination of alloys having various heat treatments and compositions covering the titanium-vanadium system was carried out in order to obtain evidence on the phase diagram. This information was supplemented by x-ray data in fixing the phase boundaries. In the preparation of metallographic specimens, standard polishing methods were employed to prepare the samples for etching. The etchant recommended for high titanium alloys is composed of one part of concentrated nitric acid, one part of hydrofluoric acid (48 per cent) and three parts of glycerol (31). This was found to etch the high titanium alloys satisfactorily but had to be modified by additions of increasing amounts of concentrated nitric acid in the higher vanadium compositions. The etching reagent was applied by vigorous swabbing with cotton tipped applicators for times up to 40 seconds.

A Bausch and Lomb Research Metallograph was used to examine and photograph the specimens. Both ordinary and polarized light were employed in order to determine what phases were present. The hexagonal alpha titanium phase can be distinguished from the cubic beta phase by noting the presence or absence of extinctions in polarized light as the metallographic stage is rotated (32). The alpha phase shows intermittent extinction on rotation of the stage, while the beta phase does not.

2. Arc melted alloys

The titanium-vanadium alloys were first examined in the arc melted state. Because of the rapid cooling rate on the copper hearth of the arc melting furnace, the arc melted metals and alloys were in essentially a quenched condition. When sponge titanium and bomb reduced vanadium are arc melted alone, they exhibit the microstructures shown in Figures 9 and 10. Hardness determinations on the titanium and the vanadium indicated that these metals probably contained less than 0.07 and 0.04 per cent oxygen, respectively, in the arc melted condition. It was consequently assumed that the alloys formed from these component metals by arc melting contained less than 0.07 per cent oxygen when prepared. The structures of a few alloys in the as-arc-melted condition are shown in Figures 11 through 15. Both of the metals, as well as the alloys show some finely dispersed phase (as an example see Figure 14), which may be due either to small amounts of impurites or to segregation on a small scale.

Figure 9. Titanium (Series II) as-arc-melted from duPont sponge. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol (by volume). X 250

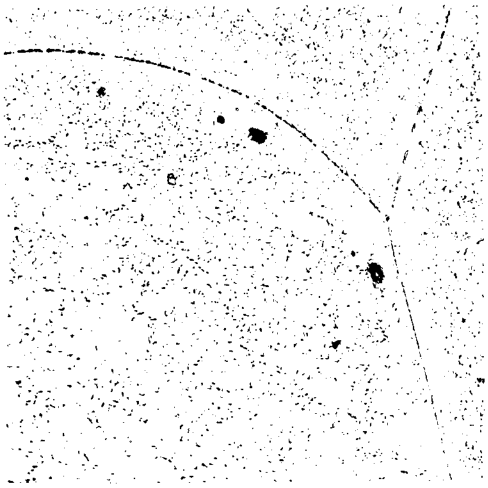


Figure 10. Vanadium (Series II) as-arc-melted from bomb reduced metal using iodine booster. Etchant 2 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

Figure 11. 1.2% vanadium (Series II) as-arc-melted alloy. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

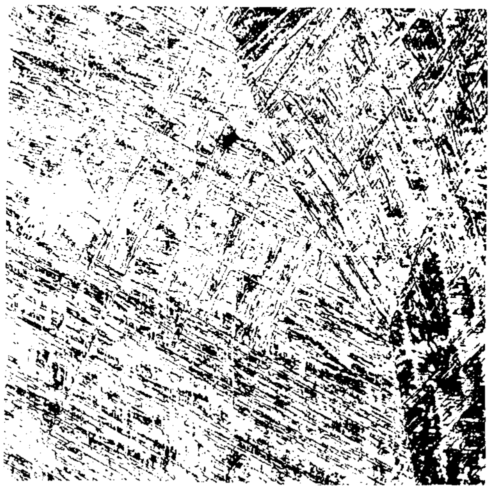


Figure 12. 5.3% vanadium (Series II) as-arc-melted showing martensitic type of transformation from beta to alpha plus beta field. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

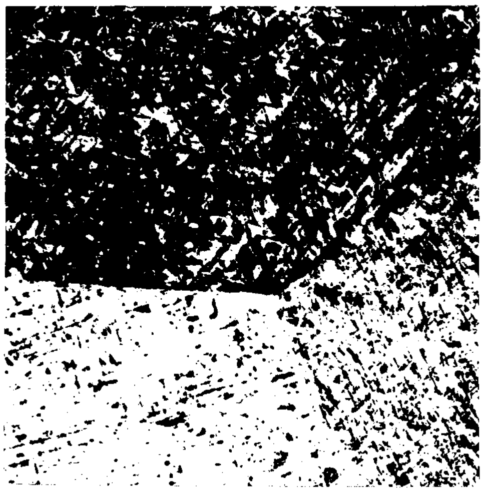


Figure 13. 7.6% vanadium (Series II) as-arc-melted showing partial transformation of beta phase on quenching. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol (by volume). X 250

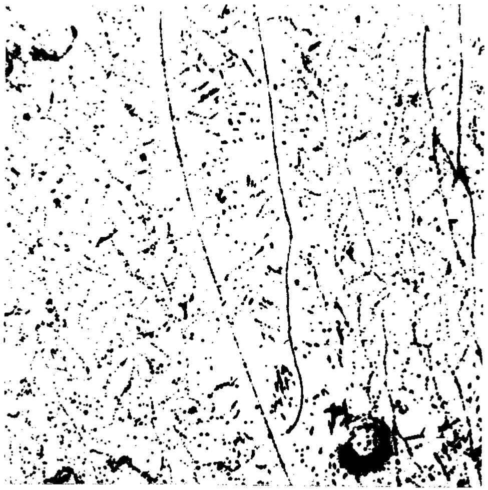


Figure 14. 26.1% vanadium (Series II) as-arc-melted showing retained beta phase widely dispersed second phase probably impurity. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

Figure 15. 69.5% vanadium (Series II) as-arc-melted showing retained beta phase second phase of impurity or slight inhomogeniety. Etchant 2 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

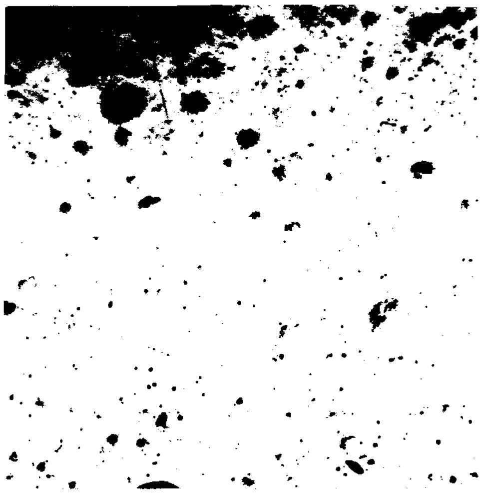


Figure 16. 26.1% vanadium (Series II) as-arc-melted showing finely dispersed second phase presumably impurity in retained beta. Unetched. X 250

The microstructure of the 1.2 per cent vanadium alloy, Figure 11, is not particularly revealing, possibly due to the irregular quenching effect and the possible presence of an impurity phase, but is typical of the as-arc-melted microstructures of high titanium alloys that exhibit high temperature solid solubility. A 5.3 per cent vanadium alloy, Figure 12, shows a martensitic structure typical of alloys that have been rapidly quenched from the single phase beta region to the alpha plus beta region. Alpha phase has apparently formed along preferred orientations within the beta grains, perhaps along the dodecahedral planes of the beta phase, by a diffusionless mechanism. The beta solid solution appears to have transformed only slightly in the 7.6 per cent vanadium alloy of Figure 13. Arc melted alloys containing more than this amount of vanadium appeared from metallographic examination to have retained the beta solid solution. This is shown for the 26.1 per cent vanadium alloy in Figure 14, and the 69.5 per cent vanadium alloy in Figure 15. It is evident from these photomicrographs and other considerations that the body-centered cubic form of titanium and the body-centered cubic vanadium are completely miscible in all proportions at high temperatures.

3. Heat treatment of the alloys

Because of the possibility of segregation or inhomogeniety, and irregular quenching effects in the arc melted alloys, both Series I and Series II alloys were given controlled annealing and quenching treatments in further studying the phase relationships. A number of Series I alloys were annealed at 910° C for 60 hours and then water quenched. Other alloys of this series were heated for 30 hours and then annealed at some lower temperature for an additional period of from 30 to 96 hours, depending on the temperature, before water quenching. Annealing was carried out in a vacuum of considerably less than 0.01 micron in most cases. A pure titanium specimen was given identical treatment with each alloy and used as a control to give some indication of the possible contamination of alloys by oxygen or nitrogen during the long time anneals. The titanium controls showed negligible increases in hardness which indicated that no appreciable exposures to oxygen or nitrogen occurred during the heat treatments of this Series I group of alloys.

Series II alloys were given a more rigorous homogenization treatment. For this purpose, the melting point furnace (Figure 6) was converted to an upright resistance furnace having a molybdenum tube 2.15 inches in diameter, and 7 inches long, with 5 inches of its length serving as the element between copper leads. Properly insulated by means of ceramic and molybdenum shields, this furnace was capable of reaching and maintaining quite high temperatures.

The high titanium compositions of Series II as-arc-melted alloys were first hot rolled at about 800° C to approximately 20 per cent reduction in area. After grinding off the oxide coating, they were stacked in the molybdenum tube furnace and heated for 16 hours at 1200° C under a 0.1 to 0.06 micron vacuum. The hardness increase of a pure titanium control sample indicated a change in oxygen content of from 0.07 to 0.25 per cent by weight during this homogenization. After grinding off the dull surface layer resulting from this high temperature homogenization, these Series II alloys were given a further short time homogenization at a lower temperature in a small quartz tube vacuum annealing furnace. The treatments consisted of annealing for from 4 to 14 hours at 910° C followed by subsequent annealing ranging from 48 hours at 850° C to 600 hours at 500° C, under a vacuum of considerably less than 0.01 micron, before water quenching.

The alloys of both series with the various heat treatments described above were examined under the microscope.

These operations were carried out with the ultimate aim of determining the effect of vanadium additions on the alpha-beta transition in titanium. Since the microstructure of the metals and alloys show possible extraneous phases, this factor must be considered in connection with the interpretation of the microstructures of the titanium-vanadium alloys. The first of these unexplained structures appeared in the unetched microstructures of both the metals and alloys, the second was developed by etching the higher vanadium alloys. In general, the x-ray powder diffraction patterns of all the alloys showed either the body-centered cubic structure of the beta phase, the hexagonal structure of the alpha phase, or a mixture of both, depending on the area of the phase diagram under consideration. No lines that could be ascribed to an impurity phase were found.

The microstructures of the unetched beta phase alloys show a widely dispersed phase which is assumed to be due to inclusions of impurities. The appearance of typical unetched fields is shown in Figures 16 and 17 for 26.1 and 75.5 per cent vanadium alloys. This phase stands out in polarized illumination as points of light. If this structure is due to impurities, the amount as indicated from spectrochemical analysis of the metal and selected alloys is comparatively small. No appreciable amounts of either copper or tungsten are introduced during the arc melting process. Several typical analyses are shown in Table 7.

Perhaps the main source of impurities in the virgin metal are due to impurities in the starting materials, reaction with the processing equipment, slag residue, and air leaks during processing. In the case of the commercial sponge titanium, oxides and nitrides may have been left in the sponge following the slag removal operation. In the case of the vanadium, slag could have been entrapped in the metal during the reduction and small amounts of it could have been dispersed in the metal during arc melting. The residual slag might well be in the nature of an oxide. In any case, what impurity phase is present after arc melting

Table 7

Spectrochemical Analysis of Arc Melted Titanium, Vanadium, and an Alloy

	Al	As	Ca	Cr	Cu	Fe	Mg	Mn	Si	Sn	Ti	W
Vanadium	M-W	FT	VW	T	T	M-W	VW	VW	W	T	W	W
Titanium (duPont)	T	T	T	VW	VW	W	T	VW	W	VW	S	-
14.8 % V	T	T	T	VW	VW	W	T	VW	VW	VW	S	-

S - strong W - weak T - trace
M - moderate VW - very weak FT - faint trace

is indicated to be semi-transparent from its behavior under polarized light. Under this illumination, the specks of this phase stand out brightly and in this respect correspond to the behavior of aniostropic oxides. Because of the known solubility of oxygen and nitrogen in titanium and the known solubility of oxygen in vanadium, it is unlikely that, at the oxygen levels of the arc melted metals indicated earlier that this phase is due to simple vanadium or titanium oxides or nitrides. The small amount of additional phase that is seen to be widely dispersed in the unetched metals and alloys is possibly a solid non-metallic inclusion of titanate or vanadate.

The second type of extraneous structure is brought out by etching the supposedly single phase high vanadium alloys and is illustrated for the 75.5 per cent vanadium alloy in Figure 18. This may be compared with the unetched appearance of the same alloy shown earlier in Figure 17. On the possibility that the structure brought out by etching might be due to small variations in the composition, the alloys were homogenized at elevated temperatures. An as-arc-melted 69.5 per cent vanadium alloy has been shown in Figure 15. After cold rolling this alloy, it was heated for one hour at 1450° C in a 0.06 micron vacuum and rapidly cooled. The results of this treatment shown in Figure 19,

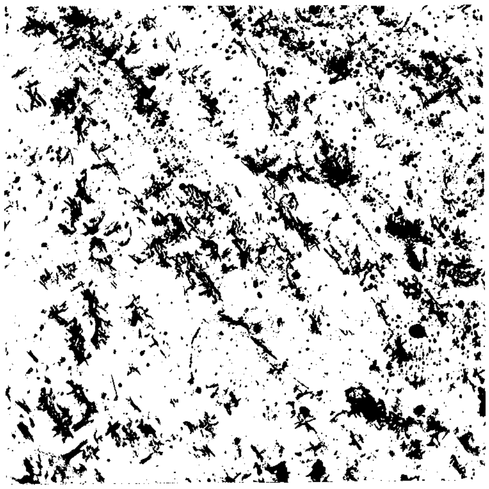


Figure 17. 75.5% vanadium as-arc-melted, showing widely dispersed second phase, presumably of impurity. Unetched. X 250

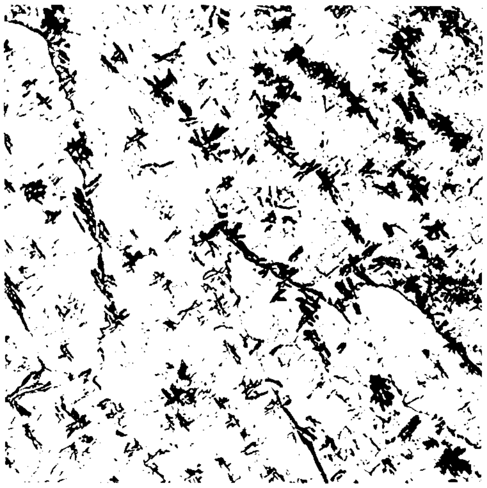


Figure 18. 75.5% vanadium as-arc-melted showing beta phase with additional structure brought out by etching that may be due to concentraction gradient. Etchant 2 HNO_3 (conc), 1 HF (48%), 3 glycerol (by volume). X 250

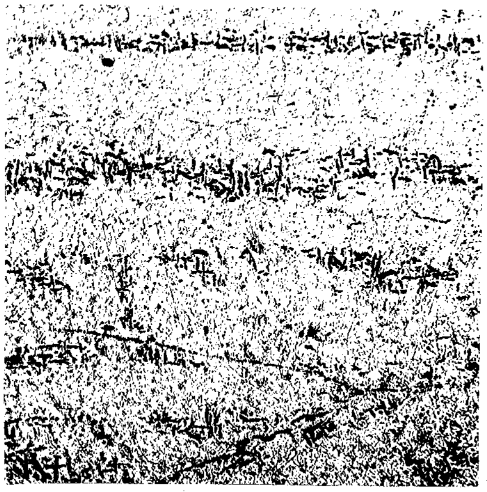


Figure 19. 69.5% vanadium cold rolled 30% heated 1 hour at 1450° C under 0.06 micron vacuum. No appreciable change in amount of structure. Etchant 2 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

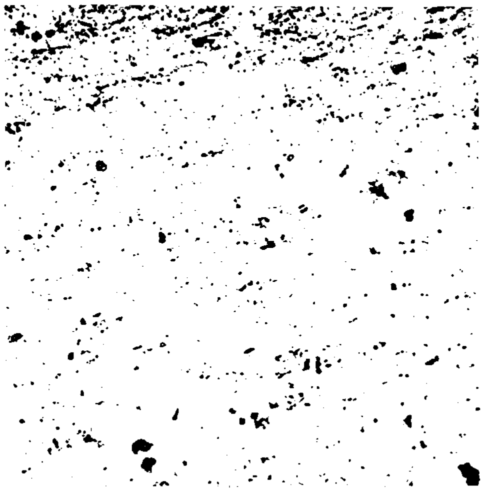


Figure 20. 75.5% vanadium after 10% reduction in area, heated 16.7 hours at 1550° C showing the finely dispersed impurity phase. Unetched. X 250

indicate that no appreciable change in the etching characteristics had occurred as a result of the high temperature homogenization.

A still higher homogenization of the 75.5 per cent vanadium alloy of Figure 18 was carried out. This alloy shows an exceptionally large amount of this structure. After a 10 per cent reduction in area, this alloy was heated between 1530° and 1585° C for 16 hours and 40 minutes in a vacuum. The unetched appearance of the alloy after the homogenization treatment is shown in Figure 20. Etching of this specimen (Figure 21) revealed much the same appearance as before the treatment. This structure in the case of the 75.5 per cent vanadium alloy is apparently not alpha phase as seen from its appearance under polarized light.

The effect of a homogenization treatment of 16 hours at 1200° C is shown in Figure 22 for an alloy of somewhat lower vanadium content, i.e., 26.1 per cent vanadium. The widely dispersed phase shown for the same composition alloy in the as-arc-melted state (Figure 14) appears to have agglomerated slightly.

The emergence of the unknown structure under the influence of etchants indicates that it may possibly be due to a concentration gradient of titanium or some minor

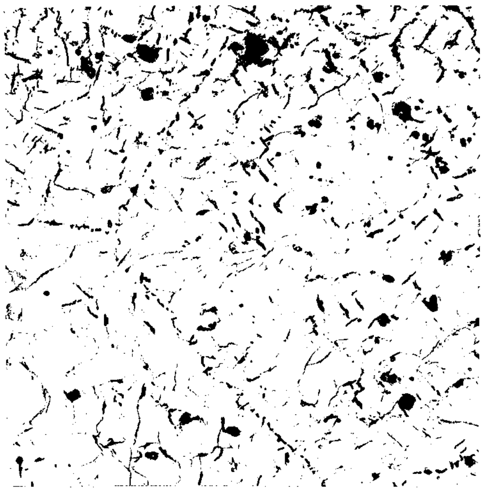


Figure 21. 75.5% vanadium after 10% reduction in area, heated 16.7 hours at 1550° C showing beta phase and additional structure brought out by etching. Etchant 2 HNO_3 (conc), 1 HF (48%), 3 glycerol (by volume). X 250

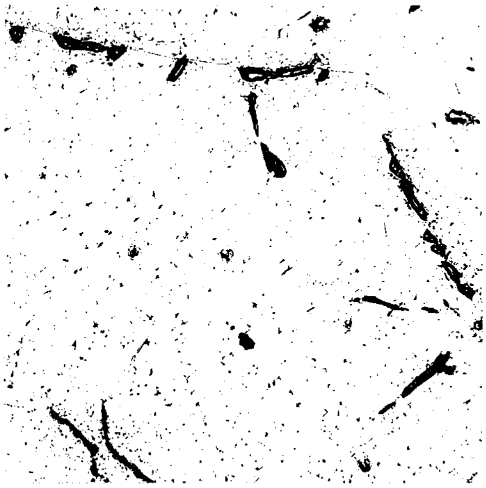


Figure 22. 26.1% vanadium (Series II) arc melted, homogenized 16 hours at 1200° C under 0.1 micron vacuum. Impurity phase somewhat agglomerated at grain boundaries and throughout the matrix. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

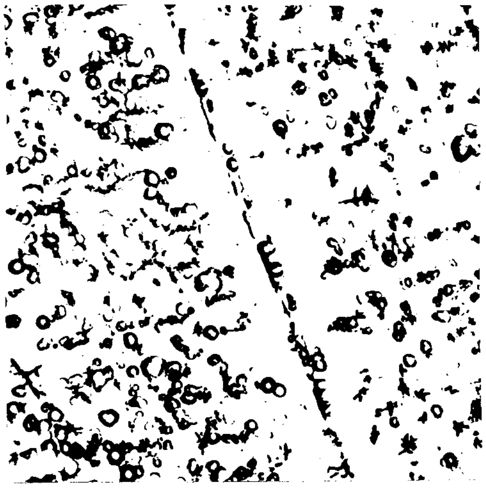


Figure 23. 51.4% vanadium as-arc-melted, showing etching pits produced in bringing out grain boundaries. Etchant 2 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 1000

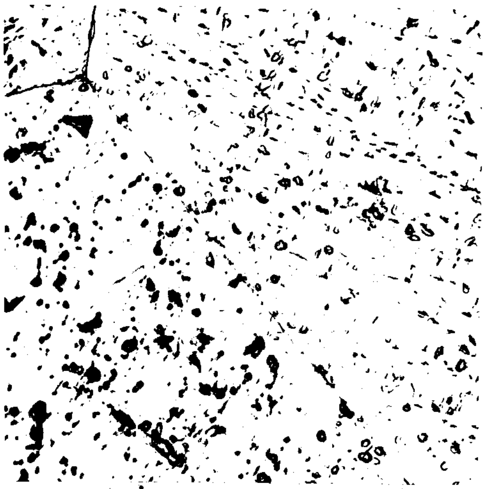


Figure 24. Vanadium (Series II) as-arc-melted from bomb reduced metal (iodine boosted). Shows etching pits produced in bringing out grain boundaries. Etchant 2 HNO_3 (conc), 1 HF (48%) 3 glycerol. X 1000

impurity in the vanadium alloy. The phase, etching at a different rate from the surrounding matrix, may be a solid solution of slightly different composition from the matrix, perhaps produced in the freezing of the rapidly stirred arc melted button. Because of the higher melting points of these alloys, the small diffusion coefficients at the homogenization temperature, and perhaps the low concentration gradients existing within the solid solution, diffusion rates of these alloys may be so slow that even the rigorous treatments given the alloys are insufficient to produce completely homogeneous alloys in the higher vanadium region.

The etching procedure necessary to bring out the grain structure of these alloys may be responsible in a large measure for the unfavorable appearance of the microstructures. The etching procedure as described earlier, may be sufficiently drastic on the solid solution grains to enhance a very small concentration gradient to give an over etched effect. In the case of an over etched 51.4 vanadium alloy, (Figure 23), severe cavitation of the alloy in the vicinity of the impurity or concentration gradient is apparent. In this connection, vanadium has a cleaner appearing microstructure under a high than a lower magnification as may be seen from a comparison of Figures 24 and 10. Some of the contaminated appearance may this be laid to over etching.

The results of the metallographic studies of the heat treated alloys in the transition region of the titanium-rich compositions are shown in Figure 25. From an examination of the microstructures of the arc melted alloys, it was seen earlier that titanium and vanadium were completely soluble in each other at high temperatures. Thus, arc melted alloys up to 7.6 per cent vanadium showed the martensitic structure often typical of unstable alloys that have been quenched from a single phase region. Beyond this composition to pure vanadium, the microstructures of the arc melted alloys indicated completely retained beta solid solution.

In the titanium-rich alloys below the beta transition temperature, two phases co-exist under equilibrium conditions. Figure 26 shows a 5.3 per cent vanadium alloy as quenched from an annealing temperature of 850° C. This microstructure exhibits a large amount of alpha phase in rod form, with partly transformed beta phase as the matrix. Studies on the determination of the boundaries of this two phase field are presented in the following sections.

The points plotted on the diagram of Figure 25 were derived from the microstructures of quenched alloys of Series II that had received a previous high temperature homogenization. The points indicate evidence of one and

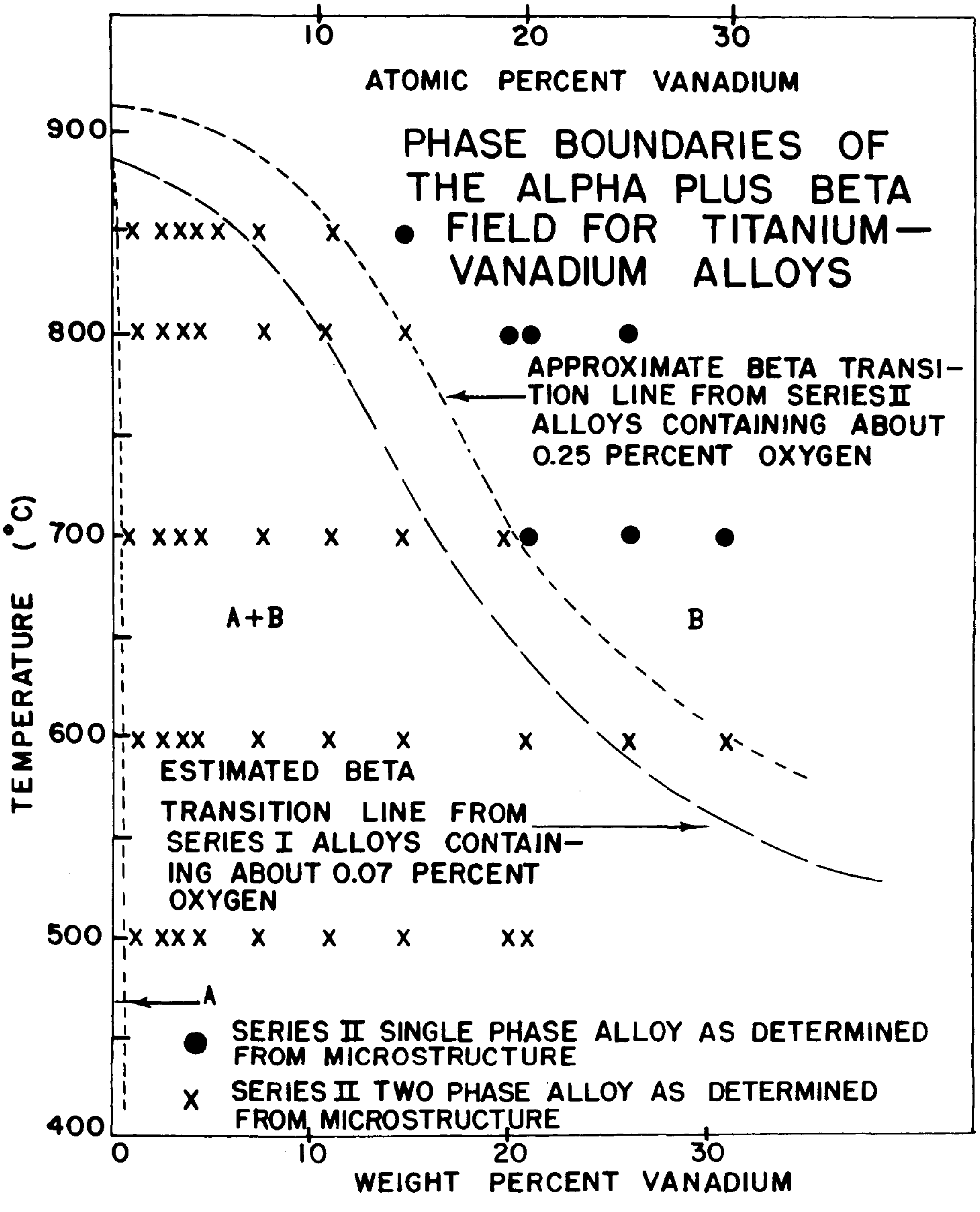


Figure 25. Phase Boundaries.

two phase alloys at the quenching temperature. During the homogenization treatment, the oxygen content increased in these alloys to an estimated 0.25 per cent by weight. Consequently the boundaries of the alpha plus beta field derived from the use of these data can be somewhat displaced from that of the ideal titanium-vanadium binary system. Microstructures of these heat treated alloys used to determine the approximate location of the beta transition are shown in Figure 27 to Figure 36. There is a definite lowering of the transition temperature with increasing amounts of vanadium. The 10.9 per cent vanadium alloy of Series II, quenched from 850° C is shown in Figure 27. This microstructure presents evidence of areas of alpha phase in equilibrium with beta at the quenching temperature. Examination of the microstructure under polarized light confirmed the existence of this phase with the partly transformed beta matrix. Evidently at this composition, the beta transformation boundary lies only slightly above 850° C for this Series II alloy. The 14.8 per cent vanadium alloy exhibits a microstructure characteristic of single phase beta when quenched from 850° C (Figure 28). Examination with polarized light showed that the dark inclusions in this microstructure stand out brightly and are probably due to impurities. When this 14.8 per cent vanadium alloy

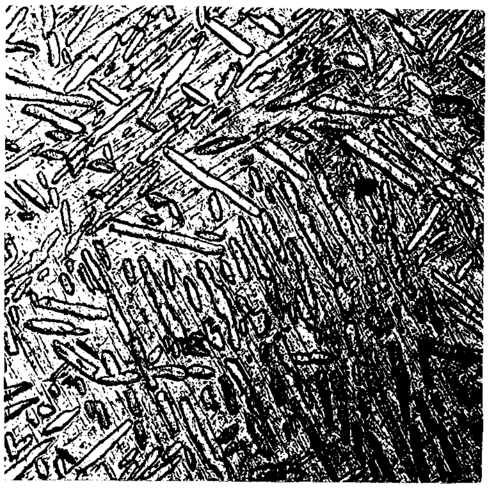


Figure 26. 5.3% vanadium (Series II) arc melted, homogenized 16 hours at 1200° C, then heated 12 hours at 900° C, 48 hours at 850° C and water quenched. Alpha rods in partly transformed beta matrix. Usual 1:1:3 etchant. X 250

Figure 27. 10.9% vanadium (Series II) arc melted, homogenized 16 hours at 1200° C, heated 12 hours at 900° C, 48 hours at 850° C and water quenched. Traces of alpha in partly transformed beta background. Usual 1:1:3 etchant. X 250

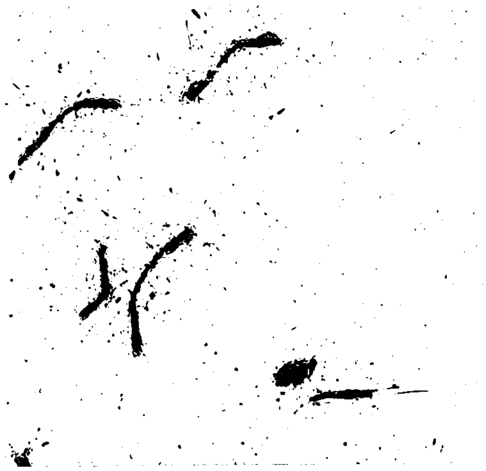


Figure 28. 14.8% vanadium (Series II) arc melted and homogenized 16 hours at 1200° C, heated 12 hours at 900° C, 48 hours at 850° C, and water quenched. Single phase beta apparently some impurity. Usual 1:1:3 etchant. X 250

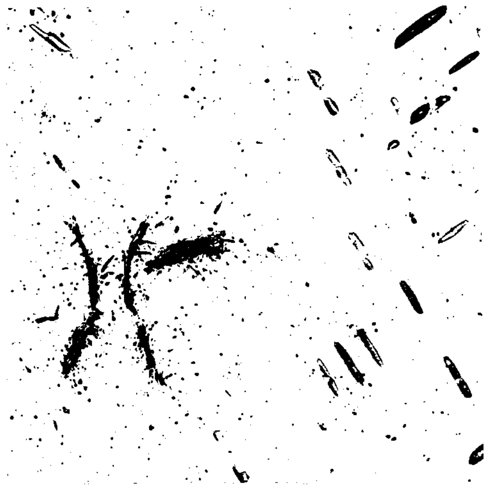


Figure 29. 14.8% vanadium (Series II) arc melted and homogenized 16 hours at 1200° C, heated 6 hours at 900° C, 60 hours at 800° C, and water quenched. Traces of primary alpha in beta matrix, also some impurity phase. Usual 1:1:3 etchant. X 250

is quenched from 800° C (Figure 29), traces of primary alpha phase are evident in what appears to be a retained beta matrix. Thus the phase boundary for the 14.8 per cent vanadium alloy is slightly above 800° C.

The microstructure of the alloy with the nominal composition of 20 per cent vanadium that was quenched from 800° C is apparently single phase (Figure 30). The alloy of the same composition that was quenched from 700° C shows some evidence of primary alpha in what appears to be retained beta phase in Figure 31. Thus the boundary line passes between 700° and 800° C at about 20 per cent vanadium.

The appearance of the 21 per cent vanadium alloy quenched from 700° C is that of a single phase alloy (Figure 32), while that of the same composition quenched from 600° C is two phase (Figure 33). The results of the 600° C quench are of doubtful accuracy however, since equilibrium may not have been attained after 57 hours at this temperature. The second phase of this 21 per cent vanadium alloy appears to be alpha in a retained beta matrix. This was inferred not only from the ordinary microstructures but from its appearance under polarized light and from the x-ray pattern which showed evidence of the presence of some alpha phase. The structure of the 21 per cent vanadium alloy quenched from 600° C shows the arrangement of phases characteristic of

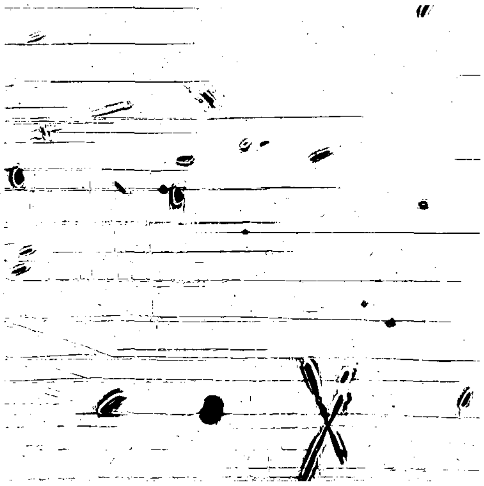


Figure 30. 20% vanadium (Series II) arc melted and homogenized 16 hours at 1200° C heated 6 hours at 900° C, 60 hours at 800° C, and water quenched. Single phase beta tending to transform a small amount impurity. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol (by volume). X 250

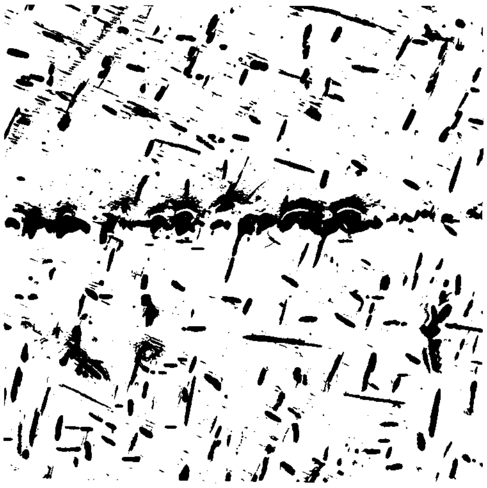


Figure 31. 20% vanadium (Series II) arc melted and homogenized at 1200° C 16 hours, heated at 900° C for 14 hours, 80 hours at 700° C and water quenched. Primary alpha in partly retained beta. Some impurity phase. Etchant 1 HNO_3 (conc), 1 HF (48%) 3 glycerol. X 250

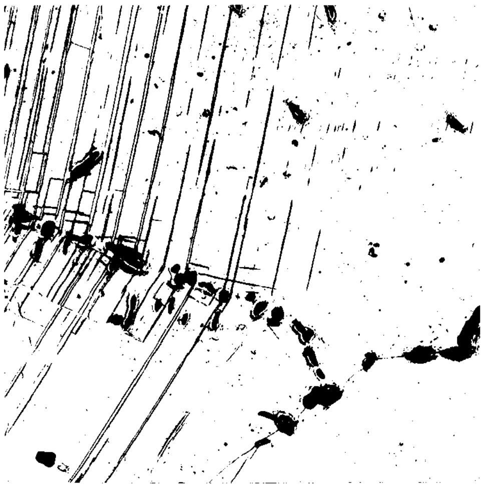


Figure 32. 21% vanadium (Series II) arc melted and homogenized 16 hours at 1200° C, heated at 900° C for 14 hours, 30 hours at 700° C and water quenched. Single phase partly retained beta with some impurity phase. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

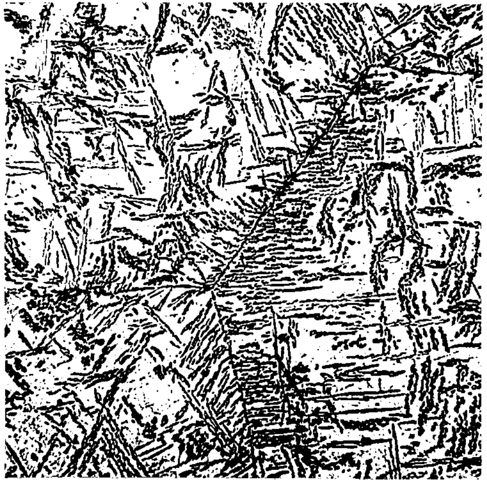


Figure 33. 21% vanadium (Series II) arc melted, homogenized 16 hours at 1200° C, heated 6 hours at 900° C, 67 hours at 600° C before water quenching. Alpha crystals in partly retained beta matrix. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

first precipitation of a second phase as the temperature is lowered. This alpha must have been formed by a nucleation and grain growth mechanism at 600° C. In such cases, grain growth is often initiated at the grain boundaries and at impurities in the metal as appears to be the case for this alloy.

The time-temperature-transformation curves for the titanium-vanadium alloys are probably similar to those of the analagous titanium-molybdenum system which have recently been investigated (33a). The martensitic transformation for the titanium-vanadium alloys is indicated from the microstructure to be suppressed when 26.1 per cent vanadium has been alloyed with titanium in these alloys, which contain about 0.25 per cent of oxygen. Furthermore, when the 26.1 per cent vanadium alloy is heated into the beta region and then quenched at a rapid enough rate to slip past the knee of the assumed TTT curve, the beta phase appears to be completely retained (Figure 14). This behavior seems to hold for arc melted alloys containing more than 26.1 per cent vanadium. When, on the other hand, the alloy which is completely in the beta condition is cooled from an elevated temperature to a given quenching temperature and held there for any length of time, the beta phase, after a characteristic nucleation period for the particular alloy, should begin to transform, eventually giving alpha and beta phases at the respective equilibrium concentrations. This transformation may or may not occur completely, depending on the length of time at the annealing temperature and the shape of the TTT curve for the particular alloy under consideration. As a general rule, if the beta phase of the alloy is increasingly stabilized by additions of a soluble alloying element having the same crystal structure, the tendency of the alpha phase to form usually becomes increasingly difficult. Thus, for the titanium-vanadium system, the addition of body-centered cubic vanadium to titanium tends to stabilize the body-centered cubic beta phase relative to the hexagonal close packed alpha phase. The formation of martensitic beta (accicular alpha) on rapid cooling is seen from metallographic examination to be inappreciable at vanadium compositions above about 21 per cent, the beta phase apparently being retained when more vanadium is alloyed with the titanium.

In spite of a 600 hour anneal, the alloys of the 500° C quench may not have reached equilibrium. The microstructures of the lower vanadium alloys that had been quenched from both 500° and 600° C were comparable, the only difference being in the more rapid etching characteristics of the alloys of the 500° C quench. Because of the increased super-cooling of the 500° C over the 600° C annealing temperature, the number of stable nuclei for initiating crystal growth is increased in the first case, while the diffusion rates are lowered. A comparison of the size of the alpha phase from the 500° and 600° C quenching runs is seen from examination of the Figures 34 and 35 for the 26.1 per cent vanadium alloy. The alpha grains are seen to be much more widely dispersed in the alloy quenched from the lower temperature. From the microstructure of the 31 per cent vanadium alloy quenched from 600° C (Figure 36), only a small amount of alpha phase is present indicating that at this temperature, the phase boundary is probably close to the 31 per cent composition.

Making use of the microstructures exhibited by these specimens, the beta transition line was sketched in Figure 25 for the Series II alloys. This is shown by the right hand dotted line of the figure. The beta to alpha transition temperature for zero per cent vanadium in this series of alloys which contain about 0.25 per cent oxygen, would be somewhere above 900° C. It is seen that additions of vanadium to titanium progressively depress the transition to about 600° C at 30 per cent vanadium.

The transition from beta to alpha in highly purified titanium is approximately 885° C (29) (30). In Figure 25,

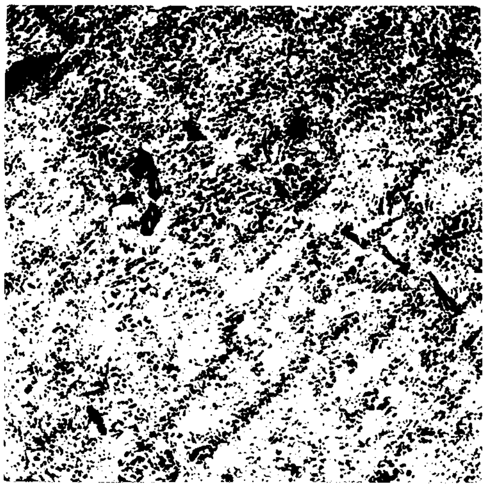


Figure 34. 26.1% vanadium (Series II) arc melted and homogenized 16 hours at 1200° C, heated 6 hours at 900° C and 600 hours at 500° C before water quenching. Apparently finely divided alpha in beta matrix. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol (by volume). X 250

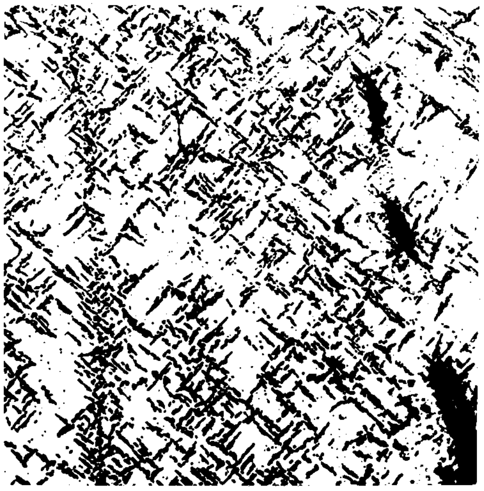


Figure 35. 26.1% vanadium (Series II) arc melted, homogenized 16 hours at 1200° C, heated 6 hours at 900° C, 67 hours at 600° C before water quenching. Alpha crystals in retained beta matrix. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

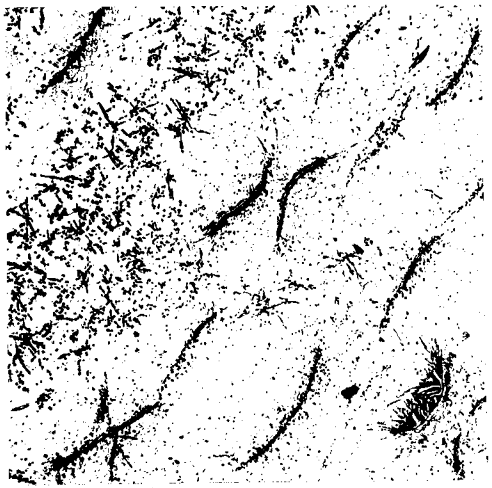


Figure 36. 31% vanadium (Series II) arc melted, homogenized 16 hours at 1200° C, heated 6 hours at 900° C, 67 hours at 600° C before water quenching. Apparently traces of alpha in beta matrix and impurities. Usual 1:1:3 etchant. X 250

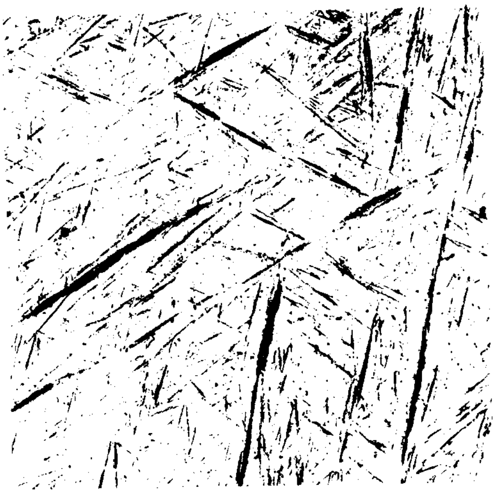


Figure 37. 10.7% vanadium (Series I) arc melted and annealed at 910° C 60 hours before water quenching shows the martensitic single phase transformed beta. Usual 1:1:3 etchant. X 250

it is to be noted that the transitions for the Series II alloys indicate that this point is about 915° C. Since the titanium, and these alloys after homogenization, contained approximately 0.25 per cent oxygen, the heavy dashed line cannot be assumed to be the correct boundary for the ideal titanium system. The 915° C transition for the 0.25 per cent oxygen in titanium was derived from the recent work by Jenkins and Worner (30).

Having obtained the general shape of this transition boundary with the alloys containing approximately 0.25 per cent oxygen, special effort was made to investigate the transition with a few alloys of much lower oxygen content. Series I alloys which contained not more than 0.07 per cent oxygen after homogenization and quenching treatments, were examined for evidence of one and two phases in a manner similar to that employed for the Series II alloys above.

Four compositions (10.7, 14.1, 33.9 and 51.4 per cent vanadium) of alloys of the low oxygen series were employed in this study. The 10.7 per cent vanadium alloy when quenched after 60 hours at 910° C gave evidence of having been in the single phase condition at that temperature by its martensitic appearance (Figure 37). When the same alloy was quenched from 800° C after 25 hours at temperature, a very small amount of primary alpha was evident (Figure 38),

Figure 38. 10.7% vanadium (Series I) arc melted and annealed 24 hours at 910° C, 24 hours at 800° C and water quenched. Traces of primary alpha and dark impurities visible in partly transformed beta matrix. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol (by volume). X 250

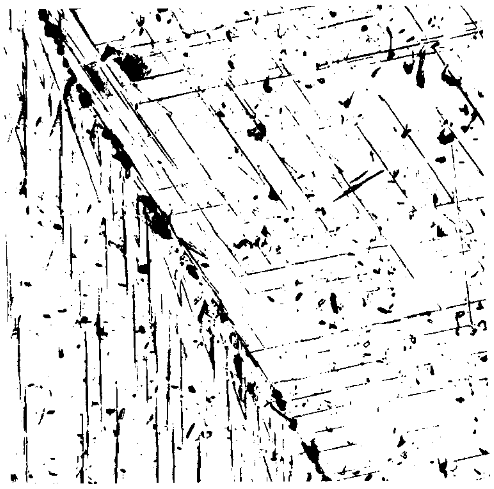


Figure 39. 14.1% vanadium (Series I) arc melted and annealed at 910° C 24 hours, 24 hours at 800° C before quenching. With exception of impurity phase, alloy essentially single phase beta, partly transformed. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

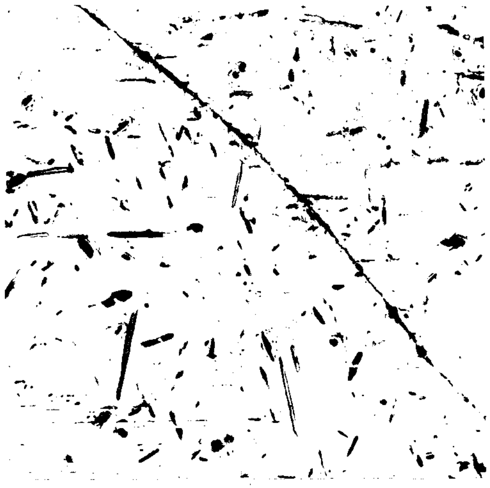


Figure 40. 14.1% vanadium (Series I) arc melted and annealed at 910° C for 36 hours at 750° C before water quenching. Primary alpha in partly retained beta background. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

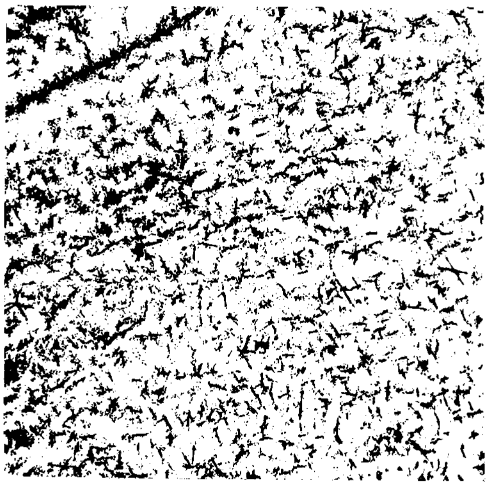


Figure 41. 33.9% vanadium (Series I) arc melted and annealed 30 hours at 910° C, 96 hours at 500° C and water quenched. Alloy shows finely divided alpha in beta matrix. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

indicating that the transition line was slightly above 800° C at this composition. The 14.1 per cent vanadium alloy of the 800° C quench is seen to be single phase in Figure 39. When quenched from 750° C, this 14.1 per cent vanadium alloy showed traces of primary alpha phase so that the phase boundary at this composition was slightly above 750° C (Figure 40. The 33.9 per cent vanadium alloy of Figures 41 and 42 that had been quenched from 500° C is seen to have a precipitate of alpha phase throughout the grain. Its unetched appearance is seen in Figure 43.

Photomicrographs of Series II alloys containing 31 per cent vanadium and quenched from 500° C are shown in Figures 44 and 45. The unetched alloy presents essentially a single phase appearance, but on etching small rods of what appear to be alpha phase develop.

Because of the rapid etching characteristics and the microscopic appearance (Figure 51) of the Series I 51.4 percent vanadium alloy, it is suspected of lying in the two phase region at 500° C.

The results of the examination of Series I alloys were summarized and then superimposed on the data for the Series

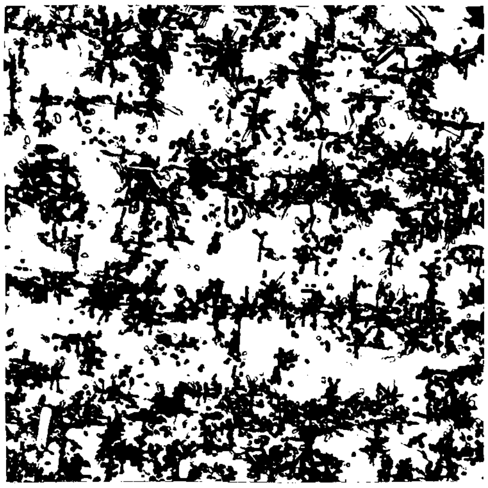


Figure 42. 33.9% vanadium (Series I) arc melted and annealed 30 hours at 910° C, 96 hours at 500° C and water quenched. Single phase beta and finely divided alpha crystals. Usual 1:1:3 etchant. X 1000

Figure 43. 33.9% vanadium (Series I) arc melted and annealed 30 hours at 910° C 96 hours at 500° C and water quenched. Beta matrix with second phase apparently alpha. Unetched. X 250

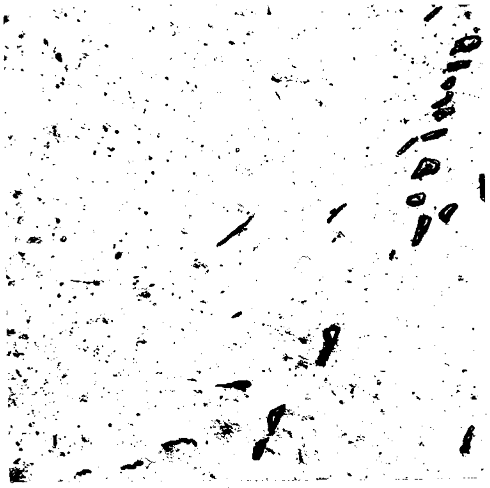


Figure 44. 31.0% vanadium (Series II) homogenized 16 hours at 1200° C, 600 hours at 500° C and water quenched. Appears single phase except for grain boundary impurities. Unetched. X 250

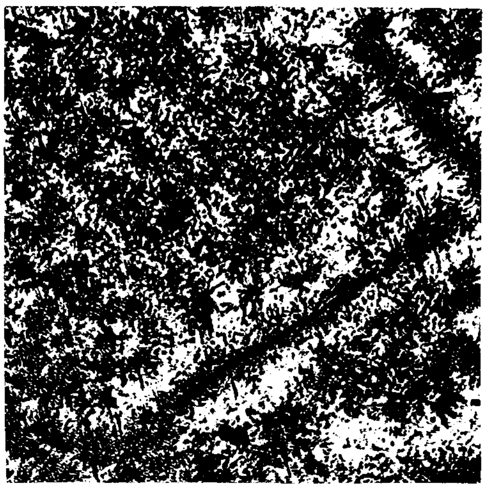


Figure 45. 31.0% vanadium (Series II) homogenized 16 hours at 1200° C annealed 600 hours at 500° C. Small alpha rods in beta matrix. Usual 1:1:3 etchant. X 250

II alloys of Figure 25. The actual points observed in locating the position of the dashed line are not indicated on this diagram. The dashed line in this figure shows the beta transition temperature of Series I alloys to lie considerably below that of Series II alloys (upper dotted line), for the lower vanadium compositions. Thus, at the 10 per cent vanadium composition, the beta transition temperature is about 50° C below that of Series II alloys. If this is assumed to be associated with the smaller oxygen content of Series I alloys, then the dashed curve represents the beta transition boundary for the titanium-vanadium binary system more closely than does the upper curve in which higher oxygen levels were employed. Thus the addition of oxygen to the higher titanium is seen to lower the solubility of titanium in vanadium at a given temperature, or to raise the transition temperature for a given vanadium composition. Since it is known that additions of oxygen to titanium raise the beta transition temperature, the similar rise in the transition temperature for the high titanium alloys with vanadium appears to be reasonable.

The effect of oxygen on the transition temperature in a titanium-vanadium alloy is clearly exemplified in Figure 46. The alloy containing 10.7 per cent vanadium and less than 0.07 per cent oxygen was annealed for several hours under a 0.1 micron vacuum at 800° C which is just above the transition temperature for this composition. The composition of the core of this alloy did not change during the annealing treatment, so consequently exhibits evidence of having been single phase (beta) when the sample was quenched. On and near the surface of the sample, however, where exposures to a slight amount of air in the furnace formed some oxide, the dissolved oxide raised the transition temperature, making this particular titanium and vanadium combination fall within the alpha plus beta area. The case of this sample, then, shows evidence of alpha plus beta phases being present at the quench, in contrast to the beta core. In this discussion, the effect of relatively small amounts of nitrogen in the samples was considered as a part of the effect assigned to oxygen, since the two elements contribute quite similar hardening effects to titanium (22) and both are soluble in solid titanium.

The question of solid solubility of vanadium in alpha titanium was approached through metallographic examination of heat treated alloys in the very low vanadium range. Series II alloys which contained approximately 0.25 per cent oxygen were employed in this study. The samples were annealed for several hours at temperatures below the beta to alpha transition for pure titanium, and then quenched.

The quenched specimens were then examined metallographically for evidence of the phase relationships existing at the quenching temperatures. The results of these examinations indicate that the solid solubility of vanadium in alpha titanium must be quite low for these samples. Samples were annealed at and quenched from 850° C, 800° C, 700° C, 600° C, and 500° C in making this investigation. The lowest per cent vanadium treated contained 1.2 per cent of that element. In all of the alloys so treated, there was evidence of beta phase with the alpha phase, indicating that, should a one phase alloy exist for this part of the system, its composition has less than 1.2 per cent vanadium. To exemplify the microstructures observed, some of the samples quenched from 700° C are shown in Figures 47 through 50. The range of compositions here are from the pure alpha titanium to 3.4 per cent vanadium. The two phase structure is quite evident in the 3.4 per cent (Figure 47) and the 2.5 per cent vanadium samples (Figure 48). The 1.2 per cent (Figure 49) vanadium sample appears to show only a little beta, but it differs definitely from the sample containing no vanadium (Figure 50).

On the basis of these observations, and some x-ray studies to be described later, the dotted line bounding the single phase alpha area on the right in Figure 25, has been sketched in at less than one per cent vanadium.

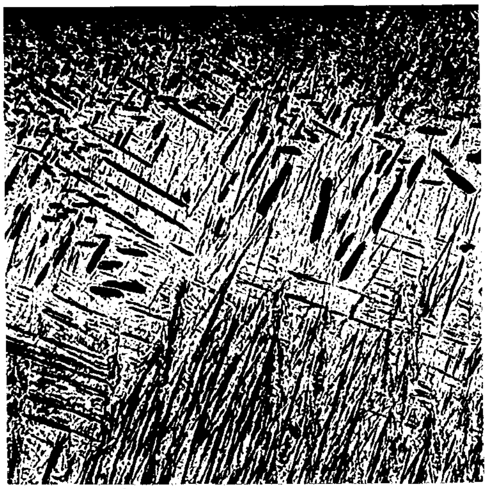


Figure 46. 10.7% vanadium (Series I) homogenized hours at 910° C, heated hours at 800° C before water quenching. Shows center martensitic structure of single phase transformed beta and at edges of specimen alpha rods that indicate two phase region. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol (by volume). X 250

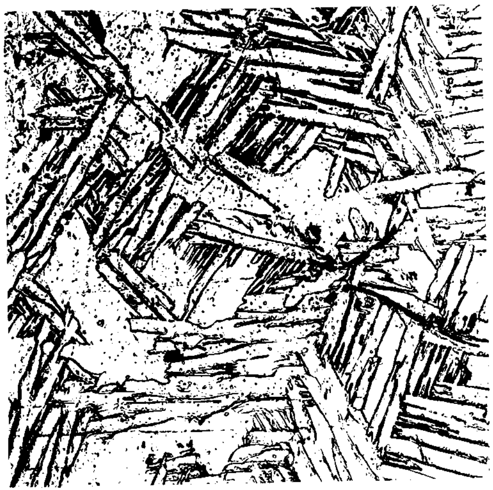


Figure 47. 3.4% vanadium (Series II) homogenized 16 hours at 1200° C, annealed 14 hours at 900° C, 80 hours at 700° C before water quenching. Alpha plus beta phase. Grains larger than in higher vanadium alloy. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

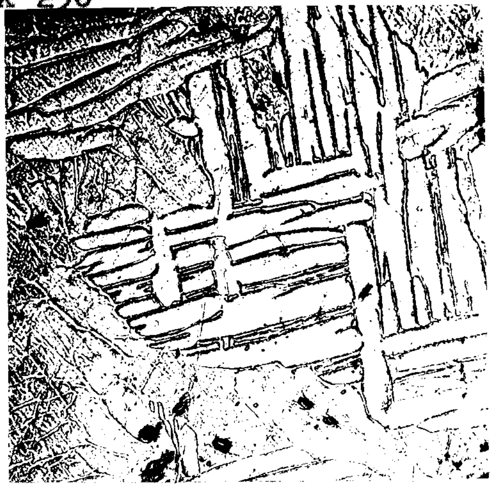


Figure 48. 2.3% vanadium (Series II) homogenized 16 hours at 1200° C, annealed 14 hours at 900° C, 80 hours at 700° C before water quenching. Alpha grains with beta phase probably located at grain boundaries. Usual 1:1:3 etchant. X250

Figure 49. 1.2% vanadium (Series II) homogenized 16 hours at 1200° C, annealed 14 hours at 900° C, 80 hours at 700° C before water quenching. Beta phase probably located at alpha grain interstices. Usual 1:1:3 etchant. X 250

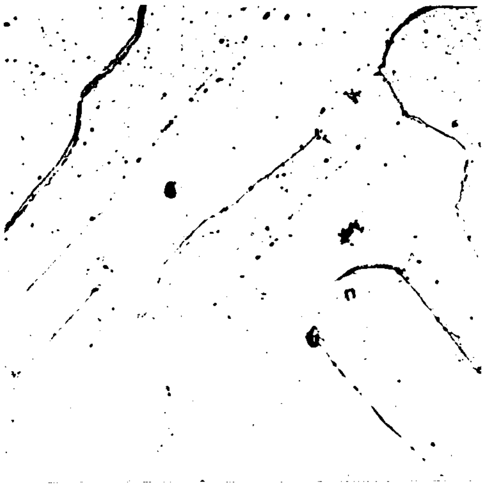


Figure 50. duPont titanium (Series II) homogenized 16 hours at 1200° C, annealed 14 hours at 900° C, 80 hours at 700° C before water quenching. Clear alpha titanium. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol (by volume). X 250

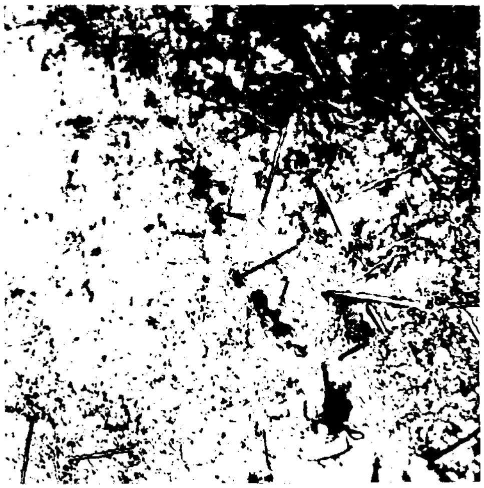


Figure 51. 51.4% vanadium (Series I) 30 hours at 910° C, 96 hours at 500° C, water quenched. Apparently alpha in rods and also finely divided alpha in beta matrix. Etchant 2 HNO_3 (conc) 1 HF (48%), 3 glycerol. X 1000

D. X-Ray Studies

X-ray studies were employed, along with metallographic examination of the titanium-vanadium alloys, for indicating the nature of the phases, for estimation of the solubility of vanadium in the hexagonal (alpha) form of titanium, and for attempting to fix the beta to alpha plus beta phase boundary. X-ray diffraction patterns were obtained for the metals and alloys in both the powdered and massive forms.

Early x-ray diffraction data indicated that widespread solubility existed for titanium in vanadium. For example, an alloy of approximately 50 per cent vanadium content showed the body-centered cubic lines of vanadium as principal constituent, but with an altered lattice parameter.

To determine the extent of the high temperature solubility of titanium in the body-centered cubic vanadium, x-ray patterns of massive arc melted alloys were examined. For this purpose, the alloys were left in the arc melted condition, essentially a quenched one, in order to retain a larger amount of titanium in the beta phase than would have been possible for some of the corresponding annealed alloys, especially in the high titanium range.

Data were gathered using a Phillips x-ray unit in conjunction with a Geiger spectrometer which gave a continuous record of the diffraction intensity as the Bragg angle was varied. In the earlier runs, the massive metal and alloy specimens were cut to fit a 1 x 2 cm sample holder. The upper surface of the specimen was polished on 600 grit covered paper, and deeply etched with a mixture of concentrated HNO_3, 48 per cent HF, and glycerol to remove the disturbed metal.

Because of the relatively few lines of body-centered cubic vanadium, the large grain size of the specimens used, and the singular motion of the sample with respect to the beam, it was difficult to obtain many reflections with this sample arrangement. Accordingly, later alloys were mounted in bakelite in order to fit a second sample holder. This sample holder allowed the specimen also to be rotated in the plane of its surface. To secure some of the reflections on these large grained alloys, it was usually necessary to scan the desired 2θ region repeatedly at a rapid rate, with rotations of the specimen in the surface plane of about 5° or so between each scan, in order to obtain a satisfactory intensity for locating the diffraction peak. Even by employing the above procedure, only a few peaks were obtained on some of the alloys. Once an appreciable peak had been located at the rapid scanning rate, further scannings were made at slower speeds, and the mean value taken in order to increase the precision of the determination. After measuring the positions of the peaks carefully, the corresponding interplanar distances (d values) were obtained by extrapolation from tables of d versus 2 θ for Cu kα_1 radiation (33b). Before making a series of determinations, the Geiger spectrometer was first standardized against a silicon standard. High angle reflections were made to coincide with standard values as closely as possible. Only the prominent diffraction peaks of the metals and alloys were chosen for following the change in lattice parameter with composition of the beta solid solution.

After ascribing the proper reflections to these peaks, lattice parameters were found for each reflection. In order to obtain a more precise value of the parameter of each metal and alloy from these data, the limiting value was obtained, at first, from a plot of lattice parameter against the corresponding $\cos^2 \theta$ values. Because of the limited number of reflections obtained for vanadium and the beta phase alloys, and because of the fact that a plot of $\cos^2 \theta$ values against the lattice values deviates considerably from linearity when low angle reflections are included, the function of Nelson and Riley (34), f(θ), was later employed. While this latter function has been tested only for powdered alloys in the usual powder cameras, where a plot of that function against lattice parameter is linear, it was nevertheless employed in this case with massive samples on the spectrometer, in the hope that it might be somewhat more satisfactory then the $\cos^2 \theta$ function. Experimentally, the Nelson and Riley function appeared to show a linear relationship with lattice parameter for the massive alloy samples employed here.

An attempt was made to place a reliability index on the limiting value of the lattice parameter determined by use of this function with massive samples. The variation of the mean deviation of the lattice parameters, as a function of twice the Bragg angle, is illustrated by data on a 51.7 per cent vanadium alloy. For 2θ values of about 40°, 74°, and 101°, the corresponding lattice parameters were determined as 3.1572 ± .0031 Å, 3.1550 ± .0014 Å, and 3.1557 ± .0003 Å, respectively. The usual tendency for the mean deviation to decrease with increase in the Bragg angle is indicated in this particular case. However, this tendency was not always found. This limiting value obtained as a result of linear extrapolation was determined as 3.1558 Å for the 51.7 per cent vanadium alloy.

A semi-analytical method (35) was used in an attempt to estimate a mean deviation for this limiting value. In this method, an average mean deviation was determined for all reflections observed for one specimen. By giving the mean deviation increasing statistical weight as the 2 θ values increased, a mean deviation of ± .0003 Å was found for the limiting value of the lattice parameter of the 51.7 per cent vanadium alloy. Similar treatment of the data taken on pure vanadium powder led to a limiting value of 3.028 ± .0005 Å. This analytical method, however, gave deviation values that appeared to be unreasonably low in comparison to that estimated by graphical examination of the data. The best estimate of the limiting value of the lattice parameter for each of the samples has been plotted against its composition as shown in Figure 52. No further attempt was made to fix a limit of precision analytically for this extrapolated value. Instead, from an examination of the data plotted against the function of Nelson and Riley, a mean deviation of 0.002 Å appeared to be reasonable.

A plot of lattice parameter versus alloy composition is presented in Figure 52. The estimated precision of the parameter values and the precision of the alloy compositions are indicated by the rectangles for each point. This figure shows the considerable expansion of the lattice parameter as titanium is added to body-centered cubic vanadium. This indicates that substitutional solid solution exists over a wide range in this system. The

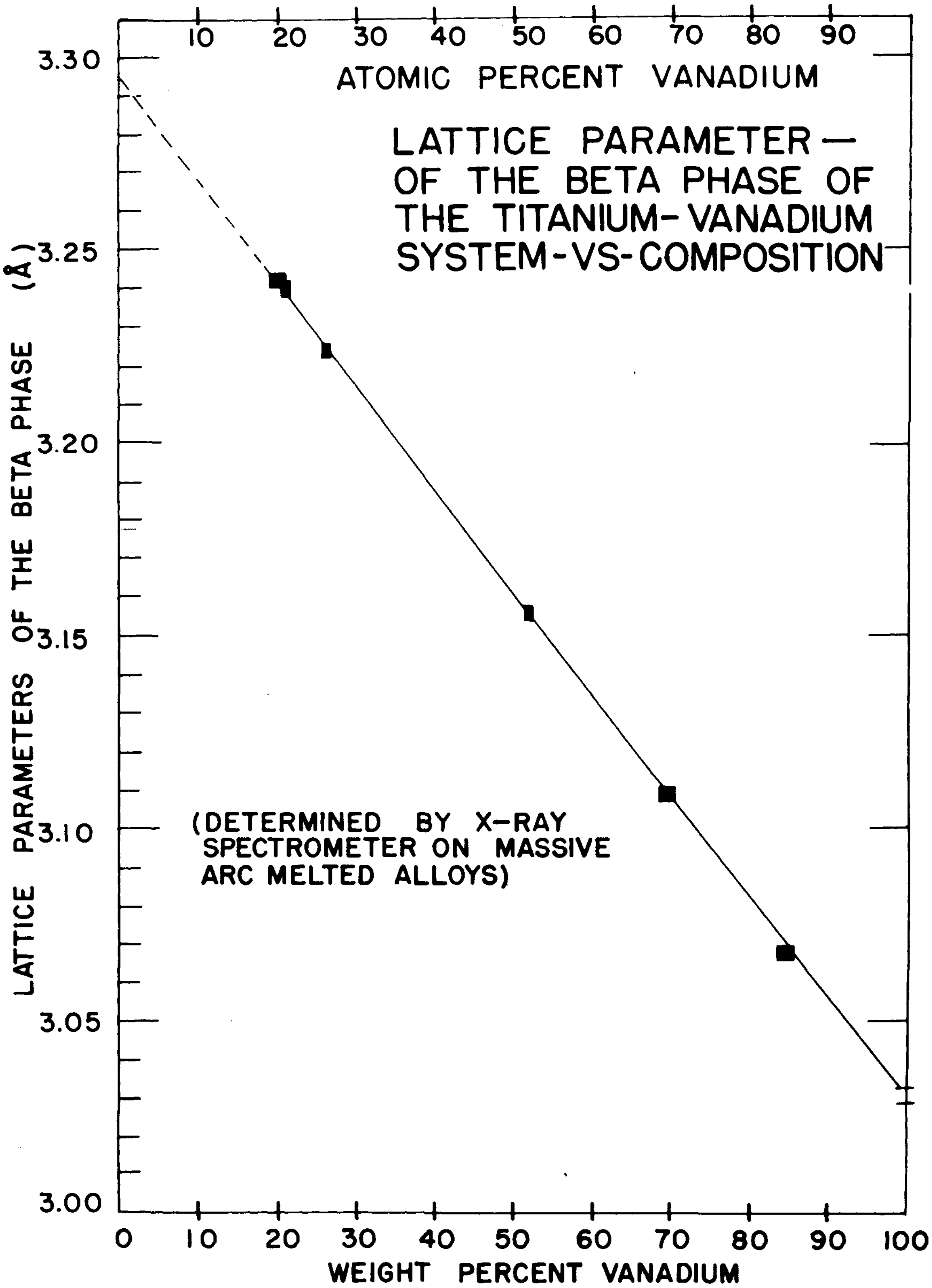


Figure 52. Lattice Parameter vs Composition.

widespread solid solubility might have been expected from the Hume-Rothery rules, and the expansion of the lattice parameter with additions of titanium to vanadium from the fact that the titanium in the body-centered cubic form has a larger lattice parameter (3.29 Å) than vanadium (3.03 Å).

In addition to the determination of the extent of solid solubility using massive arc melted samples, x-ray diffraction patterns of the alloy powders were used for phase identification in quenching experiments similar to those described earlier. X-ray powder patterns were obtained for each alloy in a 11.43 cm powder camera having the Straumanis film arrangement.

In the initial work of this part of the investigation, fine alloy filings from the arc melted specimen were sealed in zirconium-gettered silica tubes and subjected to the same homogenization, annealing, and quenching treatments as the metallographic samples. Zirconium was used because of its greater affinity for oxygen and nitrogen (36). This getter was heated repeatedly to redness to eliminate residual gas from each small annealing tube. After heat treatment, the tubes were opened and the alloy powder was screened through a 200 mesh brass screen and stuck to a fine pyrex filament with a film of Celvancene grease. X-ray photographs of these alloy powders taken earlier in the investigation were so cluttered with extraneous lines as to be useless for phase identification. These extra lines were shown to be due to wall scale which was caused by reaction of the alloy powder with the silica tube during the long time, high temperature homogenization treatment. To get around this difficulty, massive samples were first homogenized and then filed, and the powder placed in larger diameter silica tubes. A short anneal at the homogenization temperature followed by annealing at the quenching temperature reduced the amount of scale sufficiently in the quenched powders to make it possible to get some scale-free powders for the x-ray studies. These powders were sufficiently pure for satisfactory investigation of the alloy phases.

The x-ray diffraction patterns of the quenched alloys in the high titanium region usually showed a mixture of alpha and beta phases. As increasing amounts of vanadium were added to titanium at a given quenching temperature, the intensity of the body-centered cubic lines increased while that of the alpha phase showed a corresponding decrease. The hexagonal lines of the alpha phase continued to persist, however, even into the metallographically determined single phase beta region. Thus, the 14.8 per cent vanadium alloy of the 800° C quench (Series II) would be considered to be single phase beta from its metallographic appearance, which, with the exception of some impurity, is essentially single phase. However, alpha lines are evident in the x-ray diffraction patterns of the homogenized alloy of the same composition that had been powdered and subjected to identical annealing and quenching treatments. In this connection it might be pointed out that the quenching rates may have been somewhat different for powdered alloys than for the massive alloys. The small massive samples used for metallographic examination, on quenching into water were assumed to have received a rapid quench. On the other hand, the alloy powders which were enclosed in small silica tubes, owing to the relatively poor conductivity of the silica and the powder, may have required a slightly longer time for cooling when the silica tubes were dropped into water.

Because of the almost identical appearance of the alpha diffraction patterns of primary alpha and secondary alpha (transformed beta), it is not possible to determine the source of the lines by x-ray methods alone. The only difference is in the relative intensities of the lines, which may show some variation. However, by making use of the metallographic appearance of the alloys in conjunction with this x-ray evidence, it is possible to infer what type of phase is causing the reflections.

In the case of the 14.8 per cent vanadium alloy above, it is felt that the alpha lines may be produced by a martensitic type transformation of the beta phase. Metallographically, this sample shows only a small amount of impurity phase in addition to the retained beta matrix. The 21 per cent vanadium alloy of this 850° C quenching run also exhibits alpha lines in its diffraction pattern, having an estimated intensity of one tenth of that of the principal body-centered cubic beta lines. This alloy, also in a metallographically determined single phase region, is probably exhibiting martensitic type transformation. There is some metallographic evidence for a martensitic type transformation in these higher vanadium alloys. For the 21 per cent vanadium composition quenched from 700° C (Figure 32) which is single phase beta at that temperature, some accicular transformation product seems to be present.

The x-ray patterns of the 31 per cent vanadium alloy of the 500° C quenching run on Series II alloys, showed evidence of some alpha phase. In this case, the rapid attack of the alloy by etching reagents and its metallographic appearance (Figure 36) indicate that the alloy is two phase at this temperature. Even the 51.7 per cent vanadium alloy (Series II) of the same quenching run showed a faint trace of alpha phase in its diffraction pattern. This fact, and the reactivity of the alloy with etching reagents indicate that this alloy, as well, may lie in the two phase region at 500° C. Thus, the x-ray evidence on Series II alloys containing approximately 0.25 per cent oxygen indicates that a martensitic type transformation may persist up to the 21 per cent vanadium alloy and perhaps slightly above. The two phase region is indicated to extend to at least 31 per cent vanadium at 500° C and perhaps to 51.7 per cent vanadium at the same temperature.

To estimate the solubility of vanadium in the hexagonal form of titanium, x-ray patterns of the low-vanadium alloys of Series II were examined. These alloys were in the form of powders filed directly from the massive high temperature homogenized alloys and so contained about 0.25 per cent oxygen to begin with. Because of the care in removing residual gas from the annealing tubes, it is felt that no appreciable amounts of additional gas were introduced as a result of the subsequent heat treatments given these alloys.

When the results of individual runs were considered, the 1.2 and the 3.4 per cent vanadium alloys quenched from 850° C showed lines of the beta phase. From the relative intensities of these lines as visually estimated, the amounts of beta phase appeared to be 10 and 30 per cent respectively, the rest being alpha. Lines of the beta phase were also seen in the photographs of the 1.2 per cent vanadium alloy quenched from 700° C and the 2.45 per cent vanadium alloy quenched from 500° C. Because the beta phase is partially transformed on quenching, even more beta should have been present at the quenching temperature than the x-ray data would indicate. Thus it appears on the basis of x-ray data that at 700° C and above less than 1 per cent vanadium is soluble in the hexagonal form of the titanium used in these experiments.

Because of the considerable variation of lattice parameter with composition in the single phase beta region, it was hoped that by employing the usual powder techniques and the Nelson and Riley function (34) for extrapolation, that the lattice parameters should be determined with sufficient accuracy to enable the beta transition boundary to be fixed within reasonable limits. In an attempt to fix the beta to alpha plus beta transition line, the x-ray patterns obtained earlier in connection with the qualitative identification of phases from the various quenching treatments, were examined. Lines of each pattern were measured to the nearest 0.005 cm on a conventional illuminated Phillips x-ray film scale. The circumference of the x-ray film was obtained from measurements of the average mid-points of both the back and front reflection regions. The 4 θ values were obtained from this circumference value and the measured separations of corresponding lines on the film. $\sin^2 \theta$ values were then read from a prepared plot of $\sin^2 \theta$ against 4 θ. The lines of the beta phase (body-centered cubic) were indexed and a number of lattice parameters for each alloy were calculated from the various $\sin^2 \theta$ values. Values for copper $k\alpha_1$ of 1.5405 Å, $k\alpha_2$ of 1.5443 Å, and $k_2\alpha_1 + \alpha_{2/3}$ of 1.5418 Å were employed in obtaining the parameters. For each alloy these lattice parameters were plotted against the Nelson and Riley function of θ in order to determine a more precise parameter value for that composition. As may be seen from Figures 53 and 54, the function indicated at the abscissa shows the expected linear relationship with lattice parameter in most cases. The limiting value of the lattice parameter was obtained from the plot by extending the straight line to the zero value of the function. For convenience in evaluating the Nelson and Riley function more directly from the experimental data, a plot had been prepared for reading directly the values of the function from the 4 θ values. Figures 53 and 54 show the experimental points and the limiting value of the lattice

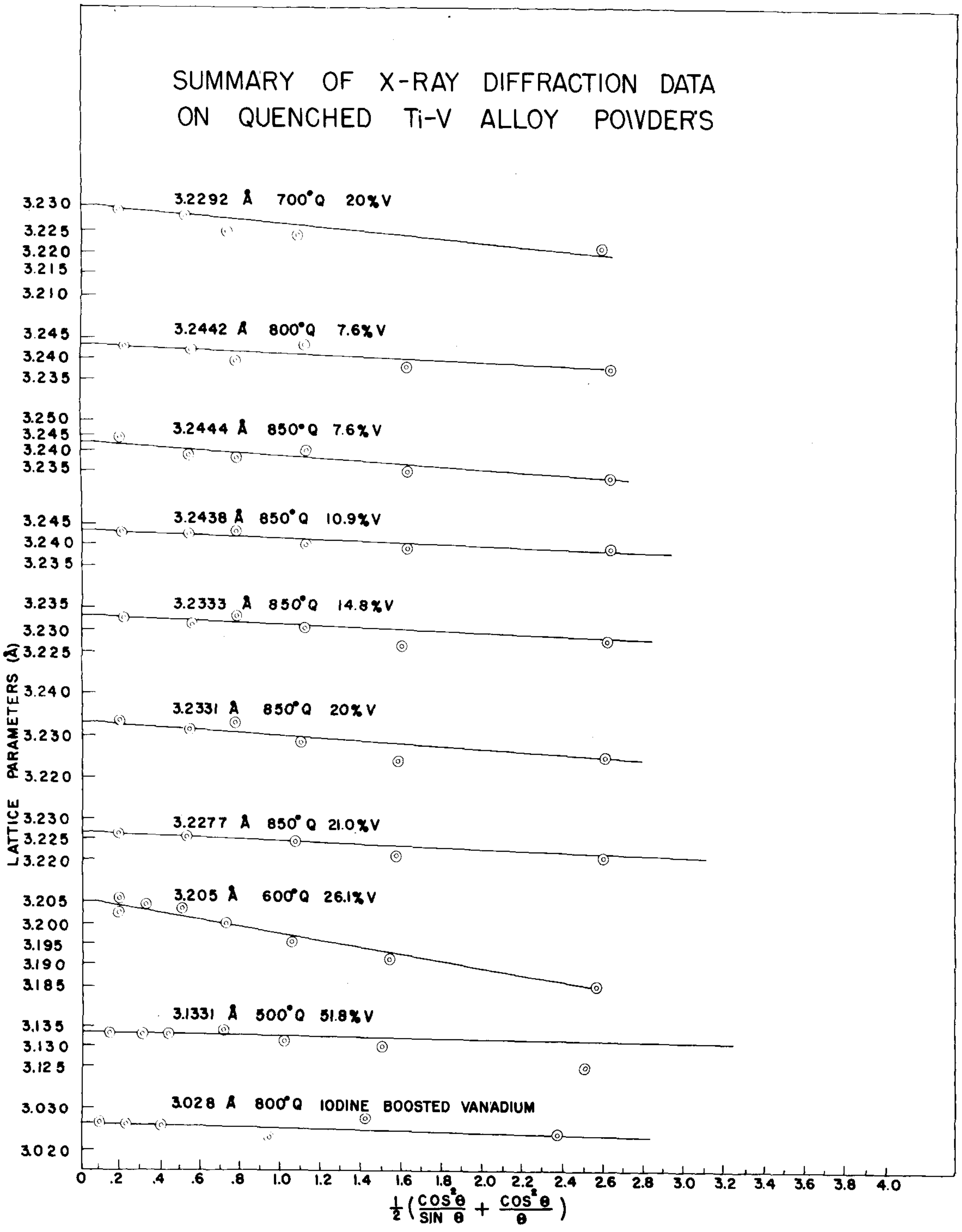


Figure 53. Summary of Diffraction Data on Powdered Alloys.

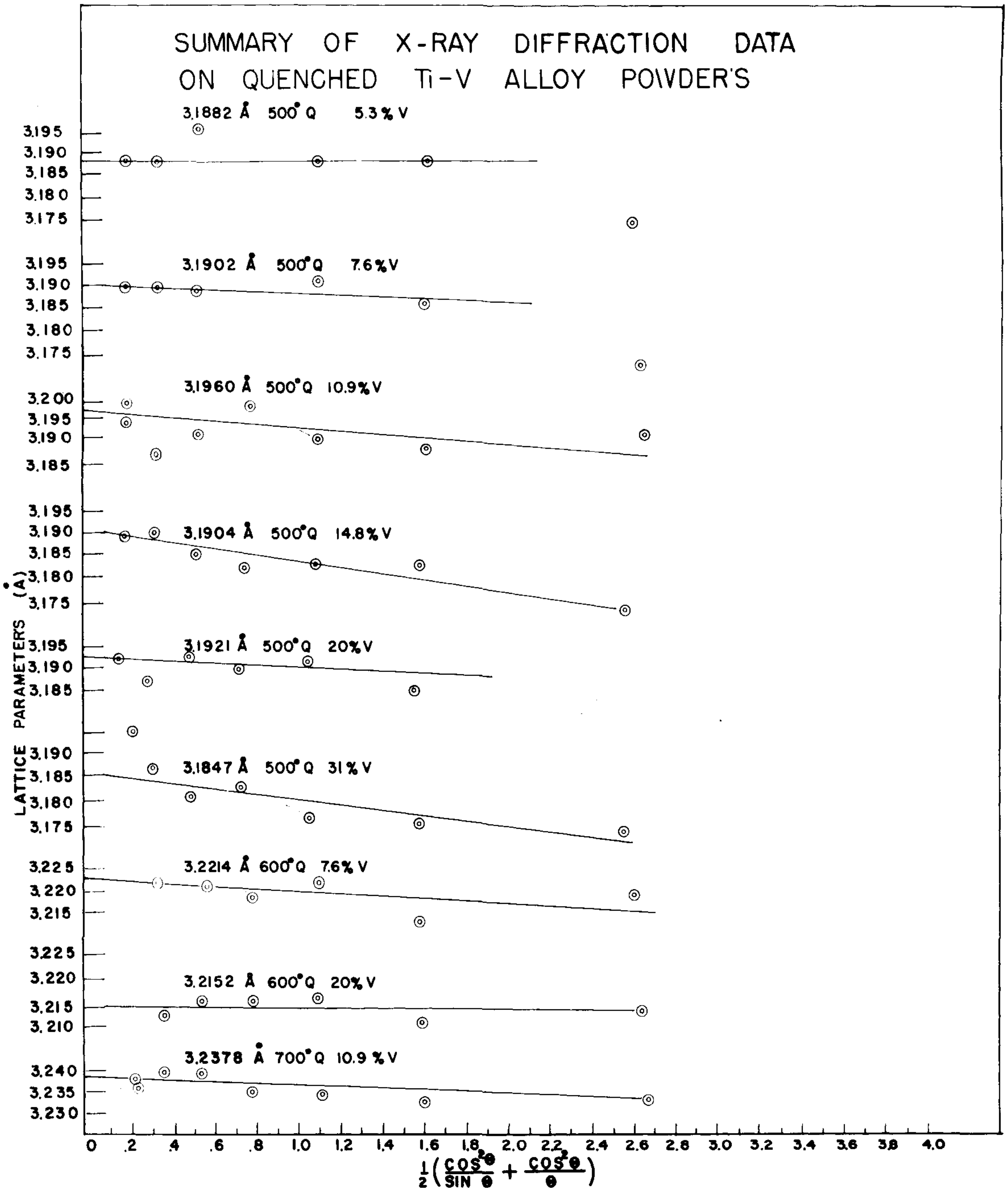


Figure 54. Summary of Diffraction Data on Powdered Alloys.

parameter for a given alloy composition. The quenching temperature is also indicated.

If it is assumed that the graph of lattice parameter against composition determined previously (Figure 52) on massive arc melted alloys by spectrometer may be used in conjunction with data obtained by Debye camera on the quenched alloy powders, then the position of the boundary between the beta and the alpha plus beta fields could be determined. Thus, reference of the beta phase lattice parameter for the two phase region to the lattice parameter versus composition curve determined for one phase alloys should give the composition of the terminal beta solid solution corresponding to any given quenching temperature. This reasoning is based on the assumption that the beta phase remains practically unchanged on quenching and that equilibrium has been established at the quenching temperature.

Results of the lattice parameter determinations on alloys quenched from the higher temperatures were not especially rewarding. The highest value of the beta phase lattice parameter that was obtained on a two phase alloy quenched from 850° C was 3.2444 Å for the 7.6 per cent vanadium alloy powder. Referring to the lattice parameter versus composition curve of Figure 52, the composition of the beta phase corresponding to this value is seen to be 18.7 per cent vanadium (81.3 per cent titanium). This lies considerably above the metallographically determined phase boundary of about 11 per cent vanadium for alloys containing 0.25 per cent of oxygen. The lattice parameter of the 7.6 per cent vanadium alloy quenched from 800° C also appeared to have essentially the same value, i.e., 3.2442 Å which corresponds to the composition of 18.7 per cent vanadium, while the metallographically determined phase boundary at this temperature is about 15 per cent vanadium.

Because no larger lattice parameter than the 3.2444 Å, indicated above, was found, it may be that an alloy richer in titanium than the 81.3 per cent cannot be retained by the quenching procedure employed. Enclosure of the powder in silica annealing tubes perhaps retarded the cooling rates enough to prevent retention of larger quantities of titanium in the beta phase. A more rapid effective quenching rate may favor the retention of more titanium than this in solid solution.

The lattice parameters of the 14.1, the 20, and the 21 per cent vanadium alloys quenched from 850° C, where all compositions lie in the metallographically determined single phase region, gave lattice parameters of 3.2333 Å, 3.2331 Å, and 3.227 Å, respectively. By reference to

Figure 52, the compositions corresponding to these values were 23, 23, and 25 per cent vanadium. None of these corresponded to the chemically analyzed values. Since the lines of the beta phase appeared to be reasonably sharp on the film, with some resolution of the alpha 1 and 2 lines in the back reflection region, and since the limiting values were determined according to established procedures, it is probable that the observed values are reasonably accurate (i.e., to about ± 0.003 Å). Assuming that these are the true observed parameters, then it appears that at the quenching rates employed both the complete retention of the beta solid solution and the use of x-ray methods to fix the beta to alpha plus beta phase boundary for the elevated temperatures are questionable.

Examination of the x-ray data from the lower temperature quenches, did not give much more satisfactory results than in the high temperature case. Perhaps because of non-attainment of equilibrium during the long-time, low-temperature anneals, the beta phase lattice parameters were not constant at a given quenching temperature, for alloys in a metallographically determined two phase region. The parameter values generally tended to decrease as the phase boundary was approached.

The two lattice parameters taken of the 700° C quenching run were 3.2378 Å for the 10.9 per cent, and 3.2292 Å for the 20 per cent vanadium alloy, and corresponded to beta phase compositions ranging from 20 to 25 per cent vanadium according to Figure 52. This range of the phase boundary composition, corresponds roughly with the metallographic boundary of 20.5 per cent vanadium for the 700° C quench, of an alloy containing approximately 0.25 per cent oxygen.

The lattice parameters of the Series II alloys quenched from 600° C were found to be 3.2214 Å, 3.2152 Å, and 3.205 Å, for the 7.6, the 20, and the 26.1 per cent vanadium alloys respectively. This corresponds to a range of compositions for the beta phase of from 26 to 34 per cent vanadium. As metallographically determined, the boundary at 600° C is at about 32 per cent vanadium for alloys containing about 0.25 per cent oxygen.

The 500° C quench showed a range for the beta phase composition of from 36 to 42 per cent vanadium if the parameters of all six alloys containing less than 32 per cent vanadium are considered. Metallographic studies indicate that the phase boundary is above 32 per cent vanadium at 500° C. However, because of the probability that the 500° C anneal did not give equilibrium, it is not possible to locate the phase boundary at this temperature with any assurance. The 51.8 per cent vanadium alloy, when annealed and quenched at 500° C, gives a beta phase parameter corresponding to 61 per cent vanadium, when compared to the arc melted alloys of Figure 52, which throws some question on the validity of the x-ray techniques here, or the true nature of the 51.7 per cent vanadium alloy.

It might be noted that if the lattice parameter against composition curve of Figure 52 is extended to 0 per cent vanadium the lattice parameter for body-centered cubic titanium would be close to 3.294 Å. This lies above the extrapolated value of 3.287 Å recently obtained by other investigators using powdered titanium-vanadium alloys (37) that had been quenched into liquid argon from 650° C. This discrepancy may be attributed perhaps to incomplete quenching of the massive beta phase alloys on the copper hearth of the arc melting furnace in the present series of experiments, to a higher oxygen content of the commercial titanium and of the alloys adjacent to it, or to a combination of these two factors.

In addition to the use of x-rays for phase identification, and for phase boundary studies, an attempt was made to test for ordering which was suspected for the 50 atomic per cent vanadium alloy. First two powdered 50.8

atomic per cent vanadium alloys were sealed in zirconium gettered silica tubes and heated to 800° C for the purpose of disordering the alloy. One sample was withdrawn and air cooled; the second was cooled to 350° C and held at that temperature for over a month, then furnace cooled. X-ray diffraction methods were found to be insufficiently sensitive, however, to detect ordering in a system having the components as closely related as titanium and vanadium (38).

Since the additional super lattice lines that would result from ordering of the body-centered cubic solid solution would occur for odd values of $(h + k + l)$, a consideration of the structure factors shows that the super-lattice line intensities will be given by the expression $F(hkl) = C(f_V - f_{Ti})^2$ whereas the intensities of the normally occurring lines of the disordered solid solution are given by $F(hkl) = C(f_V + f_{Ti})^2$. Since the atomic scattering factors of titanium and vanadium are given by the atomic numbers at 0° scattering angle, the resulting ratio of intensities of super-lattice to disordered lattice lines is given for this system by $(23-22)^2/(22-23)^2$ or 1/2025, so that no super lattice lines should be expected to be observed for this system in any reasonable exposure time.

Lattice parameters were calculated for a few of the titanium control samples using powder techniques. The hexagonal lines of titanium were measured and corrected for film shrinkage in the same manner as was done for the titanium-vanadium beta phase alloys. The lines were indexed and lattice parameters of the (hk0) and 001) reflections were calculated. Corresponding "a" and "c" values were plotted against the Nelson and Riley function of θ and a representative straight line drawn to determine the limiting value of the parameter.

The "c" values for homogenized commercial titanium containing about 0.25 per cent oxygen, differed considerably from precision values for crystal bar titanium as found in the literature (39). Two commercial titanium powder samples were filed from a given specimen of homogenized metal. These samples were sealed in quartz tubes and quenched, in one case from 850° C, and in the other case from 500° C. The "c" parameter for the 850° C quench was found to be 4.737 Å while that from the 500° C quench was 4.706 Å. These differ measurably from the reported precision "c" value determined for high purity annealed titanium of 4.683 Å. Evidently the quenching of alloys containing oxygen effectively increases the "c" values to such an extent that they correspond to "c" values in annealed titanium containing much more oxygen. For example, the commercial titanium quenched from 500° C had the lattice value of annealed metal containing 1.1 per cent oxygen, while the sample quenched from 850° C was approximately equivalent to 6 per cent oxygen in annealed titanium. These high values are assumed to be due to the quenching effect and do not represent the oxygen contents determined from hardness (22).

Thus it appears that titanium containing about 0.25 per cent oxygen is prevented from returning to its equilibrium lattice parameter corresponding to a given oxygen content when quenched from higher temperatures. The lower the quenching temperature, the closer the approach to the equilibrium value. This conjecture is admittedly based on rather limited data so it is felt that further study is warranted.

VII. PHYSICAL PROPERTIES OF THE ALLOYS

A. Density

Because the alloys prepared by arc melting were almost invariably void-free, portions of these alloy buttons were used for density determinations. An alloy sample, suspended by a fine copper wire, was weighed first in air, then while standing in water. From the two weights, together with the water temperature, the metal density was calculated.

An analytical balance was used, along with class "S" weights in the density determinations. The metal hanging from the left balance arm by fine wire was carefully weighed. Then a beaker of water supported on a wooden stand was slipped up under the specimen till it was completely submerged and this weight recorded. To insure that no air bubbles would cling to the metal and thus decrease the observed density, the metal was first carefully cleaned with acetone and wiped dry with clean laboratory towel. The surface tension of the water was reduced by addition of a few grains of detergent (Dreft) so that the metal was completely wetted. Water temperature was read to the nearest tenth of a degree on a mercury-in-glass thermometer, and was never far from 25° C.

As an example of a typical density determination, data for the 14.1 per cent vanadium 85.9 per cent titanium alloy of Series I is given below. The arc melted button was sectioned and appeared to be free from holes or segregation. Chemical analysis performed later on this specimen indicated the atomic percentage of vanadium to be 13.38 per cent instead of the calculated 13.30 atomic per cent derived from the charge.

Sample RP7-18 (15V-85Ti)

Wgt wire + alloy	7.8611 g
Wgt wire suspension	0.0613 g
Wgt alloy	7.7998 g

Wgt wire + alloy in water	6.2018 g
Wgt wire suspension	0.0613 g
Wgt alloy in water	6.1405 g

Length submerged wire 2-1/8"
Volume submerged wire (2.125")(.0013 cc/") = 0.0028 cc

Wgt displaced water equivalent to alloy volume	7.7998 g
	6.1405 g
	1.6593 g

Density of water at 25.1° C = 0.997018 g/cc

Alloy + wire volume 1.6593 g/0.997018 g/cc =	1.6643 cc
wire volume	0.0028 cc
alloy volume	1.6615 cc

Alloy density 7.7998 g/1.6615 cc = 4.694 g/cc

An indication of the reproducibility of the determinations of density is given by citing results for several measurements on the 4.22 per cent vanadium alloy. In the arc melted condition, this alloy gave for a mean value of two readings 4.5718 ± .0008 g/cc. For three of the hot-rolled alloys of this composition which were surface ground after rolling, the mean value was 4.5705 ± .0017 g/cc. An additional determination on the hot-rolled alloy in which the oxide skin was not removed before the determination gave the value of 4.4681 g/cc., and thus emphasized the importance of completely removing this layer. Hot-rolled densities were run as a check on possible voids in the arc melted specimens. The two sets of densities, as-arc-melted and as-hot-rolled, corresponded fairly well in most cases. A table of densities for Series I alloys, Table 8 follows, together with the corresponding chemical analysis when available. A similar table for Series II alloys is also included as Table 9.

The considerable number of titanium-vanadium alloy densities were measured for several reasons, one being that at the beginning of the investigation, it was not known how many chemical analyses could be obtained for these alloys so that densities might have had to be used as a check on the composition. This use implies that a

Table 8

Experimental Densities of Titanium-Vanadium Alloys of Series I

Charged to furnace (atomic %)	Analyzed alloy (atomic %)	Analyzed alloy (wgt %)	Density at 25° C
National Lead Co. Ti		99.6 % Ti	4.5197
5.76% V	5.80% V	5.96% V	4.583
10.07% V	10.15% V	10.7 % V	--
13.30% V	13.38% V	14.1% V	4.6944
49.97% V	49.9 % V	51.4 % V	5.2417
(sulfur boosted vanadium)		99.55% V	6.1042

series of standards could be prepared merely by co-melting known mixtures. As may be seen from a comparison of the composition charged to the furnace and then analyzed, this is not too erroneous an assumption in most cases. In addition to this, the calculation of the surface tensions of the titanium-vanadium alloys required this quantity.

A plot of density as a function of composition is shown in Figure 55 for both Series I and Series II alloys. This was used to estimate the composition of alloys produced by co-reduction of the mixed oxides with calcium, as well as the composition of a few unanalyzed alloys of

Table 9

Experimental Densities of Titanium-Vanadium Alloys of Series II

Charged to furnace (atomic %)	Analyzed alloy (atomic %)	Analyzed alloy (wgt %)	Arc melted density (g/cc)	Hot rolled density at 25° C (g/cc)
(duPont sponge Ti)		98.2 % Ti	4.5146	4.5141
1.04% V	1.07% V	1.20 % V	4.5286	4.5258
2.05% V	2.33% V	2.475% V	4.5549	4.5594
2.98% V	2.96% V	3.14 % V	4.5528	4.5522
3.94% V 3.94% V	4.00% V 4.00% V	4.22 % V 4.22 % V	4.5726 4.5711	4.5682 4.5710 4.5723 4.4681
4.94% V	5.01% V	5.31 % V	4.5837	4.5820
6.94% V	7.13% V	7.55 % V	4.6082	4.6119
10.0 % V	10.34% V	10.9 % V	4.6595	(not hot rolled)
13.96% V 13.96% V	13.97% V 14.07% V	14.73 % V 14.81 % V	4.7291	4.6703
20.1 % V	20.0 % V	21.0 % V	4.7827	4.7487
25.0 % V	24.92% V	26.1 % V	4.8557	4.8428
30.2 % V 30.2 % V	30.0 % V 30.0 % V	31.27 % V 31.27 % V	4.9294 4.9312	4.9332
50.8 % V	50.15% V	51.67 % V	5.2559	5.2846
75.05% V 75.05% V	74.32% V 74.32% V	75.48 % V 75.48 % V	5.6584 5.6554	5.6758* 5.6681*
(iodine boosted vanadium)	99.06		6.0948	6.1090

*Alloys exhibited some segregation

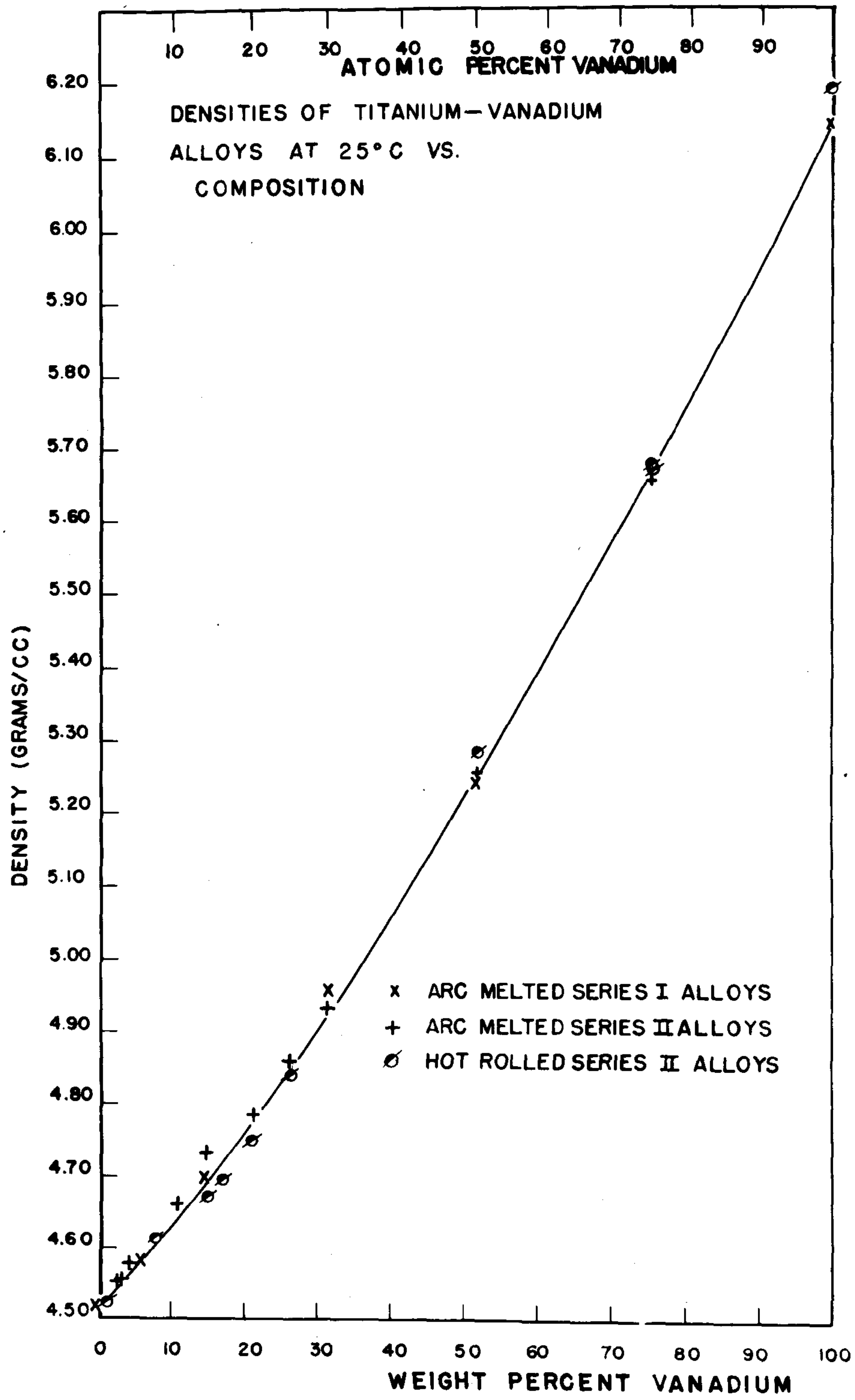


Figure 55. Density vs Composition.

both series. Both series follow the curve closely, with no significant difference between the two.

Using the values of the lattice parameters determined earlier, the x-ray densities of the beta phase alloys were calculated at several compositions using the expression $\rho = nA/VN$, where n is the number of atoms in a unit cell, 2 in the case of the body-centered cubic beta phase; A the mean atomic weight; N the Avogadro number; and V the cell volume as calculated from the lattice parameter. Values derived in this manner are listed in Table 10 along with densities determined by water displacement. Contrary to expectation, the x-ray densities were less than the measured water displacement densities. The x-ray density of powdered iodine boosted vanadium was calculated to be 6.094 Å, which was somewhat closer to the measured value.

Table 10

Densities of Several Titanium-Vanadium Alloys as Arc Melted

Composition (wgt % V)	Water displacement density (g/cc)	X-ray density of massive samples (g/cc)
V	6.1042	6.076
85V	5.850	5.806
70V	5.572	5.534
50V	5.227	5.201
30V	4.900	4.880
20V	4.760	4.732

Since the data of Table 10 were obtained on metal in the as-arc-melted condition, there might possibly be a difference in data obtained by the two methods for density because of strain set up in the metal. It might be assumed that the water displacement method gives somewhat of an average density for the piece which is perhaps under compression in its center, and under tension on its surface, while the x-ray value of density can be obtained by measurements involving only the surface metal, assumed to be under tension.

Another factor not taken into account in calculating the x-ray density of these samples is the additional weight associated with the structure due to interstitial impurities such as oxygen, and to substitutional impurities such as iron.

From an examination of the density against composition curve (Figure 55), it is evident that the observed density for the 50 per cent vanadium alloy, for example, is less than that of a mechanical mixture of equal parts of titanium and vanadium. This could be interpreted as indicating that the atoms in the alloy are not so compatible as either atom surrounded by its own kind. The limiting case of this tendency for like atoms to associate together is exhibited by eutectic formation. In the case of the titanium-vanadium alloys, the tendency of the melting temperature to form a eutectic is shown by the minimum in the liquidus curve.

B. Emissivity Determinations

Approximate emissivities were determined on Series II titanium-vanadium alloys. This was done primarily as a check on the amount of oxidation, since the melting points of these alloys were apt to be influenced by introduction of appreciable amounts of oxygen or nitrogen. It was hoped that a change in surface or bulk oxidation would be accompanied by a marked change in the spectral emissivities of the alloys.

Reference to a table of emissivities (40), for example, shows that titanium in the unoxidized state has a value of emissivity at the 6500 Å wavelength, of 0.63, while the value for titanium oxide is listed as 0.50. For vanadium, the value of the metal is listed as 0.35 while that of the pentoxide, 0.70 (40). While some of these values are open to question in view of later determinations (41) the at least indicate that some difference might be expected between oxidized and non-oxidized metals.

1. Method

Emissivities were obtained from a measurement of the surface temperature of a metal or alloy that corresponded to a given true temperature. These determinations were carried out in conjunction with the melting temperature determinations, the usual melting point specimens being employed. The temperature of the specimen, both inside and outside of a black-body hole drilled in it, was measured by an optical pyrometer as the metal was being heated stepwise to the melting range. The temperature was allowed to level off after each increase in current through the specimen until fairly constant readings were obtained, for areas both inside and outside the hole, after which the temperature would again be increased. The usual corrections were made to the observed temperatures and these were plotted, the surface temperature against the true temperature. Emissivities were found by reference to a table of emissivities (e_λ) as a function of the true temperature (T) for specified surface temperatures (S). The table (42) shows surface temperatures for every 100° C between 700° and 1400° C, then at 200° C intervals to 2000° C. It represents the tabular solution of the equation $\ln e_\lambda = c_2 (1/T' - 1/S')/\lambda$ for specified values of S and for $c_2 = 1.432$ cm deg, $\lambda = 6500\ \text{Å} = 0.65 \times 10^{-4}$ cm, and where T' and S' are the true and surface temperatures in °K.

2. Emissivity of nickel

Electrolytic nickel was used to check the method which was used for emissivity determination. The initial specimens were prepared from two pieces of 1/8 inch nickel sheet cut to identical size. One piece was completely pierced by a 0.04 inch drill, the other drilled to a depth of 1/16 inch with a sharply tapered drill of the same size. The holes were placed at the center constricted part of the specimen so that melting would occur at that point. The upper surface of the first sheet of nickel was polished down to and including the 600 grit paper covered wheel. After placing one piece above the other so that the holes coincided, and clamping tightly between the electrode jaws, the metal was heated stepwise in a 1 to 2 micron vacuum by passing high amperage current through it. Good results were often obtained using this method, but because of the occasional tendency of the two pieces to buckle and separate slightly, thus losing part of the black body character of the hole, these specimens were later supplanted by pressed nickel melting point bars prepared in the manner indicated in section VI.-A-1. The surface of some of these bars was finished on the 600 grit paper while that of others were given an even higher polish on a cloth covered wheel with a 600 mesh carborundum-soap slurry.

To illustrate how typical data were condensed to obtain emissivity values, some data are given in Table 11. Surface temperatures (°C) are indicated by parentheses, the rest being temperatures (°C) within the black-body hole. Underlined values to the right of the column of figures are average values of surface and true temperature as determined from the temperature readings lying between the black lines. Corrected temperatures are also shown.

True temperatures were plotted against surface temperatures for the runs on the pressed nickel bars, and the best line representing the data drawn through the points. Where the curve of true temperature against surface temperature intersected observed temperatures of 700°, 800°, 900° C etc., the corresponding true temperatures were read off, and using these two temperatures, emissivities were interpolated from a table (42). The average emissivity of pressed nickel powder is shown as a function of temperature in Table 12.

Table 11

Melting Point and Emissivity Data for Electrolytic Nickel*

Pressure 1.5 microns					
3:00 P.M. run on			....		
			(1263)		
823			(1259)		
832			(1261)		
827			1368		Corrected
832			1365		Temperatures
(787)			1368	1367	1381
(792)			(1265)	(1264)	(1273)
832		Corrected	(1262)		
829	831	Temperatures	1367		
832	(785)	834	1365		
(787)		(787)	(1252)		
(784)			1335		
(784)			1345		
830			....		
826			1430		Corrected
			1436		Temperature
1.4 microns			1440 melted at hole		1457
3:10 P.M.					
....			4:10 P.M. run off	92.7	Avg.
			0.9 micron	92.6	
			Per cent transmission	92.4	92.6%

*Specimen surrounded by a 2 inch molybdenum shield with 3/8 inch frontal opening. Front face polished on cloth wheel with 600 grit carborundum soap-water slurry following the 600 grit paper wheel.

An examination of the results for nickel shows no marked difference in emissivities between samples that had been polished on the 600 grit paper wheel and those subjected to a further wet polishing operation to give the metal an even higher polish. Burnishing or

Table 12

Emissivities of Pressed and Presintered Nickel Powder
(Averaged Values)

Surface temp. (° C)	True temp. (° C)	Spectral emissivity at 6500 Å
800	847	0.422
900	958	0.413
1000	1070	0.406
1100	1183	0.40
1200	1295	0.396
1300	1407	0.41
1400	1463	0.414

self-polishing that takes place on heating the alloys to a high temperature under vacuum has been found to have no effect on emissivity (41). There is also no apparent difference in emissivities between specimens that had been surrounded by a 2 inch molybdenum shield, and unshielded specimens. The effect of a shield might be expected to increase the observed surface temperature for a given true temperature of the metal, somewhat above that measured when nothing but the dark walls of the cooling jacket were fronting the specimen. This would increase the emissivity over that of an unshielded sample. However, this effect was not observed up to temperatures of 1400° C for nickel. As an example, a sample of nickel with a surface temperature of 1375° C showed an apparent shield temperature of 915° C. If this effect is proportional to the fourth power of the temperature difference between the shield and the metal surface, it should be inappreciable, even at higher temperatures. Besides the shield, the metal or alloy surface in this apparatus "sees" both the top and the bottom of the cool copper electrode faces which were not especially reflecting because of filming by the metal vapors.

The mean value of the emissivity over the above temperature range, i.e., 800° to 1350° C, is 0.409 ± .008. The fact that this lies appreciably above the accepted literature values for nickel may be attributed to the nature of the metal, which was formed by pressing nickel powder and partially sintering it. The presence of pores in the nickel and interstices between the powder granules would tend to give increased black-body character to the surface and hence increase the apparent surface temperature over that of massive metal. This would lead to an increase in the observed emissivity.

Results of an emissivity run on a massive nickel sample led to a mean value of 0.361 ± .015 between 900°

and 1300° C. This was close enough to the literature values of 0.36 (40) (43) (44) to indicate that the method was of sufficient accuracy to enable marked changes in emissivity to be observed.

The emissivities of two unpolished, pressed nickel powder specimens were found to decrease steadily from 0.725 to 0.56 as the temperature was increased from 900° C to 1300° C, suggesting that, in the absence of oxidation, the progress of sintering might be followed by emissivity determinations. The values of the emissivity might approach a limiting value for a completely sintered sample.

The determination of accurate emissivities is inherently a difficult one. Aside from the effect of surface condition and degree of oxidation on this measurement, a small error in temperature will alter the observed emissivity considerably. For emissivities near 0.40, a 2° error in the difference between true and surface temperatures would be reflected in an error of about 0.01 in emissivity at 1000° C, while at 1300° C for the same emissivity, an error of 2° C would change the emissivity by 0.007 units.

3. Emissivity of the titanium-vanadium alloys

Similar measurements were carried out for the titanium-vanadium alloys as were done for nickel, the only difference being that higher vacua were employed, 0.1 instead of 1.1 microns. Most of the alloy surfaces were finished on the 600 mesh paper wheel. Plots of the true against the surface temperature for titanium and vanadium are shown in Figures 56 and 57. A similar graph of the alloys has been omitted because of the considerable number of overlapping lines. All these values have been used, however, to determine emissivities in the same manner as previously described for nickel. Emissivities as a function of true temperature have been plotted in Figures 58 and 59 for titanium, vanadium, and some of their alloys.

For most of the alloys heated under a 0.1 micron vacuum a change in emissivity was observed to take place as the specimen was heated above a certain temperature. This temperature apparently depended on a number of unascertained variables such as composition, the total pressure in the system, prior number of meltings, etc. A darkening of the area about the black-body hole was seen to begin at this temperature and to spread over most of the heated portions of the specimen.

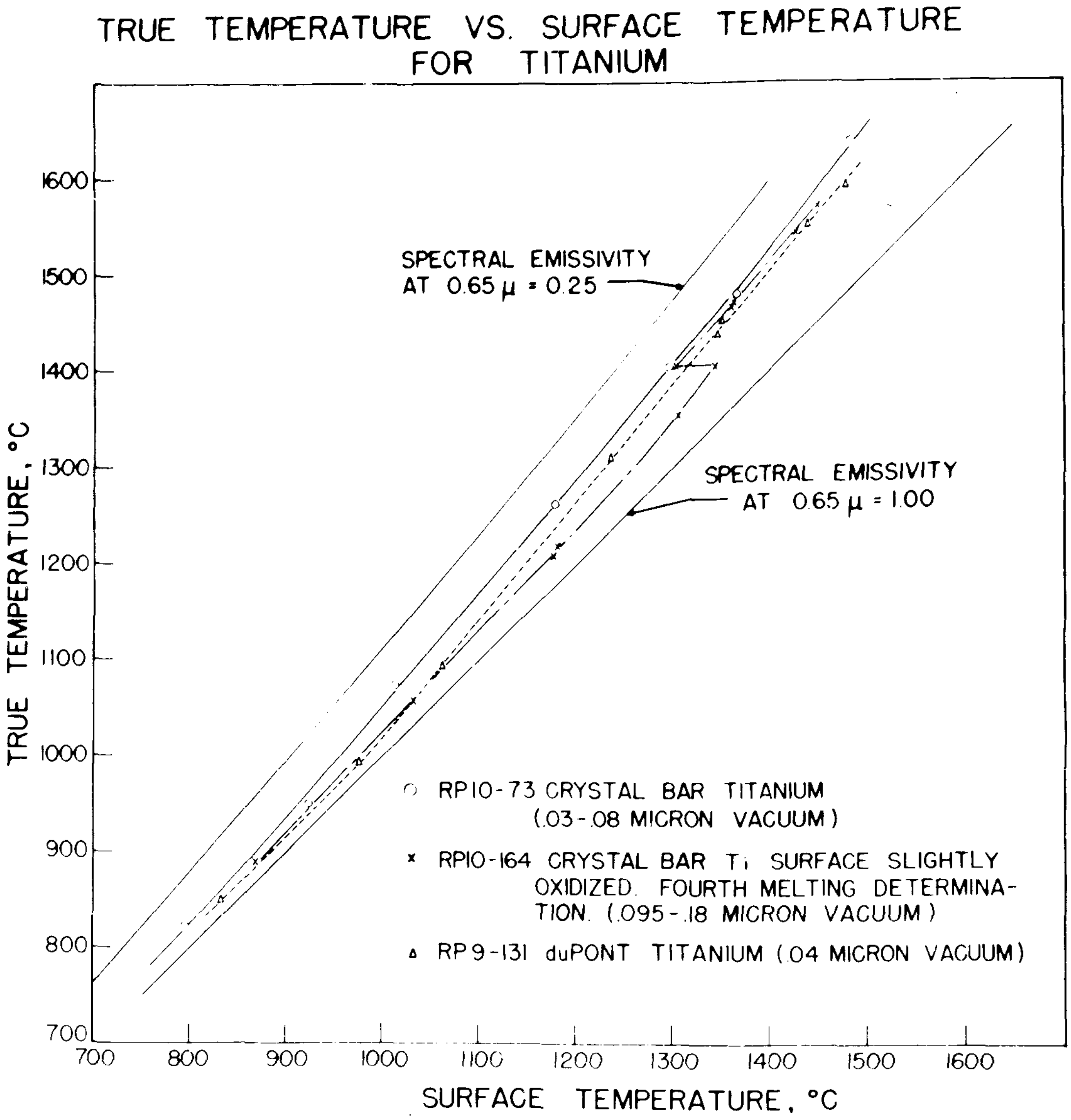


Figure 56. Surface Temperature of Titanium vs True Temperature.

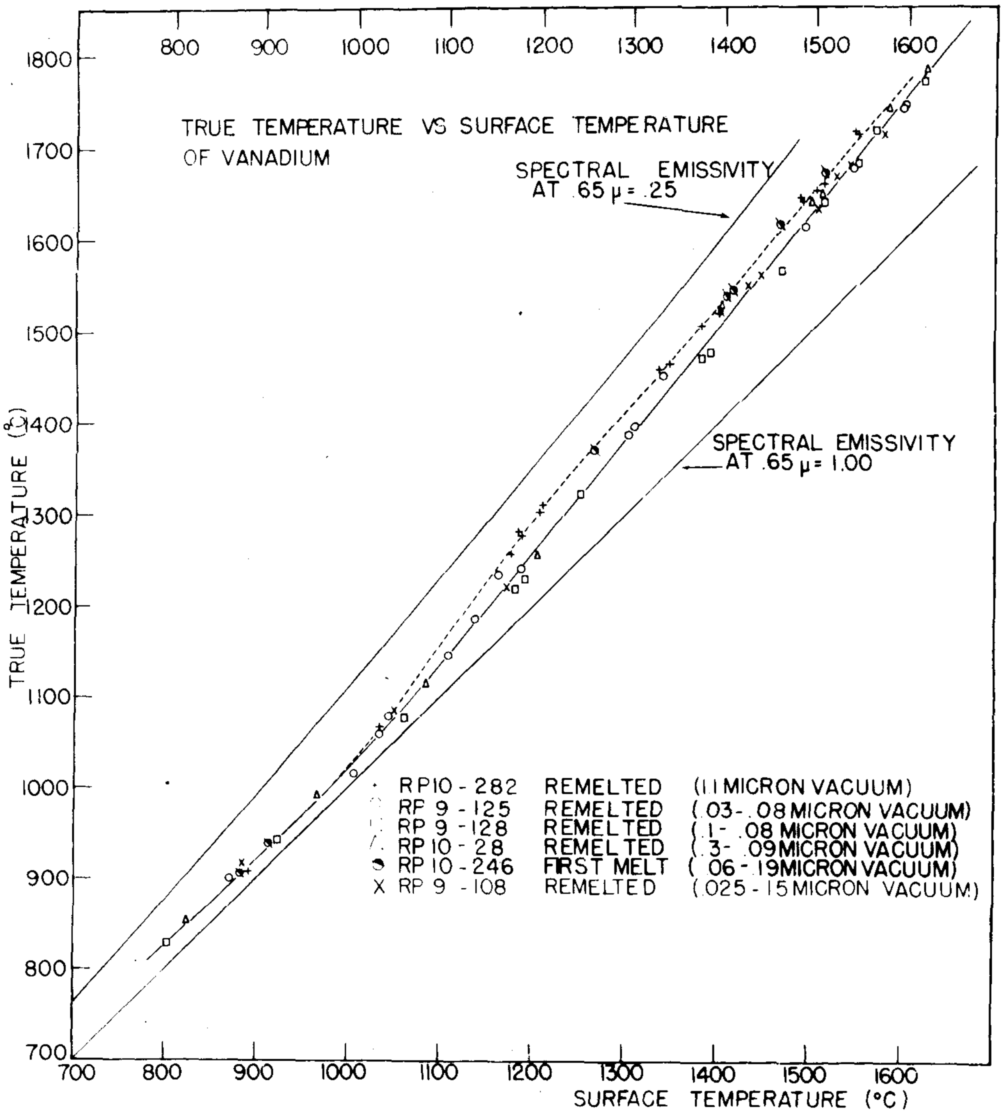


Figure 57. Surface Temperature of Vanadium vs True Temperature.

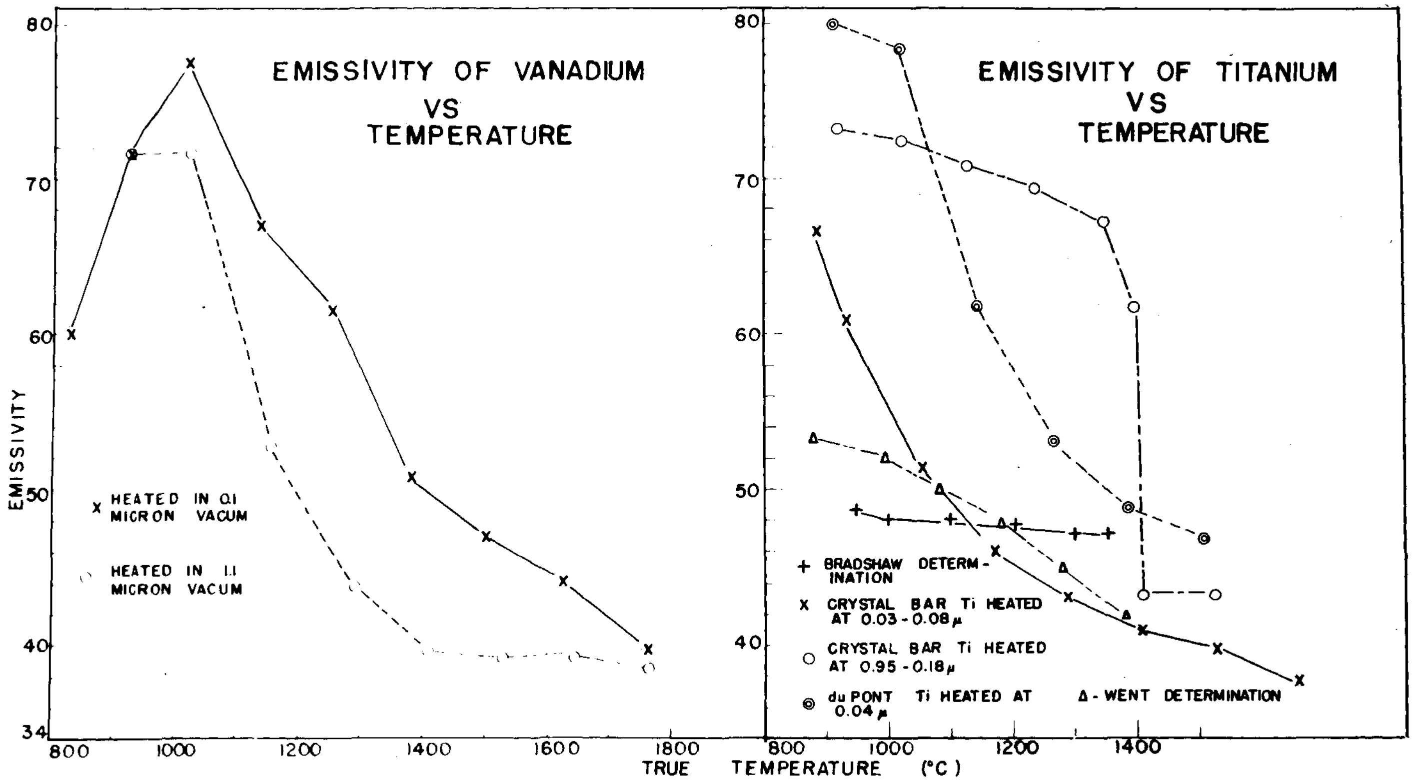


Figure 58. Emissivities of Titanium and Vanadium vs Temperature.

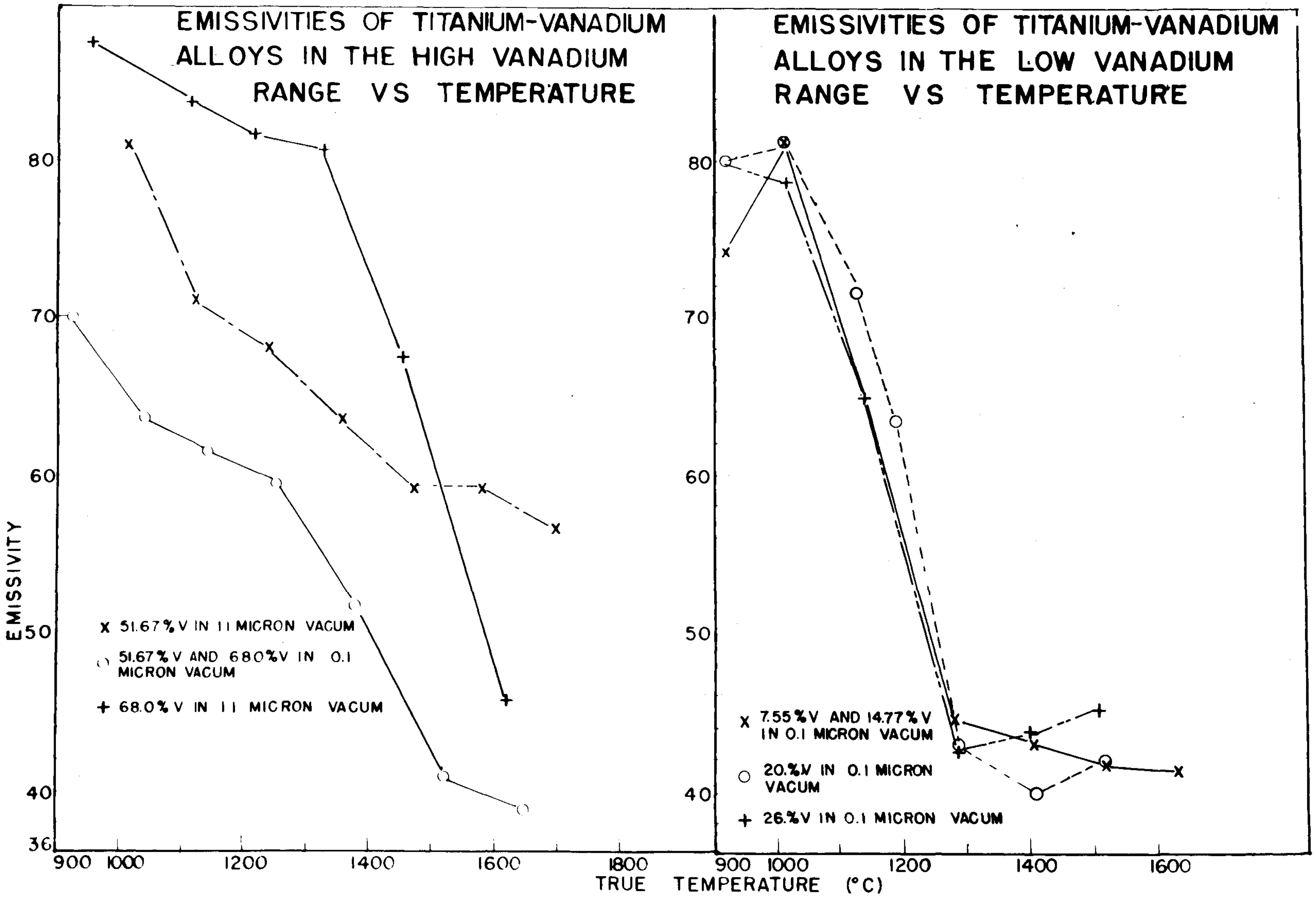


Figure 59. Emissivities of Titanium-Vanadium Alloys.

An examination of the graphs of emissivity of the metals and alloys as a function of temperature shows that emissivities tend to decrease as the temperature increases, with a few exceptions that show an initial increase in emissivity with increasing temperature. In the present series of experiments, pure vanadium is seen to exhibit an overall decrease in emissivity from 800° to 1700° C, but with intermediate values passing through a maximum near 1000° C. The contour of the emissivity against temperature curve is much the same if the melting is carried out in the presence of greater quantities of oxygen or nitrogen as when melting in the 1.1 micron vacuum. On removing the metal specimens from the melting point furnace after a determination, the surface of the metal or alloy was usually found to be much more reflecting than before the determination. The metal was apparently taking on the emissivity characteristics of the more highly reflecting metals. This alteration of the emissivity values is undoubtedly due to the progressive absorption of oxygen or nitrogen or both on the metal surface. That this is largely a surface phenomenon may be seen from an examination of the melting point specimens that were heated under a 0.1 micron vacuum. By carefully grinding off the thin surface layer, the underlying metal, possessing approximately its original appearance and hardness, is revealed.

Results of the present determinations may be compared with values of Michels and Wilford (45) on commercial titanium. Their determinations were carried out in a 10^{-6} millimeter vacuum, as compared to the 10^{-4} to 10^{-5} range of the present work. However, their metal in the form of 1/4 inch rod, drilled to form a black-body tube, had been annealed in air at 1200° C several times during the drawing operation and given a vacuum anneal at 1400° C. Some superficial oxygen or nitrogen could very well have been present as a result of the drawing operation. The high temperature limit for emissivity data was restricted by the vapor pressure of the titanium at these low pressures. Their values ranged from 0.72 at 777° C to 0.69 at 1127° C, passing through a minimum of 0.59 at 877° C.

Determinations of Bradshaw (41), apparently carried out with considerable care at 10^{-6} millimeters vacuum showed values that are given in Figure 58. Oxygen and nitrogen contents given for this titanium were 0.073 and 0.19 per cent, respectively, and no increase in either could be detected after a run.

Values of Went are also shown in Figure 58 (46).

4. Summary of emissivity results

The results of the determination of emissivities in a 0.1 micron vacuum of the titanium, vanadium, and their alloys have been summarized in the graphs of the preceding section. Some of these values show an initial increase in emissivity before a decrease as the temperature is raised, but all eventually decrease as the temperature is raised further. This appears to be associated with the superficial absorption of oxygen or nitrogen. The results may be explained in a very qualitative manner by consideration of the reverse process to light emission, that of the light absorption of these alloys.

In general, good absorbers are good radiators and good reflectors are poor radiators. Thus metals showing higher values of light absorption or smaller reflectivity for a given wavelength, 6500 Å in this case, have larger spectral emissivities at this wavelength. It is likely that the high spectral emissivities at 6500 Å may be related to the extent of overlapping of the d, s, and p bands or orbitals, and to the availability of free electrons in the metals and alloys.

The initial increase in emissivity observed for vanadium seems reasonable in the light of the effect of impurity level in increasing the available energy states. According to Seitz (47, p 326), " * * * impurity atoms or lattice imperfections induce additional energy states * * * These states lie in the regions between continuous bands." Thus by increasing the available number of levels in vanadium by traces of oxygen, for example, the light absorption and, consequently, the emissivity will increase. If it is assumed that still further amounts of oxygen reduce the number of free electrons available for interaction with the low energy 6500 Å radiation, then less absorption can occur for the oxidized metal at that wavelength. As a result, the radiation properties are similarly affected and the metal becomes less like a black body. In other words, the emissivity decreases. These same considerations should apply to titanium and its alloys with vanadium, as well as to other reactive metals of sufficient purity.

From the results of the emissivity runs and the proposed explanation of the results as being due to progressive up-take of oxygen, the inference is that the melting points of titanium and vanadium are considerably altered because of the presence of oxygen in the metal. However, it must be remembered that the emissivity effects are restricted to the surface, or to within about 200 Å of it (48), and that the condition of the surface may be considerably different from the bulk of the metal, the thin golden layer on crystal bar titanium being an example, a layer that could be ground off to uncover the underlying base metal which presented almost the original hardness and appearance.

The results of the determinations of Bradshaw (41) that have been mentioned earlier indicate by the very slight change in emissivity with temperature that only a trace of oxygen was being introduced by melting in the 10^{-6} micron vacuum. The oxygen level of that metal was 0.73, the nitrogen 0.19 per cent. The determination by Went (46) probably duplicates the present experiments more closely as far as vacua are concerned, the decrease in emissivity that he found being probably a result of oxygen or nitrogen up-take.

5. Melting temperature from emissivity measurements

A further use for emissivity measurements was to determine the melting temperatures of the titanium-vanadium alloys. By measuring the temperature immediately above the sight hole just after it had closed, and referring to the plot of surface temperature against true temperature, the melting point of the metal could be estimated, and, in the case of the alloys, a temperature could be determined for estimating the liquidus. The assumptions involved are that the temperature has not dropped following hole closure, and that the emissivity of the outer surface does not change appreciably up to melting.

Melting temperatures obtained by this method are shown in Table 13 along with values obtained by the previous method of taking the maximum temperature in the black-body hole before that hole closed. This table also includes data on the vacuum under which each test was made and the maximum surface temperatures from which the melting temperatures by surface measurement were estimated.

An examination of Table 13 shows that in most cases, roughly the same melting values are obtained by either method. More reliance should be attached to determinations by the hole closure method, since more unknown factors are involved in the maximum surface temperature method. For example, the result on crystal bar titanium is more likely to be in error when compared to determination by the hole closure method. This value of 1631° C was obtained on the fourth melting of a sample which originally melted at 1677° C as shown in Table 4. Deviation of the two methods may be ascribed to the breakdown

Table 13

Melting Temperatures (M. T.) of Titanium-Vanadium Alloys by Maximum Surface Temperature and Hole Closure Methods

Sample comp. by wgt.	Vacuum (microns)	Max. surface temp. (°C)	M. T. (°C) by surface	M. T. by hole closure (°C)
Pure V	1.1	1726	1910	1877
84.5% V	.07	1581	1720	1692
	.07	1559	1708	1697 (R1)
	.06	1556	1720	1728 (R2)
75.5% V	.09	1484	1626	1651
	.08	1525	1690	1662 (R)
68.0% V	.09	1501	1647	1669
	.07	1479	1631	1651 (R1)
	1.1	1553	1721	1710 (R2)
51.7% V	.085	1465	1603	1605
	1.1	1610	1710	1687 (R)
31.0% V	.1	1445	1580	1575
	.06	1462	1583	1579
26.1% V	.095	1454	1565	1567
	.085	1448	1568	1579 (R)
21.0% V	.1	1462	1584	1580
	.13	1448	1583	1579 (R)
20.0% V	.1	1459	1580	1590
14.8% V	.13	1485	1615	1605
3.14% V	--	1510	1636	1633
	.04	1486	1604	1626 (R)
Crystal Bar Ti	.095	1447	1567	1631

R -- Repeated melting determination carried out on same specimen just above in the table.

of the principal assumptions on which the maximum surface temperature method is based.

The results of both methods appear to indicate that small amounts of oxygen which were introduced at each melting tend to lower the melting temperature of the metals and alloys and further additions of oxygen increase the melting temperature. Thus, the alloy-oxygen system probably exhibits a slight minimum, followed by a sizable increase of melting temperature with appreciable amounts of oxygen.

C. Surface Tension

Approximate surface tensions were measured on arc melted titanium and vanadium, and on most of their arc melted alloys by the method of sessile drops (49), as a check on the melting temperatures of these materials. From an empirical standpoint, surface tensions of isomorphous metals generally tend to increase with melting point. This is undoubtedly the result of the tendency of both of these quantities to reflect the binding forces in a metal. Because of the tedious nature of melting temperature determinations in the case of the high melting reactive metals, it was originally hoped that by measuring the surface tensions of the metals at their melting points, and reference to a plot of surface tension against temperature, the melting temperatures could be approximated with much less effort.

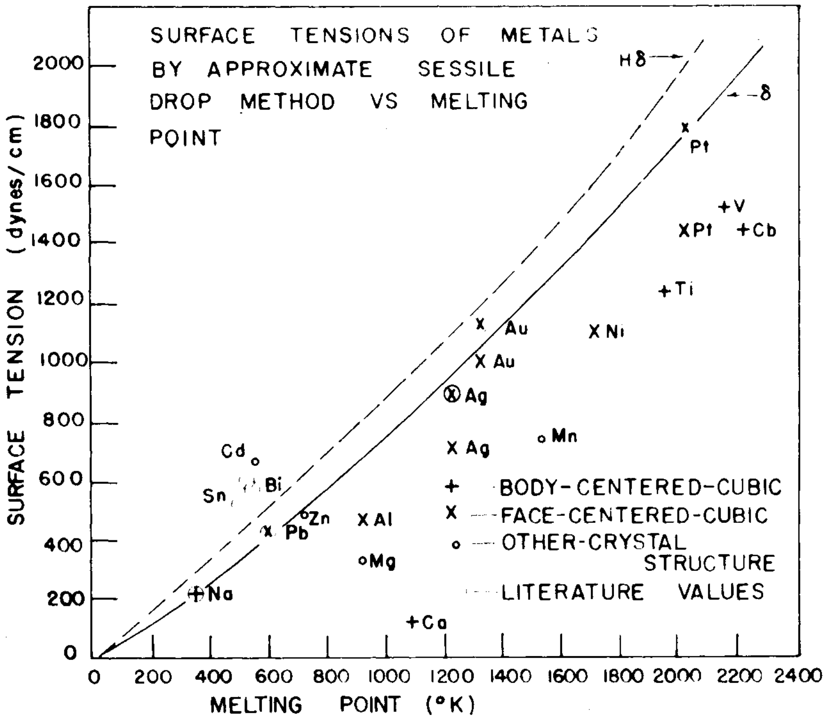
In the present experiments, the as-arc-melted alloy and metal buttons were taken to be sessile drops. The method involves first heating a metal or alloy under purified argon. The resulting solid button is then cut through the center so as to present a maximum cross-section which is somewhat elliptical in shape. This elliptical shape is especially characteristic of the upper portion of a button of a certain size range, where it is quite free to assume a shape independent of the form of the container while still in the liquid condition. The major axis of this ellipse is measured with calipers, and the maximum height above this axis is next measured. From these two measurements and the alloy density, the surface tension may be calculated for the metal using the approximate formula of Worthington for large sessile drops (50). Thus

$$\gamma = \tfrac{1}{2} h^2 g\, d\, (1.641\, L/(1.641\, L + h)$$

where h is the maximum height above the maximum radius L, g the gravitational constant (980.6 dynes), and d the alloy density at the melting point. The drop height is seen to be the important parameter since it enters as a squared quantity.

The interrelation of the surface tensions of liquid metals at their melting points and the melting points on the absolute scale is shown graphically in the lower graph of Figure 60. The solid line curve is drawn from the literature values (51) for sodium, lead, silver, gold and platinum as determined by various methods. Experimental values of surface tension have been determined on a number of metals by the sessile drop approximation and are included in Figure 60. These values are generally lower than the established values that were used to draw the curve, indicating that for determination of absolute surface tensions, the sessile drop method is inadequate under the conditions employed.

These determinations were made on drops of varying sizes, as the amounts of certain metals available for the measurements were limited. The effect of the drop size of solidified arc melted crops on the observed surface tension of vanadium is shown in the upper part of Figure 60. It may be noted that as the drop diameter increased to somewhat greater than 3 centimeters, a fairly constant value of the observed surface tension by the sessile drop



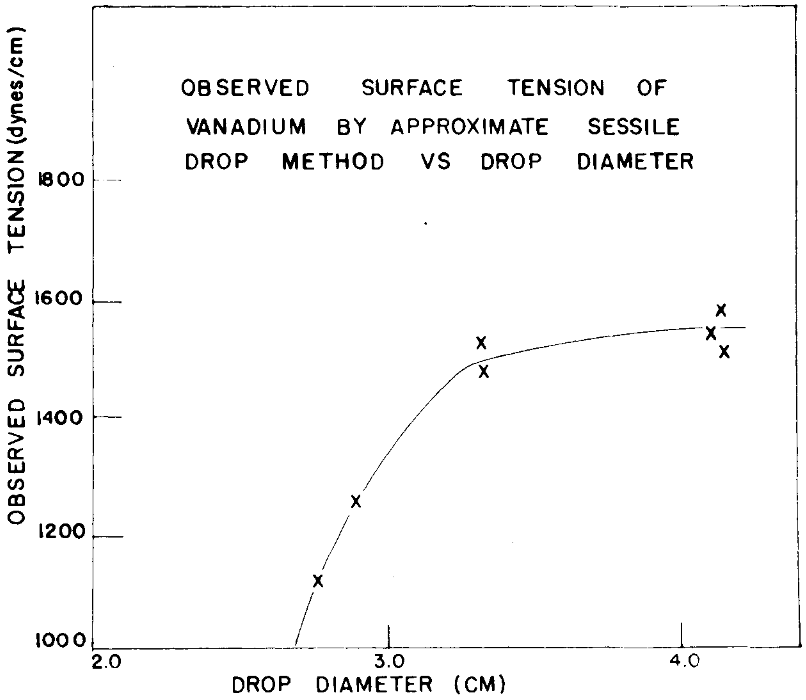


Figure 60. Surface Tensions.

method was obtained. The same trend of observed surface tension with solidified drop size was also found for thorium and nickel. In the case of thorium, the average surface tension of 915 dynes/cm was found for the 3.21 cm drop diameter, and 1006 dynes/cm for the 4.13 cm drop. For nickel, the surface tension of 1120 dynes/cm for the 2.78 cm drop diameter increased to 1200 dynes/cm for the 3.03 cm drop.

The effect of employing the room temperature density instead of the lower density at the melting point is to increase the observed surface tension somewhat. The effect of drop size on the accuracy of surface tension measurements has been reviewed by Porter (52) and has been shown to be a function of density and drop radius for liquids. Since much greater deviations in surface tension were observed in the case of the solidified sessile drops than have been covered by Porter's discussion, some other variable such as the cooling characteristics of the drop is undoubtedly of greater importance.

Each metal button was melted under argon which had been purified by zirconium as a getter. The arc was played upon the metal and moved over the surface till the entire upper part of the drop was molten. The metal was well stirred by the arc during this operation so that no impervious oxide skin had a chance to form over the surface such as might have occurred in the case of the pendant drop method (53). Freezing of the molten drop usually began at the edges and progressed radially towards the center, with the last liquid to freeze at the center of the drop. A tendency to pipe, i.e., to form a depression in the top of the button, was evident in most cases. Cooling from the edges tended to reduce the observed height, which is the most important variable to be measured, and consequently the observed surface tension. The value of h used in the equation for the calculation of surface tension was taken to be the maximum observed height above the maximum drop diameter, rather than the height at the midpoint. The maximum height was usually located midway between the drop edge and its center.

Determinations of the surface tensions of the titanium-vanadium alloys were carried out on approximately constant volume drops in order to give drops of about the same diameter and cooling characteristics. It was hoped that the diameter would be sufficiently large that the observed surface tension would lie on the plateau of the surface tension against drop diameter curve (Figure 60). The averaged results of these determinations are shown graphically in Figure 61. In addition, most of the drop

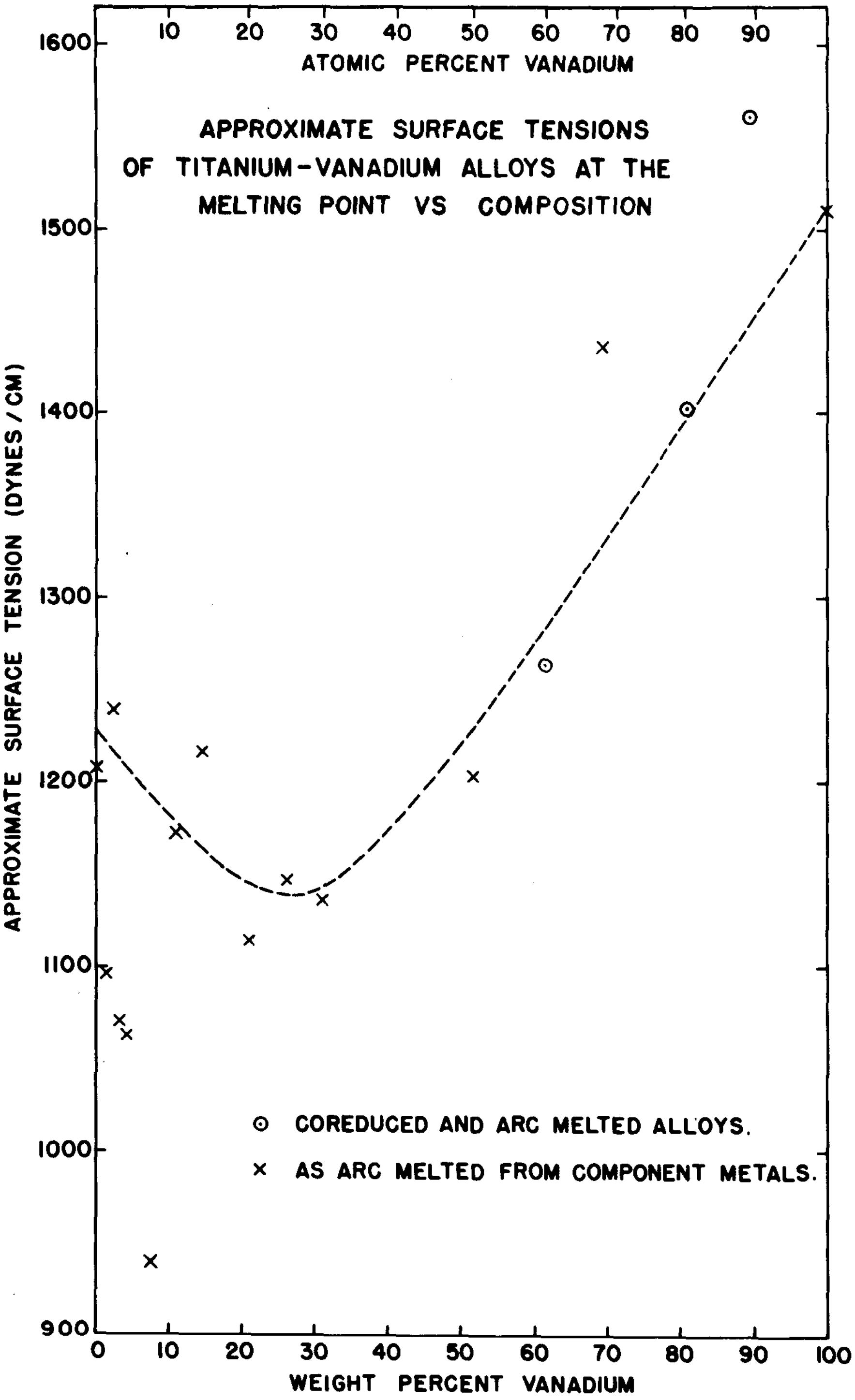


Figure 61. Approximate Surface Tensions of Titanium-Vanadium Alloys.

diameters and densities are tabulated in Table 14. With the exception of a few low values that resulted in some cases from the use of smaller drops, surface tensions tend to follow the course of the solidus curve, exhibiting a minimum at approximately 30 per cent vanadium. Thus it would seem in the case of the titanium-vanadium system at least, a system in which each metal has the same high temperature crystal structure and exhibits complete high temperature solubility, that empirically, surface tension furnishes an index of the melting point, and is directly proportional to it.

Instead of being proportional to the surface tension, it has been suggested (54) that the melting point on the absolute scale might be proportional to the surface enthalpy, H . A curve drawn from calculated values of the surface enthalpy for sodium, lead, silver, gold and platinum against the absolute melting point is shown by the dotted line in Figure 60. The enthalpy relationship, of course, follows the same general trend as surface tension and on the graph has the same ordinate units.

There may be some justification for this relationship involving enthalpy (55). Stefan hypothesized that an increase of the surface of the liquid by the cross section of a molecule requires the same expenditure of energy as

Table 14

Approximate Surface Tensions of the Titanium-Vanadium Alloys

Sample (wgt. %)	Drop height (cm)	Drop diameter (cm)	Density (g/cc)	Surface tension (dynes/cm)	
duPont Ti	.825	4.565	4.52	1237	1208
	.82	3.78	4.52	1179	
1.2% V	.785	4.39	4.529	1120	1097
	.76	4.37	4.529	1073	
2.5% V	.83	4.40	4.56	1252	1240
	.82	4.417	4.56	1228	
3.1% V	.78	4.18	4.553	1109	1071
	.75	4.20	4.553	1032	
4.2% V	.76	4.25	4.57	1064	1064
	.76	4.24	4.57	1064	
5.3% V	.79	4.78	4.58	1168	1168
	.79	4.68	4.58	1168	
7.6% V	.70	3.80	4.61	905	940
	.73	3.79	4.61	974	
10.9% V	.795	4.32	4.66	1181	1174
	.785	4.32	4.66	1167	
14.8% V	.80	4.39	4.73	1217	1217
	.80	4.39	4.73	1217	
20.0% V	.78	4.34	4.76	1162	1189
	.79	4.41	4.76	1196	
	.80	4.25	4.76	1210	
21.0% V	.76	4.18	4.78	1110	1116
	.765	4.18	4.78	1122	
26.1% V	.775	4.18	4.86	1168	1148
	.76	4.20	4.86	1127	

Table 14 (Cont'd)

Sample (wgt. %)	Drop height (cm)	Drop diameter (cm)	Density (g/cc)	Surface tension (dynes/cm)	
31.0% V	.76	4.058	4.93	1138	
51.7% V	.765	4.08	5.26	1228	1204
	.76	4.08	5.26	1212	
	.745	4.085	5.256	1172	
69.5% V	.80	4.32	5.54	1417	1436
	.81	4.33	5.54	1455	
75.5% V (rough surface)	.775	4.125	5.66	1358	
84.5% V (surface shows asterism)	.865	4.374	5.843	1725	
V	.80	4.10	6.10	1548	1511
	.79	4.06	6.10	1508	
	.78	4.10	6.10	1477	
Arc melted co-reduced alloys**					
100% Ti***	.78	3.60	4.058	961	
10.4% V***	.73	3.48	4.528	945	
21.0% V***	.76	3.34	4.944	1100	
61.5% V	.785	3.185	5.413	1264	
81.0% V	.79	3.756	5.756	1402	
89.5% V	.83	3.39	5.908	1561	

*Drop diameter possibly too small.

**Where possible resulting alloy compositions have been estimated from alloy densities.

***Composition in weight per cent charged to bomb.

the evaporation of the molecule. He developed the following relation

$$2\ (V/N)^{2/3}\ (\ \gamma\ -\ T\,{}^{\Delta\gamma}/\Delta T)\ =\ \Delta H_v/N$$

where V is the molar or atomic volume, N is the Avogadro number, γ the surface tension, T the absolute temperature, and ΔH_v the heat of vaporization. In general, the heat of vaporization is given by the expression $\Delta H_v = T\ \Delta S_v + V\ \Delta P$, where ΔH_v is the heat required to convert one mol of liquid to vapor at a given temperature, T; ΔS_v the entropy of vaporization, V the volume of the system, and ΔP the pressure change during vaporization. As long as the change in pressure is small enough to render the last term negligible as compared to the first, the approximation $\Delta H_v = T\ \Delta S_v$ results. The entropy change in passing from liquid to vapor has been found to be fairly constant, at least at the boiling point, Trouton (56), or for a constant vapor concentration, Hildebrand (56), for analagous liquids, although the entropy change of associated differs from non-associated liquids. It might be expected that the change in entropy of atoms in passing from the solid in a given crystal modification, body-centered cubic for example, to a given volume at constant pressure in the vapor state, would be constant in that crystal system at least, as that atom is passing from an environment possessing a certain degree of order to a disordered state (vapor at a given pressure and volume). As long as the entropy change in fusion is constant from metal to metal, and this is not a bad approximation for many metals (57), then the entropy of vaporization, which is given by the difference of the entropys of sublimation and fusion, should be somewhat constant. Substitution of $T \Delta S_V$ for ΔH_V leads to the expression

$$2\,(V/N)^{2/3}\,(\gamma - T\,{}^{\Delta\gamma}/\,\Delta T) = T\ \Delta S_V/N$$

where $(\gamma - T\,{}^{\Delta\gamma}/\,\Delta T)$ is equal to the surface enthalpy, H_γ.

In the case of the Stefan equation it has been necessary in the case of ether (58) to substitute for the 2 a factor of 2.76. This indicates that more energy is required to evaporate an ether molecule than to transfer it into the surface layer. In the present instance, solution of the above equation for ΔS_V gives a measure of the applicability of the constant entropy of vaporization assumption from metal to metal. Values of this quantity have been calculated and are shown below in Table 15.

Table 15

Apparent Entropies of Vaporization of Several Metals

Metal	Melting point (°K)	Estimated density at M. P. (g/cc)	Surface enthalpy dynes/cm	Apparent entropy of vaporization cal/mol°
Na	370.5	0.93	248	42.8
Pb	600	10.61	506	24.75
Ag	1233	9.17	1088	18.45
Au	1336	17.13	1268	19.52
Pt	2047	19.2	2051	19.0

Data on melting points, room temperature densities, and coefficients of expansion obtained from the literature (59), have been employed to calculate densities at the melting point. Values of the surface enthalpy have been calculated from literature values of the surface tension and the temperature coefficient of surface tension (51). As an example of the required data for calculation of a value for the entropy of vaporization ΔS_v in the case of silver we have:

Melting point = 1233° K
Surface tension at 1323° K = 916 dynes/cm
$\Delta \gamma / \Delta T$ (in the 1300° K range) = -0.13

Coefficient of linear expansion = 19.7×10^{-6} in/°C = 50×10^{-6} cm/°C .

Density at 20° C = 10.49 g/cc .

The surface tension of silver at its melting point is seen to be

$$1323 - (1323^\circ - 1233^\circ)\ \Delta\gamma / \Delta T = 916 - (90^\circ)(-0.13)$$

$$\gamma = 928 \text{ dynes/cm} .$$

The surface enthalpy given by the expression $H_\gamma = \gamma - T\ \Delta\gamma / \Delta T$ gives the value of 1088 dynes/cm for silver at the melting point.

From the coefficient of linear expansion, the coefficient of cubic expansion may be approximated by multiplying by 3 (60), giving in the case of silver a value of 150×10^{-6} cm^3/° .

The estimated volume occupied by 1 cc of silver after heating to the melting point is $1 + (1233 - 293)(150 \times 10^{-6}) = 1.144$ cc. The density at the melting point is consequently given by the

$$(10.49 \text{ g/cc})\ (1.0/1.144) = 9.17 \text{ g/cc} \quad @\ 1233^\circ \text{ K} .$$

Substitution of the data for silver in the equation $\Delta S_V = 2\ (M/N\ d)^{2/3}\ H_\gamma\ (N/T)$ enables the entropy change to be found. In the equation, M/d has been substituted for V the molar or atomic volume, M being the atomic weight in this case, and d the density at the melting point. Thus,

$$\Delta S_v = (2)\ \ (107.9)/(9.17)(6.023 \times 10^{23})^{2/3}$$
$$(1088)\ (6.023 \times 10^{23}/1233)$$

$$\Delta S_v = 77.15 \times 10^7 \text{ ergs/mol}^\circ \text{ or } 77.15 \times 10^7 \text{ ergs/mol}^\circ$$
$$(1.987 \text{ cal}/8.314 \times 10^7 \text{ ergs}) = 18.45 \text{ cal/mol}^\circ$$

Results obtained in a similar manner for several other metals which were used to prepare the graph of surface enthalpy against melting point of Figure 60 are shown in Table 15.

It is seen that the values of entropy of vaporization obtained by this method differ considerably when high and low melting metals are compared. Consequently, melting points calculated by using the constant entropy assumption will be in error if an attempt is made to apply the modified Stefan equation over too wide a temperature range.

The entropy values calculated in this same manner for the alloys of the titanium-vanadium system are shown in Table 16. Because the temperature coefficient of the surface tension has not been determined for these alloys, the surface enthalpy could not be calculated directly. It is seen that for a number of metals (51), however,

Table 16

Apparent Entropies of Vaporization of Titanium-Vanadium Alloys

Alloy (atomic %)	Melting point (°K)	Density (g/cc)	Atomic wgt. (g/cc)	Surface enthalpy (ergs/cm)	Apparent entropy of vaporization (e.u.)
100% Ti	1953	4.518	47.90	1403	13.96
5.01% V	1903	4.58	48.04	1358	13.82
10.34% V	1888	4.66	48.22	1363	13.83
14.02% V	1873	4.73	48.38	1404	14.23
20.0 % V	1853	4.78	48.47	1301	13.25
24.92% V	1843	4.86	48.67	1332	13.53
30.0 % V	1851	4.93	48.81	1323	13.32
50.15% V	1878	5.26	49.44	1392	13.29
68.0 % V	1933	5.54	49.98	1629	14.78
80.0 % V	1984	5.76	50.33	1600	13.80
(coreduced and uncorrected for fogging)					
100% V	2133	6.10	50.95	1722	13.40

that this coefficient is approximately -0.1 dynes/cm°. By assuming this value over the entire phase diagram, an approximate value of the surface enthalpy and in turn a corresponding entropy of vaporization may be found. Contributing to the approximate nature of the results is the fact that values of the surface tension as determined by the sessile drop method in these experiments are undoubtedly too low. A further approximation for these particular alloys is the use of the room temperature density instead of the density at the melting point.

Except for the value for the 68 atomic per cent vanadium alloy, the mean value of 13.64 ± .31 entropy units for the other samples is considerably more constant than was found for the metals in Table 15. The value for the titanium-vanadium alloys is to be compared with the entropy of vaporization at the normal boiling point of about 21 cal/mol° (56), or the value at a vapor concentration of 0.005 mols per liter of between 26 and 27.8 entropy units for non-associated liquids (56). The value for zinc, for example (56), at 0.005 mols per liter concentration of the vapor is 26.4 e.u.

The lower values obtained for the apparent entropies of the titanium-vanadium alloys may be due to a number of causes. First, the premise upon which the surface enthalpy-temperature relation is based may be faulty. Instead of the factor 2 before the previous expression for apparent entropy, a larger number may be required even if the proper value of the surface enthalpy be employed. This would indicate that it takes more energy to vaporize an atom than to bring it from the bulk of the liquid to the surface and would certainly be a reasonable modification of the equation. The low values obtained for the surface tension by the method of sessile drops (Figure 61) undoubtedly are responsible for much of the discrepancy in entropy values.

Thus the relative constancy of the apparent entropy values in the titanium-vanadium system warrants a more thorough study of the surface enthalpy against melting temperature relation of this and other systems and metals by a more exact method.

The values of surface enthalpy have been arrived at by assuming a constant temperature coefficient of surface tension of -0.1 dynes/cm°. Since this temperature coefficient has not been measured by estimated, it might properly be left out of an admittedly approximate equation. Thus by substituting the surface tension for the surface enthalpy and employing the same experimentally determined liquidus temperatures densities, and compositions as before, the mean value of the constant corresponding to the entropy of vaporization was found to be 11.91 ± .30 e.u. for the same samples. This indicates that surface tensions alone should give a fairly reliable measure of the relative melting temperatures of the various titanium-vanadium alloys when such a modification of the Stefan equation is used.

An improvement in the surface tension measurements at the melting point could be effected by some such modification as the following. A large drop of metal or alloy could be photographed in the arc melting furnace. This would give the drop contour without the distortion that occurs on cooling. The same drop could next be photographed at room temperature while still in the arc melting furnace. These two photographs and a separate measurement of the density at room temperature would permit the coefficient of expansion and the density at the melting point to be estimated more closely. By repeating measurements several times on a single alloy so as to get a true representation of the drop contour, a good value of surface tension at the melting point should be possible with less inconvenience than by the use of other methods.

A further study of the relation of surface tension to melting temperature should be made. The method of sessile drops, suitably modified, should prove satisfactory for this purpose. This work will indicate how far the correlation of surface tension at the melting point and the melting point can be extended.

D. Electrical Resistivity

Electrical resistivities were measured in order to obtain additional evidence on the nature of the titanium-vanadium alloys. Both resistivities and tensile strengths were measured on the same specimens which were exclusively of Series II alloys. Pretreatment in the form of hot or cold work is usually indicated for each sample. After the alloys had been rolled into strips of approximately 1 millimeter in thickness, tensile specimens were milled from each. A Kelvin bridge, filled with silver knife-edge contacts at a separation of 1.5 inches was used to measure the resistance of the alloys. Usually three to five resistance measurements were taken for each sample and an average value was obtained. A ball point micrometer was used for making measurements of both the thickness and width for finding an average cross-sectional area. As-arc-melted metal was used as the starting material for preparation of tensile specimens in practically all cases. Slabs of about 1.75 inches in thickness, 0.5 inches in width and 0.25 inches in thickness were cut from arc melted buttons, placed on a heated nickel sheet in a silica tube furnace and allowed to heat up under an atmosphere of argon. After approaching the furnace temperature of about

800° C in a two minute heating period, the alloys were quickly withdrawn from the furnace and passed through the rolls at reductions ranging from 1 to 20 per cent per pass, then returned to the furnace immediately for reheating. The last passes were carried out without resetting the rolls so that the resulting alloy sheet would be of more uniform thickness of about 1 millimeter. The smaller per cent reductions were employed for the hardest alloys, i.e., those ranging from 7 to 20 per cent vanadium and from 50 to 85 per cent vanadium.

So that the specimens might be milled without dulling of the milling cutter, they were given a final one or two minute soak at the furnace temperature, and a water quench. All but four of the hot-rolled alloys were rolled at approximately 800° C; those four, however, were rolled between 550° and 600° C. Oxide scale was removed mechanically by careful hand grinding and polishing in order to provide good electrical contact for the resistivity measurements. A typical set of resistance measurements is given for the 51.8 per cent vanadium alloy. The approximate sample size and usual number of readings are indicated here.

Width	Thickness	Resistance between contacts (ohms)
.2468	.0471	.004419
.2464	.0474	.004416
.2455	.0474	.004415
.2446	.0476	.004422
.2454	.0474	.004415
.2453	.0473	
.2451	.0470	.004417 average
.2462	.0472	
.2457" average	.0473" average	

From these average values, the resistivity may be calculated from the expression $\sigma = A \cdot R/L$; where L, the specimen length, is the distance between contacts on the specimen, in this case 1.5 inches; A, the cross-sectional area of the specimen as obtained from the average width and thickness measurements; and R, the measured resistance in ohms. The resistivity determined for the above run was 108.5 ± .8 microhm-cm.

Values of the resistivities determined in this manner for a number of alloys are included in Table 17 and shown graphically in Figure 62. The treatment of the hot-rolled Series II alloys included a final water quench from about 800° C. The hot-rolled and vacuum annealed alloys were furnace cooled from about 800° C.

An indication of the reproducibility of the results is given by measurements on the 21 per cent vanadium

Table 17

Resistivities of the Titanium-Vanadium System

Composition (wgt. %)	Treatment	Resistivity at 25° C (microhm-cm)	Resistivity at 25° C after 800° anneal (microhm-cm)
100 % V	88.1% H.R.	31.43	29.3
100 % V	84.9% C.R.	29.7	28.4
100 % V	82.5% H.R.*	29.8	
100 % V	C.R.	23.6	28.54
75.5% V	77.2% H.R.	70.5	65.9
69.5% V	66.4% H.R.	73.8	76.9
51.7% V	81.3% H.R.	108.5	
31.0% V	89.0% H.R.	153.8	
26.1% V	87.3% H.R.*	157.4	
26.1% V	87.3% H.R.*	158.6	
21.0% V	77.8% H.R.	175.5	
21.0% V	77.8% H.R.	173.4	171.2
21.0% V	77.8% H.R.	172.4	
20.0% V	92.2% H.R.	196.6	
14.8% V	77.4% H.R.	182.6	111.1
7.6% V	85.1% H.R.	121.2	99.3 104.7
7.6% V	18.5% C.R. then 78.8% H.R.	117.9	92.5 87.8

Table 17 (Cont'd)

Composition (wgt. %)	Treatment	Resistivity at 25° C (microhm-cm)	Resistivity at 25° C after 800° anneal (microhm-cm)
4.2% V	90.6% H.R.	107.3	81.0
2.5% V	85.5% H.R.*	87.8	86.1
1.20% V	86.9% H.R.*	72.5	68.6
Ti % V	86.6% H.R.*	67.4	65.3

Alloys hot-rolled between 850° and 800° C followed by a two minute stress relief and water quench.

*Alloys hot-rolled at 550° to 600° C, stress relieved at that temperature and water quenched.

alloy. After hot-rolling at about 800° C with a reduction of 77.8 per cent, three determinations on three separate samples of this alloy gave a mean value of 173.8 ± 1.3 microhm-cm for the resistivity. Following a vacuum anneal at 800° C and furnace cooling from that temperature, the somewhat lower value of 171.2 microhm-cm was found for this alloy in a single determination.

Resistivities of the hot-rolled quenched alloys increase rapidly with additions of vanadium up to a maximum for about 20 weight per cent vanadium. Inspection of the graph (Figure 62) shows that annealing these

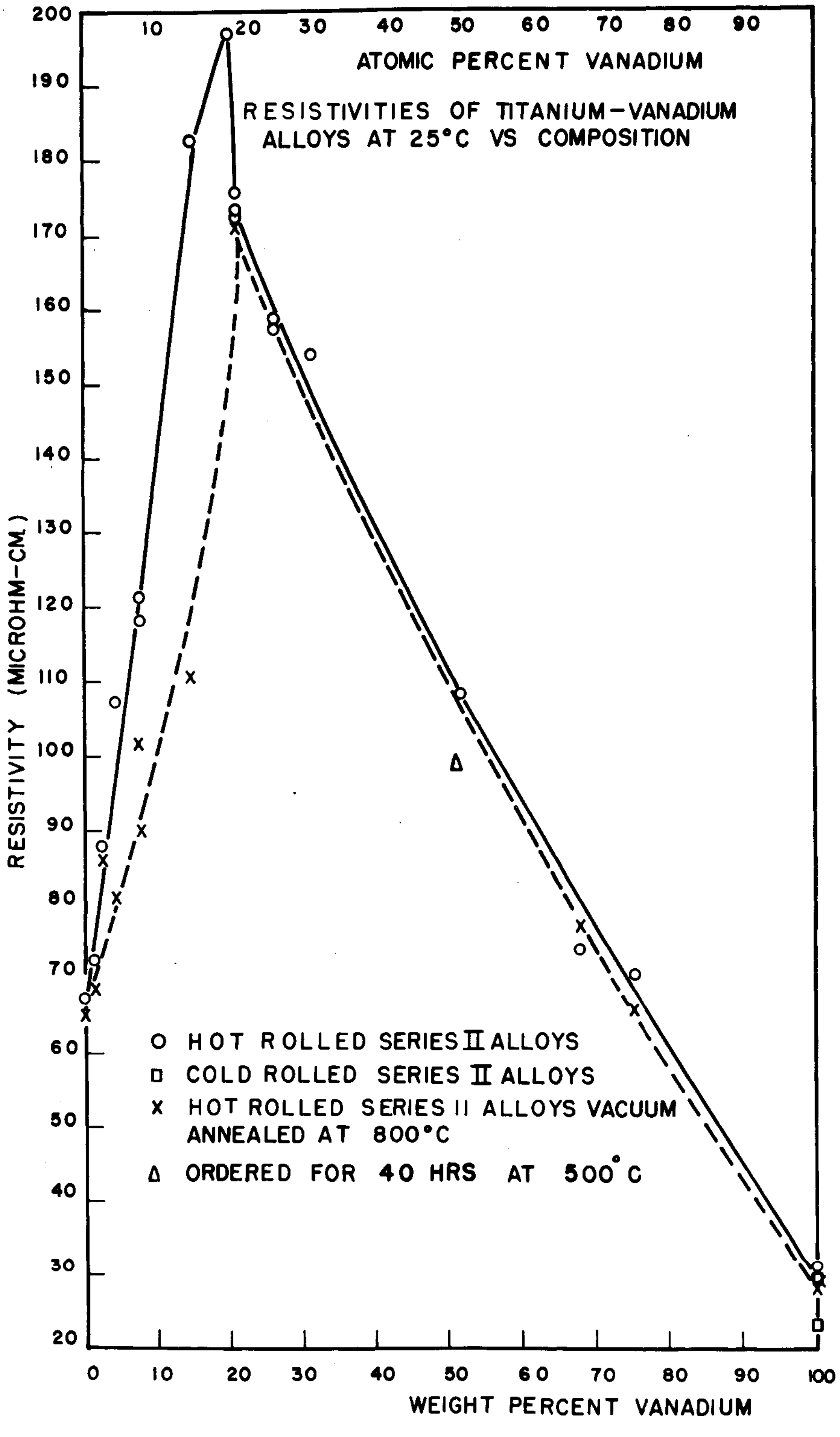


Figure 62. Resistivity vs Composition.

samples drops the resistivity markedly for the high-titanium alloys. The most remarkable drop in resistivity as a result of the 800° C vacuum anneal occurred for the 14.8 per cent vanadium alloy which exhibited a decrease from 182.6 to 111.1 microhm-cm on annealing. This composition is close to the maximum in the hardness curve for the as-arc-melted alloys of Series II. The stress relief anneal given these alloys might be expected to lower the hardness as well as the resistivity. The high titanium alloy undergoing the least change in resistivity on annealing is the 2.5 per cent vanadium alloy. The abnormal resistivity in this case is undoubtedly related to the increased hardness accompanying the "diffusionless transition" (24) that apparently occurs at that composition.

A consideration of the annealed alloys and their resistivities as a function of composition in Figure 62, shows that the resistivity rises steadily from pure vanadium to the 21 per cent vanadium alloy. This range corresponds to that of the beta solid solution. Thus, as the body-centered cubic structure of vanadium is increasingly distorted by the larger titanium atoms in substitutional solid solution, the resistivity is seen to increase to a maximum. With still higher titanium content, the alloy enters the two phase alpha plus beta region where the resistivity is some combination of the resistivity of the alpha and the beta phases.

Resistivities of both the hot-rolled and quenched, and the hot-rolled and annealed alloys lie close to one another in the beta solid solution range. The fact that the hot-rolled alloys were given a final stress relief anneal and quench undoubtedly brought these values closer to one another than if the resistivities had been taken of un-annealed hot-rolled alloys.

The data on Figure 62 does not lend any support for a solid solution of vanadium in alpha titanium since no real discontinuity in the curves is evident in the very low (1.2 per cent) vanadium range.

The only resistivity values originally available for a titanium-vanadium alloy were for two 5 per cent vanadium alloys (5a). These two alloys, although showing somewhat different tensile properties, each gave the same resistivity value of 75.5 microhm-cm. The value obtained by interpolation of the resistivity against composition curve in the present series of experiments for the 5 per cent vanadium alloy, was about 83.0 microhm-cm, for an annealed sample. This difference is not too remarkable in view of the strong dependence of this quantity on the source of the component metals.

According to van Arkel, the resistivity of the best grade of titanium is 47.5 microhm-cm (25). The titanium used in the present series of experiments of resistivity 65.3 microhm-cm, is seen to be of somewhat higher quality than the usual run of commercial metal of resistivity 79.8 microhm-cm (43) (61).

The vanadium used in these experiments had a resistivity of 28.5 in the annealed state as compared with the high purity metal prepared by Marden and Rich (11) having a resistivity of 26.1 microhm-cm. One sample of vanadium prepared here exhibited a resistivity of about 24 microhm-cm.

The resistivities of the entire titanium-vanadium system have been recently measured by Adenstedt and others (5b). Their values on furnace cooled alloys were lower than the values obtained in the present work partly because the measurements were carried out at 0° C. In the high titanium end of the system, this difference undoubtedly was in part due to the use of crystal bar titanium rather than commercial sponge metal. These investigators did not give values for the resistivity of vanadium but extrapolation of the curve in the beta region led to the unalloyed resistivity of 20 microhm-cm at 0^{o} C for that metal.

In view of the fact that vanadium forms a continuous series of body-centered cubic solid solutions over quite an extensive composition range, a distinct possibility exists for the formation of an ordered structure at the 50 atomic per cent vanadium composition. At this composition, the titanium atoms, for example, might be pictured as occupying the body-centered positions with vanadium atoms filling the corner positions.

According to Hume-Rothery, the introduction of a second kind of atom to form a substitutional solid solution with the first introduces strain into the resulting crystal in proportion to the difference in size of the two atoms. Too small a difference will cause little tendency towards ordering while too great a difference will cause precipitation such as occurs in eutectic formation (27). The effect of strain in the titanium-vanadium system is exhibited by the liquidus curve which shows this tendency towards eutectic formation. A dip in the liquidus which indicates a certain amount of incompatibility of the two species of atom, seems to be characteristic of most of the binary systems in which long range ordering has been found. The iron-cobalt system appears to be somewhat analagous to the present one in that both pairs are adjacent transition elements, have comparable crystal structures, and show the liquidus minimum. Ordering in the iron-cobalt system is indicated to begin at approximately 700° C (62) on cooling.

A 50.8 atomic per cent vanadium alloy was first heated to 800° C and held at that temperature 6 hours for the purpose of disordering it. The temperature was then dropped stepwise, allowing 16 hours at 650° C, 24 hours at 600° C, 32 hours at 550° C and 40 hours at 500° C. As a result of this treatment in a vacuum of less than 0.001 micron, the resistivity as measured on a Kelvin bridge had decreased from an estimated 106 microhm-cm to 99.3 microhm-cm.

This apparent drop in resistivity may be due to at least two causes. First, ordering may be present, and second, this alloy may lie in a two phase region at the lowest ordering temperature.

The presence of ordering could be tested, for example, by preparing alloys on either side of the 50 per cent composition. Annealing a 45, a 50, and a 55 atomic per cent vanadium alloy, for example, for considerable lengths of time at several possible ordering temperatures and measuring the resistivities before and after the anneals might reveal the nature of the alloys. A maximum drop in resistivity of these three should occur at the 50 per cent vanadium composition if ordering is present.

On the other hand, the 50 per cent vanadium alloy may actually lie in a two phase region at 500° C which is slow to attain equilibrium. If this is the case, the resistivity should also decrease, since the alpha phase that forms from the solid solution would have a lower specific resistivity than the original beta solid solution and at the same time in the course of formation would leave behind a beta solid solution that is lower in titanium than before and as a result has a lower specific resistivity. In this case, the alloy that rejects the most alpha phase will show the largest decrease in resistivity. Prolonged annealing of the 45, the 50, and the 55 per cent vanadium alloys at lower temperatures (500° C) and measurement of the resistivities before and after the treatment might indicate whether this were the valid explanation of the resistivity drop that was assumed. In this case, the greatest drop in resistivity should be observed for the 45 per cent alloy where the largest amount of alpha would be precipitated.

It is not possible, on the basis of the present experiments to distinguish with any certainty which of the two explanations of the drop in the observed resistivity is the correct one. However, on the basis of the reactivity of the 50 per cent vanadium alloy with etchants, and some metallographic data, the ordering seems the less probable.

E. Mechanical Properties

1. Cold rolling characteristics

The response of titanium-vanadium alloys to cold rolling was first determined on portions of the small specimens that had been quenched from 600° C for metallographic studies. The effect of cold working these alloys of Series I on their hardness is shown in Figure 63. Hardness generally tends to increase with amount of cold work for the pure metals and their alloys, in line with increasing amounts of strain introduced by the working.

A rather abrupt increase may be seen for pure annealed vanadium, initially at Rockwell "A" 36.2, which rises to a value of about R_A 47 with as little as 5 per cent reduction by cold work. Further reduction increases the hardness of the vanadium only moderately. With the exception of the 14.7 per cent vanadium alloy which broke

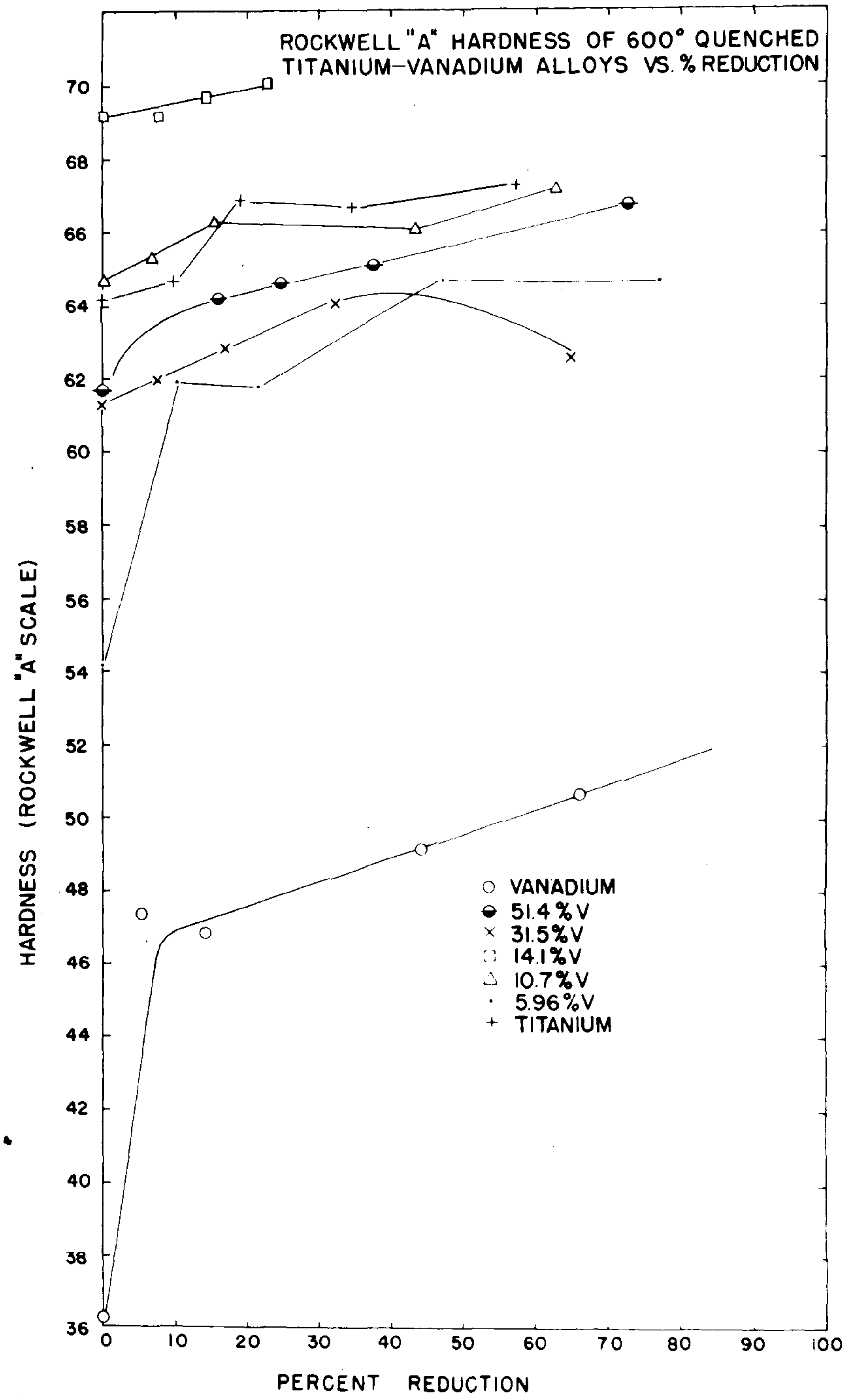


Figure 63. Cold Rolling Characteristics of Titanium-Vanadium Alloys.

after work hardening to R_A 70 at 23 per cent reduction, alloys were subjected to from 62 to 77 per cent reduction. Reductions ranging from about 2 to 10 per cent per pass were found to be satisfactory for all but the hardest alloys.

Similar treatment of the Series II alloys gave essentially the same relationship between hardness and cold working, the Series II alloys being slightly harder, however.

2. Hot rolling characteristics

Hot rolling characteristics of Series II alloys were determined at two temperatures. Alloy slabs with almost parallel sides were cut from arc melted buttons, the edges rounded to minimize stress concentration, and placed in an argon atmosphere furnace to heat. A 2 inch quartz tube surrounded by an electrical resistance furnace held the samples. The tube extended about 8 inches outside the furnace where it was reduced to 1/4 inch in diameter and connected by rubber tubing to an argon supply. To increase the rate of heat transfer to the alloy, they were placed on a nickel sheet within the furnace tube. Usually one or two minutes were allowed for the alloy to approach the furnace temperature after which it was hastily withdrawn, rolled, and returned immediately to the furnace for reheating before the next pass.

The first run was carried out with the furnace temperature between 520° and 620° C on samples ranging from 0.25 to 0.36 inches in thickness. For the most part, these samples were given an overall reduction in thickness of approximately 30 per cent, although the 4.2 per cent vanadium alloy was reduced 68 per cent, and the hard 10.9 per cent vanadium alloy by only 14 per cent. With only a few exceptions, hot rolling increased the hardness over that of the as-arc-melted alloys. Exceptions were the hard alloys ranging from 7.6 to 14.8 per cent vanadium. In this composition range, observed hardness was decreased by hot rolling. All but the 10.9 and 51.8 per cent vanadium alloys rolled without cracking appreciably under these conditions. An 8 per cent reduction cracked the 10.9 per cent vanadium alloy on the first pass into many pieces and a 7 per cent reduction per pass was too great for the 51.8 per cent vanadium alloy. In cases other than the two mentioned, reductions of from 5 to 15 per cent per pass proved to be satisfactory at this temperature.

After grinding off the scale left as a result of the preceding hot rolling operation, many of the same alloys were subjected to a further hot rolling under the same heating and rolling conditions. Reductions were considerably greater than before, most of them being in the neighborhood of 85 per cent, with this reduction being effected in from 10 to 15 passes. If the total reduction over both stages is considered, values of about 92 per cent reduction were obtained for most of the alloys.

This second stage of hot rolling was carried out in the same temperature range as before. Most of the alloys could be withdrawn from the furnace which was held between 520° and 620° C, and hot rolled so long as sufficiently small reductions per pass were employed for the harder compositions. For example, a 90 per cent reduction was obtained in the case of the 10.9 per cent vanadium alloy when 20 passes were used, instead of roughly half that number for the softer alloys. The 51.8 per cent vanadium alloy was hot rolled for 12, 18, and 28 per cent reductions in thickness per pass in successive passes, but cracked on the subsequent pass of 38 per cent reduction. As in the case of the first stage of the hot rolling involving smaller per cent reductions, alloy hardnesses increased somewhat with hot rolling except in regions of the harder compositions.

Hot rolling data were also obtained in connection with the preparation of tensile test specimens. This rolling was done on samples heated under argon in a furnace at 800° C. By employing reductions of from 5 to 10 per cent per pass, most of the alloys rolled satisfactorily at this elevated temperature, to give an overall reduction of from 66 to 92 per cent. As-arc-melted metal furnished the starting material for must of the alloys, though in the case of the 85 per cent vanadium alloy, the metal had been given a high temperature homogenization prior to the hot roll.

Some difficulty was experienced at this temperature with the 10.9 per cent vanadium alloy which failed on the first pass with about 5 per cent reduction. By employing smaller reductions per pass, even this alloy could probably have been rolled under these conditions.

To reduce the residual stresses and consequently the hardness in these alloys so that the milling cutter could be employed to shape tensile specimens without its being excessively dulled in the process, each alloy was replaced in the annealing furnace for approximately one minute following the last hot roll, then water quenched.

The temperature of all 800° C anneals was presumably above the recrystallization temperatures of the alloys.

Photomicrographs of representative hot rolled alloys are shown in Figures 64 through 67.

3. Hardness

a. General considerations. Hardness readings were taken on all alloys of both series in order to determine the effect of different treatments on this quantity. The Rockwell "A" scale was chosen since its range covered hardnesses encountered in these alloys quite well. For the most part, hardness readings were taken on small quenched specimens (approximately 1/8 x 1/4 x 1/4 inches) with parallel sides. A representative number of readings of hardness, usually from 3 to 8 were taken on each specimen and the average value was tabulated.

A disturbing feature of the hardness measurements on the Series II alloys was the fact that towards the end of the hardness determinations, it was discovered that a small imperfection existed in the point of the diamond Brale. An indication of the error to be introduced by this damaged point may be obtained from measurements on an alloy specimen where the average value was R_A 59.4 instead of the 61.5 for the sound point. As a result,

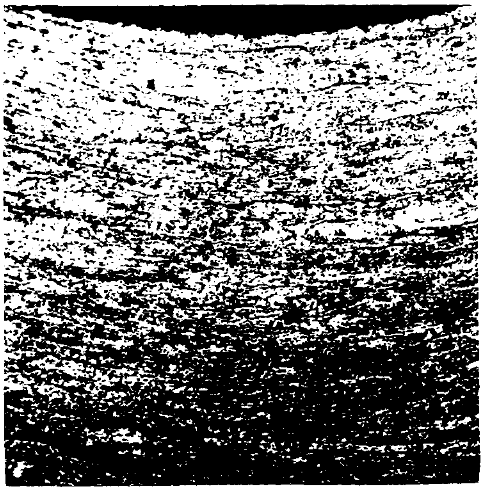


Figure 64. 2.5% vanadium (Series II) hot rolled at 550° C to 86% reduction. Alloy strip bent. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

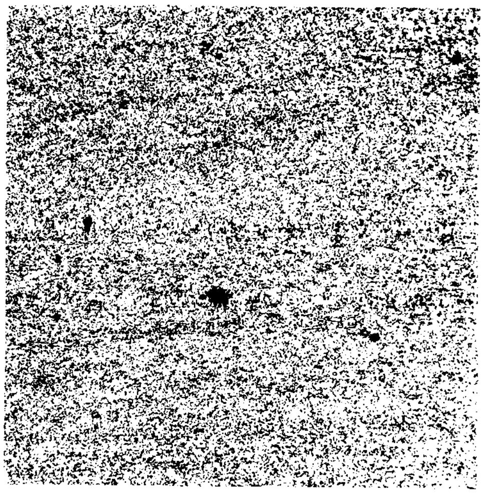


Figure 65. 10.9% vanadium (Series II) hot rolled at 550° C to 90% reduction. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

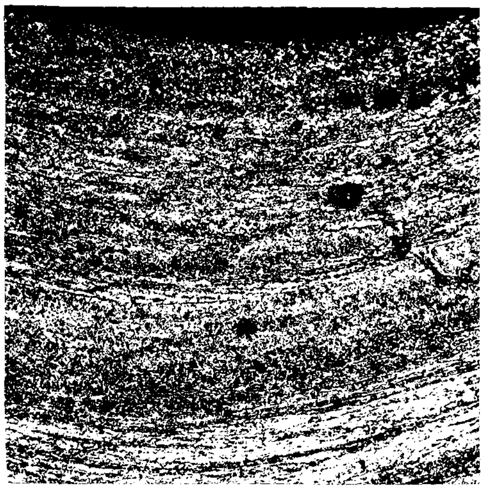


Figure 66. 26.1% vanadium hot rolled at 550° C to 87% reduction. Alloy strip bent. Etchant 1 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

Figure 67. 69.5% vanadium hot rolled at 800° C to 66% reduction. Alloy strip bent. Etchant 2 HNO_3 (conc), 1 HF (48%), 3 glycerol. X 250

important values of hardness, such as those used to determine the oxygen level in pure titanium and vanadium, were repeated with a sound point.

b. Series I alloys. Hardness values were plotted as a function of composition for the limited number of compositions of the Series I alloys. Three of these curves involving different heat treatments are shown in Figure 68. The data for other heat treatments generally followed the same trends and are given in Table 18. From this graph, it is seen that the maximum hardness is encountered in the alpha plus beta region. Microstructures of the hardest alloys usually showed the partial martensitic decomposition of beta to alpha in this region. Additional evidence for the hardness maximum in this region is shown by the difficulty encountered in hot or cold rolling of 10 per cent vanadium alloys.

A second small maximum is found around the 50 per cent vanadium alloy composition. This maximum near the center of the beta region, conforms to the usual behavior of substitutional solid solutions. The only 50 per cent vanadium alloy that failed to exhibit this shallow maximum was in the 700° C quenching run. Here the deviation is small and could possibly be attributed to the small size of the sample employed. The maximum

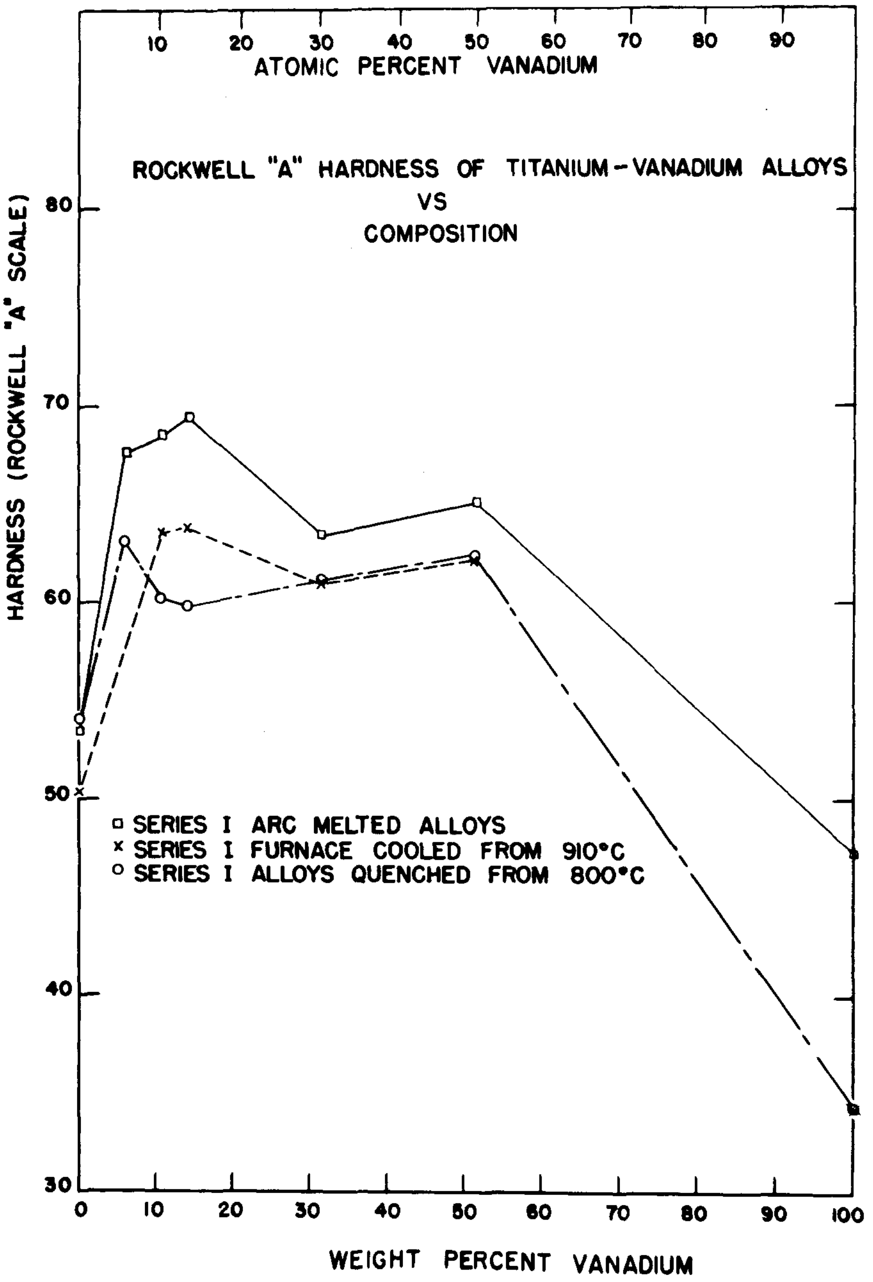


Figure 68. Hardness of Series I Alloys.

Table 18

Rockwell "A" Hardness of Series I Titanium-Vanadium Alloys

Composition (wgt. %)	As-arc-melted	Furnace cooled	Quenched from					
			910°	800°	750°	700°	600°	500°
100 % Ti	52.7	50.4	53.6	54.1	52.7	54.6	54.9	55.7
5.96% V	65.4	--	66.4	63.1	65.9	64.4	--	64.7
10.7 % V	71.0	63.6	64.1	60.3	69.0	66.6	61.7	63.7
14.1 % V	68.8	63.8	68.4	59.9	66.6	65.7	61.8	64.1
33.8 % V	60.9	61.0	60.9	61.0	60.6	61.5	59.6	61.8
51.4 % V	62.3	62.2	62.9	62.3	61.9	60.9	--	63.8
100 % V	51.5	--	--	34.2	47.4	36.9	--	37.7

hardness at this composition was reached by the 500° C quenched sample. Any of the annealing treatments gives a marked reduction in hardness of vanadium that has been arc melted.

c. <u>Series II alloys</u>. Hardness readings were taken of almost all of the Series II alloys. These, in contrast to the alloys of Series I, had been given a high temperature homogenization before beginning the quenching runs. Because of the higher oxygen levels in these alloys, the quenched hardnesses are somewhat higher. For example, the arc melted hardness of the 51.8 per cent vanadium alloy of R_A 65 was increased after the high temperature homogenization to 70.5. Because the results of these runs appeared to follow those of Series I alloys as far as general trends were concerned, these data are presented only in graphical form, Figure 69. In addition to the maxima observed for the Series I alloys, the Series II alloys exhibited a still further maximum in hardness in the case of the 2.5 per cent vanadium alloy. As may be seen from Figure 69, the maximum hardness at this composition decreases as the quenching temperature is lowered. The Series I alloys did not cover this particular percentage range, so this maximum could not possibly have been observed. This unusually high hardness

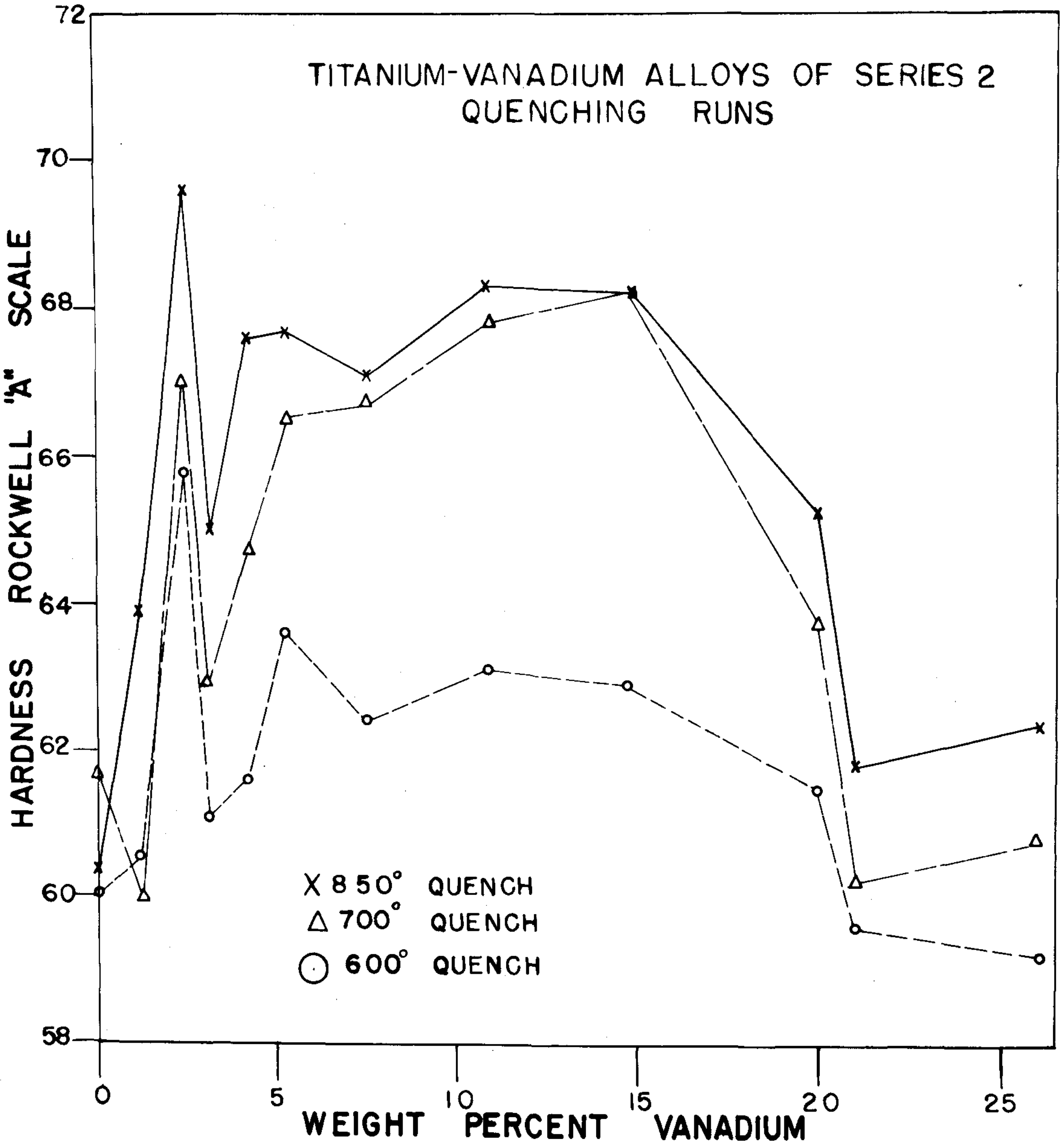


Figure 69. Hardness of Series II Alloys.

was first reported for a 2 per cent alloy by Adenstedt and others (5b, p 996). These investigators assumed that:

> * * * the hardness peak at 2 per cent vanadium is caused by a diffusionless transformation occurring during the cooling of the ingot, whereas the peak at 15 per cent vanadium must be due to precipitation of alpha from the metastable retained beta solid solution.

4. Tensile properties

The principal tensile properties of the titanium-vanadium alloys were determined on Series II alloys. The same strip specimens used for the electrical resistivity measurements were used for tensile strength measurements. A typical specimen size has already been illustrated in the discussion of resistivities.

Following the resistivity measurements, Baldwin strain gages were glued to each specimen with Duco cement, clamped tightly, and allowed to dry for 24 hours. These strain gages were of type A 12 with an internal resistance of 120.4 ohms and a gage factor of 2.05. After they had dried, the clamps were removed and each tensile specimen was placed between the jaws of a Dillon Dynamometer, where, one at a time, they were stretched to rupture. Before stretching, the strain gage leads were soldered to the leads of a Baldwin SR-4 strain indicator. Strain readings were determined at convenient intervals on the dynamometer scale, i.e., every 20 pounds on the 1000 pound scale or every 50 pounds on the 5000 pound scale. To reduce the dynamometer scale lag as the load was being applied, a stirring motor with a loaded rubber tubing extension tapped the dynamometer head continuously.

Elongation was determined separately on each specimen. For this purpose, parallel marks were scratched at known intervals on the surface of the specimen. After rupture, the specimen was fitted together again and the increase in length determined on the broken part of the alloy.

In order to obtain the desired tensile data, it was first necessary to plot stress against strain for every alloy, the stress being found from the applied load and the average initial cross-sectional area of the alloy, the strain directly from the strain gage readings. No effort was made to make the linear portion of the stress-strain curve pass through the origin, but the desired quantities were taken directly from each curve. Representative curves in both the high vanadium and high titanium ranges are shown in Figures 70 and 71. The ultimate tensile strength was found from the maximum load applied before the specimen broke. The yield

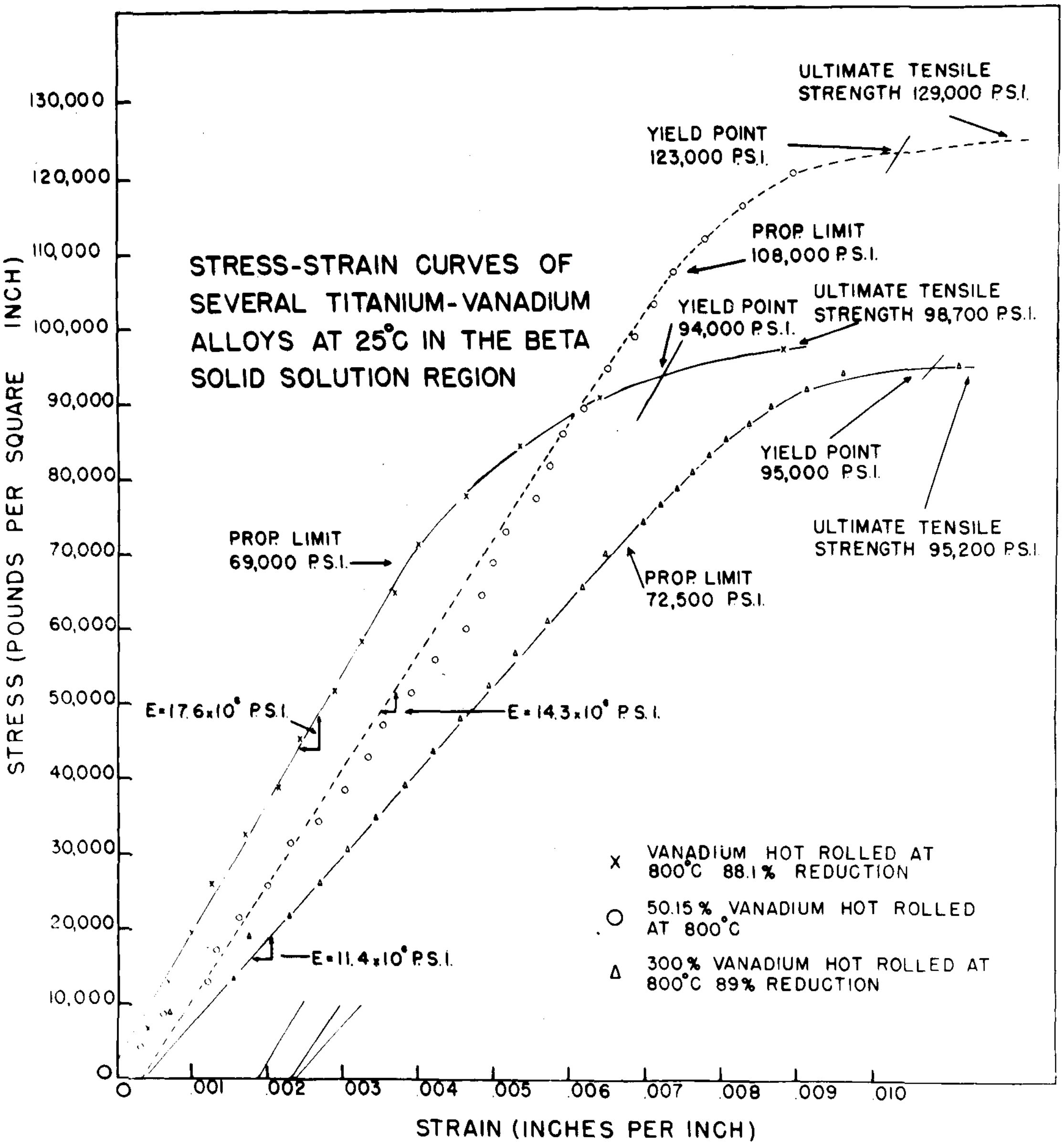


Figure 70. Stress-Strain Curves.

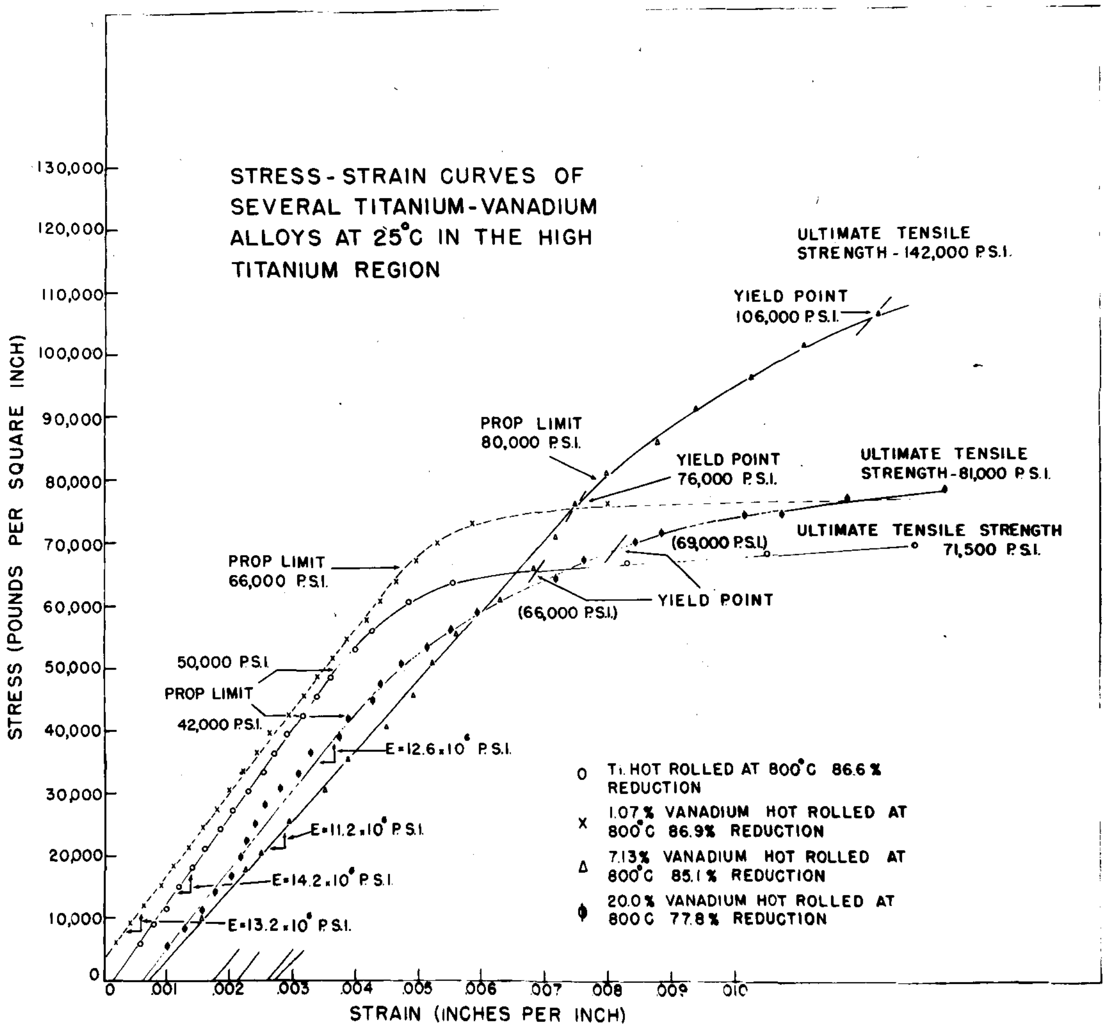


Figure 71. Stress-Strain Curves.

strength was determined at 0.2 per cent offset strain. Proportional limits were estimated from the stress-strain curves, as the end of the linear part of the graph. This data has been tabulated in Table 19.

The plot of ultimate tensile strength, of yield strength, and of proportional limit data from Table 19 as a function of composition shows, in Figure 72, that these properties approximately parallel one another, exhibiting two maxima at compositions close to two of the hardness maxima found earlier. The higher maximum occurs in the low vanadium range containing alpha plus beta phases, while the lower occurs near the center of the beta solid solution region. Tensile test data did not give an indication of any maximum corresponding to the hardness maximum found at the 2.5 per cent vanadium composition.

The modulus of elasticity as determined from the slope of the stress-strain curve for each alloy, is shown in the upper curve of Figure 73. The modulus appears to increase steadily for the hot rolled alloys, from about the 25 per cent vanadium alloy to pure vanadium. For pure vanadium, the modulus, ultimate tensile strength, proportional limit, and yield strength

Table 19

Tensile Properties of the Titanium-Vanadium Alloys*

Composition (wgt. %)	Ult. T. S. (p.s.i.)	Prop. limit (p.s.i.)	Yield str. (p.s.i.)	Young's modulus	Elongation (% in 1")
100 % Ti	71,500	50,000	66,000	14.2	18.8
1.2% V	81,000	66,000	76,000	13.2	21.9
2.5% V	105,900	72,000	102,000	14.3	12.5
4.2% V	136,800	75,000	113,000	14.1	8.7
7.6% V	142,000	80,000	106,000	11.2	13.7
7.6% V	139,000	80,000	107,000	10.0**	10.0
14.8% V	134,000	--	--	14.4***	17.5
20.0% V	113,000	42,000	69,000	12.6	17.7
26.1% V	100,800	67,000	93,000	10.7	5.3
26.1% V	109,200	66,000	95,000	10.8	7.8
31.0% V	95,200	72,500	95,000	11.4	4.7
51.7% V	129,000	108,000	123,000	14.8	13.5
69.5% V	113,200	--	111,000	16.7	2.2
75.5% V	92,900	81,000	91,300	16.4	2.2
100 % V	98,700	69,000	94,000	17.6	2.7
C.R. V	104,000	74,000	104,000	14.8	4.0

*The table above is continued from the table of resistivities. There, identical specimens are used and the amounts of hot rolling are listed along with hardness values.

**Specimen slipped in jaws - repeated.

***Specimen slipped twice in jaws - repeated.

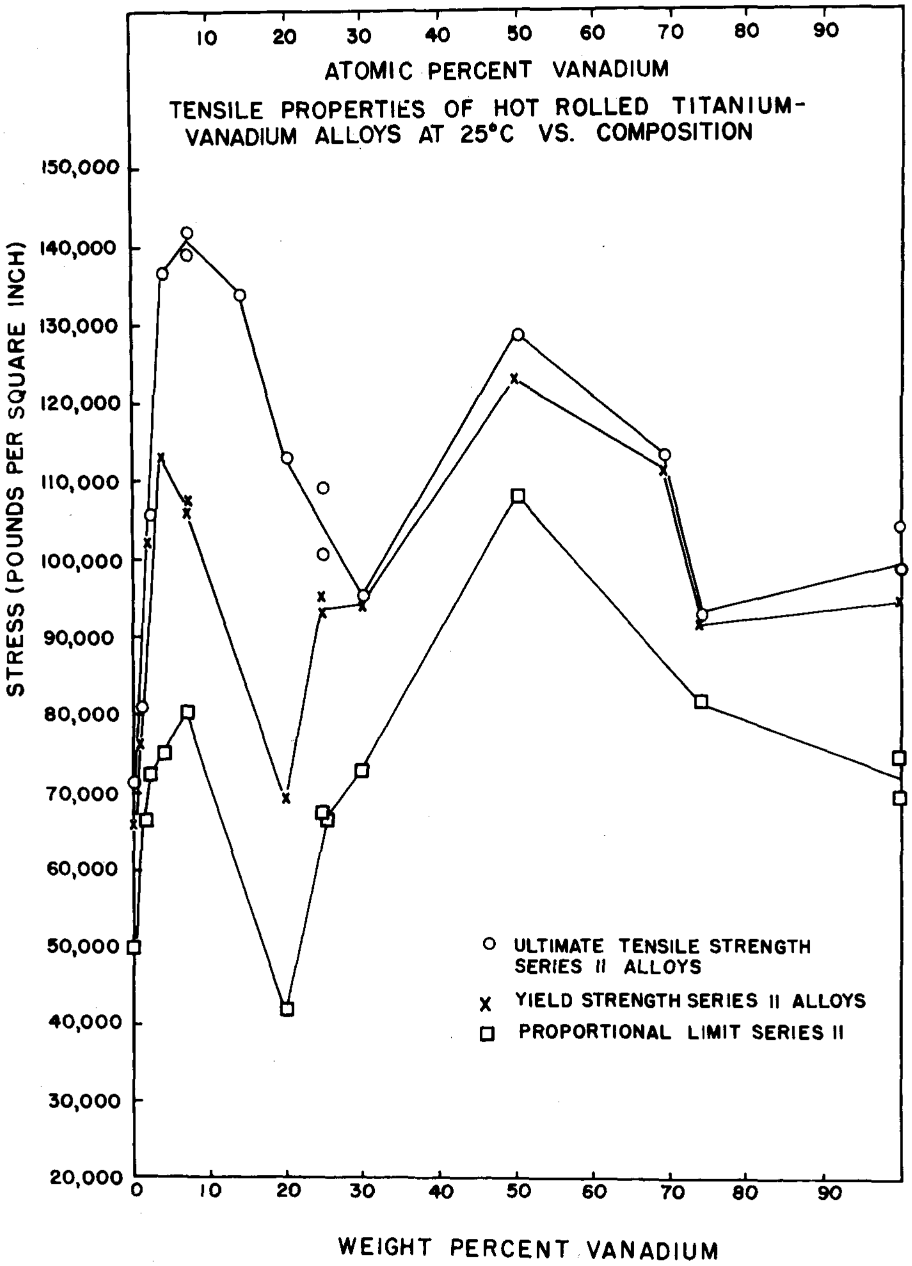


Figure 72. Tensile Properties.

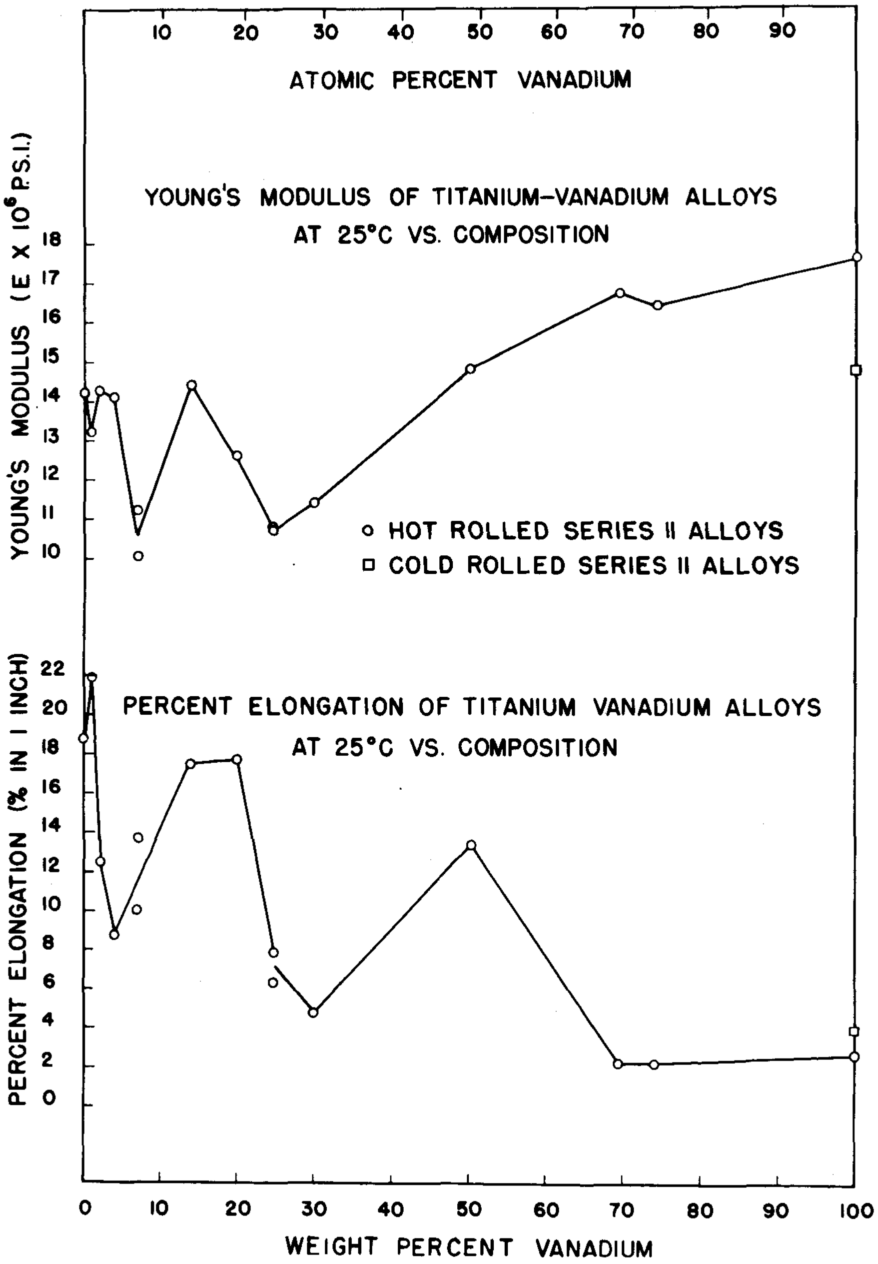


Figure 73. Moduli and Elongation.

are seen to be greater than for the commercial titanium when subjected to comparable amounts of hot work.

The per cent elongation in one inch, shown in the lower curve of Figure 73 is greater for titanium than vanadium, being 19 per cent for the first and 2 per cent for the latter. Vanadium is seen to have a lower per cent elongation than most of its alloys with titanium that were tested. Several maxima appear in the curve of per cent elongation as a function of composition, one at about 50 per cent vanadium, another between 14 and 20 per cent vanadium, and still another at about 1 per cent vanadium. These may or may not all be significant maxima.

For comparison purposes, a recent article (63) on a commercial grade of vanadium gave ultimate tensile strength values of 100,000 p.s.i. for the annealed metal. The per cent reduction, however, was unspecified and the metal was said to contain appreciable amounts ofoxygen and nitrogen. Cited in the same article were results on vanadium metal that had been prepared by calcium reduction of V_2O_3 to give a powder which was leached to remove the calcium oxide. Compact vanadium metal was then formed by sintering the pressed powder under argon. This metal was consistently produced within the limits of 0.05 to 0.12

per cent oxygen, 0.001 to 0.114 per cent hydrogen, 0.02 to 0.04 per cent nitrogen, 0.03 to 0.07 per cent carbon, and 99.9 to 99.8 per cent vanadium. A comparison of the cold rolling properties of this metal and those of vanadium which was produced by calcium reduction of the pentoxide and employed in the present investigation is given below in Table 20.

Table 20

Tensile Properties of Vanadium

	Vanadium by Ca reduction of V_2O_3			Vanadium by Ca reduction of V_2O_5
Per cent reduction	60	75	80	85
Prop. limit (p.s.i.)	63,000	68,000	69,000	74,000
Yield str. (p.s.i.)	101,000	110,000	142,000	104,000
Ult. tensile str. (p.s.i.)	107,000	117,000	155,000	104,000
Elong.				
(% in 2")	1 to 2.5	1 to 2.5	1 to 2.5	
(% in 1")				4

At the titanium rich end of the titanium-vanadium system, results of measurements on two hot forged 5 per cent vanadium alloys, were found by Busch and Dickenson (5a) to be quite different. Table 21 presents the data on these samples along with data on similarly treated 4.2 and 7.6 per cent vanadium alloys that were prepared in connection with the present work.

Table 21

Tensile Properties of Several High Titanium Alloys

	Alloy comp. (% V)			
	5	5	4.2	7.6
Prop. limit (p.s.i.)	75,000	108,000	75,000	80,000
Ult. tensile str. (p.s.i.)	128,000	144,200	136,800	142,000
Young's mod. (E x 10^6)	16.7	17.9	14.1	11.2
Elong.				
(% in 2")	14.1	8.6		
(% in 1")			8.7	13.7

The elongations and ultimate tensile strengths are seen to be in reasonable agreement, but the moduli differ considerably. The lack of agreement between the two 5 per cent alloys was assumed by the authors (5a) to be caused by variation of the cooling rate after forging, or in the forging technique.

VIII. CHEMICAL PROPERTIES OF THE TITANIUM-VANADIUM ALLOYS

A. Rate of Oxidation in Air

Two series of experiments on oxidation were carried out to determine a satisfactory hot working temperature for the titanium-vanadium alloys that would not produce a prohibitive amount of scaling. Experiments were carried out in a muffle furnace set at 775° C and at 600° C. Small samples were rolled out to increase the area and weighed on an analytical balance with class "S" weights. After placing in a preheated silica boat, they were rapidly transferred to the muffle which was closed immediately to prevent much heat loss. The alloys were heated for periods of from 5 to 250 minutes at 775° C, and up to 73 hours at 600° C, with time enough allowed for bringing the alloys up to the furnace temperature. At the end of the desired heating time, the boat was removed from the muffle, the metal specimens cooled rapidly, and the boat returned to the muffle for reheating. Specimens were weighed and returned to the heated boat for continued heating, usually for twice the duration of the previous heat. From the data of Tables 22 and 23, a curve of weight gain versus time, Figures 74 and 75, was obtained for each run.

The first oxidation tests were carried out at a temperature of 775° C on all Series I alloys. When the specimens were withdrawn from the furnace after five minutes at temperature, liquid vanadium pentoxide was seen to be running off the surface of the pure vanadium and into the bottom of the boat. Approximately 23 per cent of the original weight of 0.6344 g of metal had been lost. This corresponded to an oxidation rate of at least 700 mg/cm^2/hr. On cooling, the oxide formed purple star shaped spangles over the surface of the vanadium. As a result of this behavior, pure vanadium was left out of the rest of the higher temperature oxidation tests. A constant oxidation rate for vanadium has been recently reported by other investigators (64) for all temperatures above the melting point of vanadium pentoxide of 660° C (65). This constant rate is perhaps due to the liquid film that must flow off the metal and continuously expose it to the atmosphere.

Colors of the oxide coatings resulting from long time exposures at 775° C, ranged from the milky white scale on pure titanium, to the blue-gray oxide of the 51.4 per cent

Table 22

Air Oxidation of Titanium-Vanadium Alloys at 775° C

			Cumulative weight gain (mg/cm^2) at 775° C in total time of				
Alloy	Area	Weight	5 min.	10 min.	20 min.	42 min.	245 min.
V	2.51	.6344	(58.2)	--	--	--	--
51.4 % V	2.95	.6683	.373	.543	1.09	1.90	8.30
31.3 % V	1.341	.3289	4.03	5.89	12.08	20.95	100.3
14.1 % V	2.251	.8978	.756	.889	1.51	2.31	10.09
10.7 % V	4.813	1.2382	.395	.665	1.12	1.556	4.245
5.96% V	2.722	.6326	.33	.551	.735	1.138	2.64
Ti	2.285	.5065	.131	.306	.568	.613	1.312

Table 23

Air Oxidation of Titanium-Vanadium Alloys at 600° C

			Cumulative weight gain (mg/cm^2) at 600° C in total time of						
Alloy	Area (cm^2)	Weight (g)	5 min.	15 min.	35 min.	75 min.	115 min.	195 min.	4435 min.
V	1.657	1.4485	.241	.422	.724	1.448	2.112	2.897	9.475
51.4 % V	.851	.2273	.470	.823	1.293	2.703	3.408	4.113	12.690
33.8 % V	2.284	.8088	.088	.263	.657	1.445	1.927	2.716	16.994
14.1 % V	.979	.2432	.204	.409	.613	1.736	2.145	3.166	14.606
10.7 % V	3.917	1.5358	.026	.077	.281	.894	1.353	2.093	15.164
5.96% V	3.143	1.1353	.032	.066	.096	.286	.477	.986	7.382
Ti	2.464	.7745	.447	.487	.487	.609	.650	.690	.812
Ti	1.762	.6059	.738	.738	.738	.795	.966	1.022	1.193

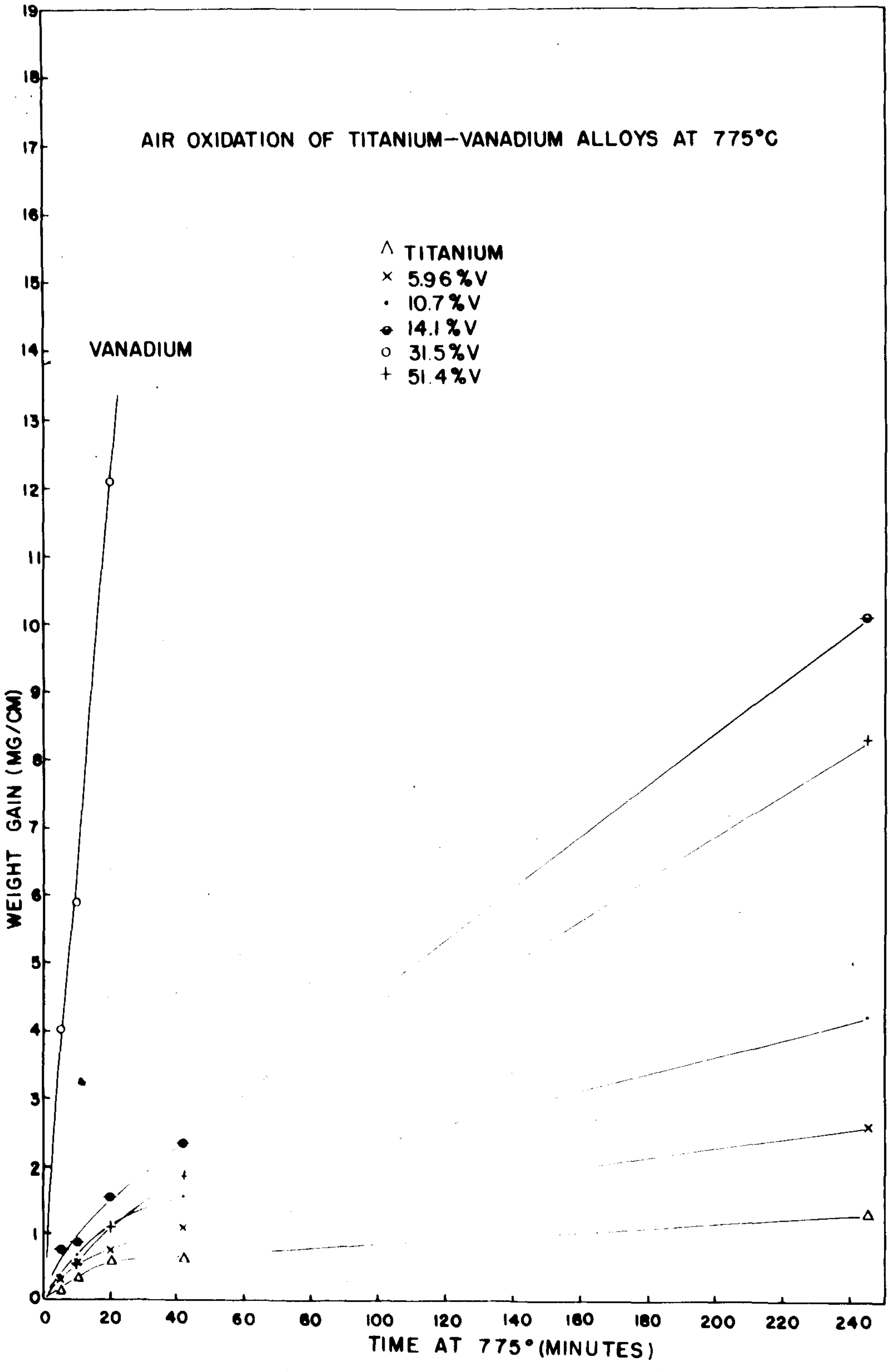


Figure 74. Weight Gain at 775° C.

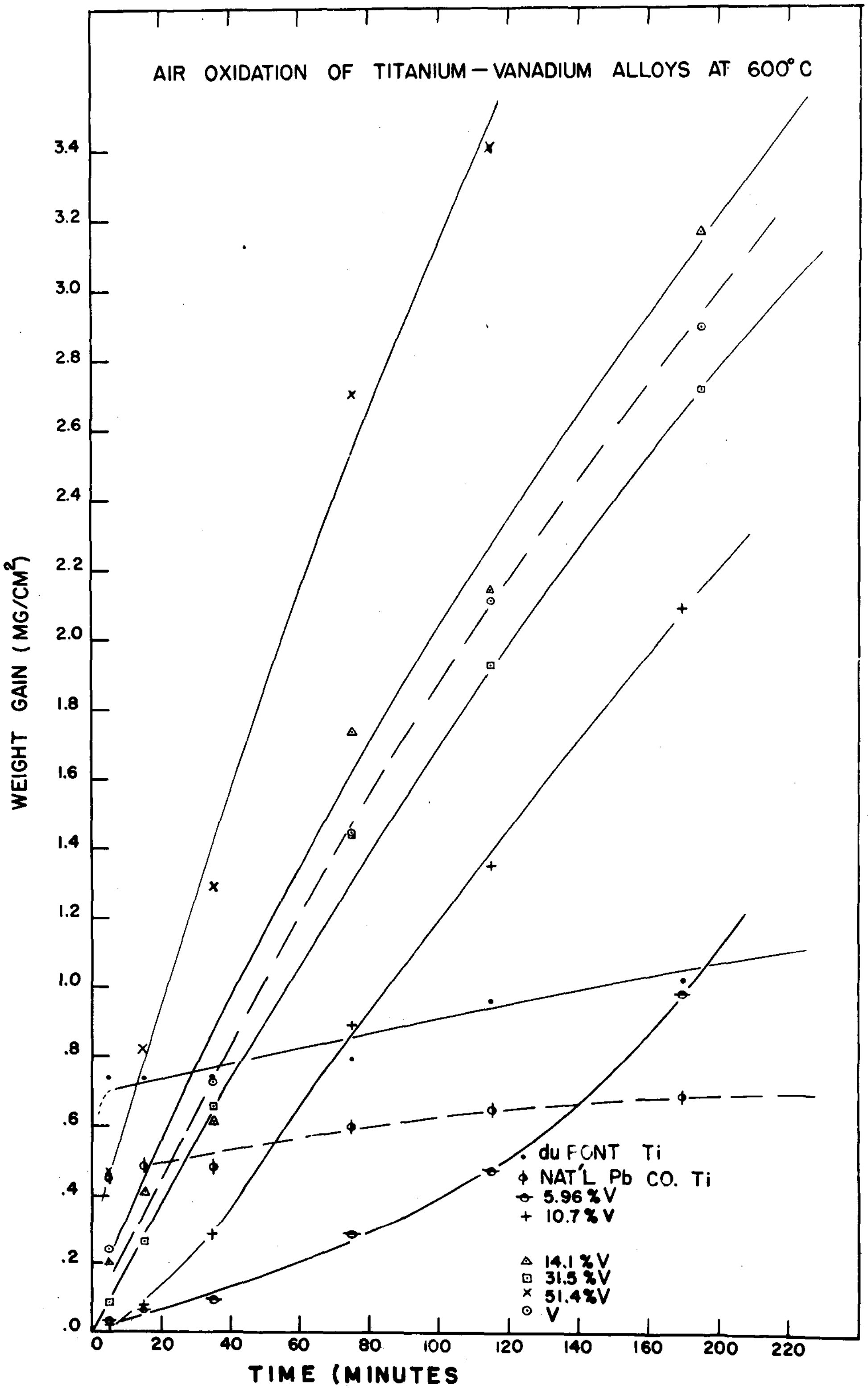


Figure 75. Weight Gain at 600° C.

vanadium alloy. The scale on titanium was very adherent, that on the 5.96 per cent vanadium alloy had begun to buckle, and that on the 10.7 per cent vanadium alloy showed an even greater buckling. The 14.1 per cent vanadium alloy exhibited considerable flaking, and loose scale was included in the weight gain. The scale on the 33.8 per cent vanadium alloy appeared to be quite dense but had parted at the edges, and a good share of the alloy was well converted to blue-gray oxide. The blue-gray film on the 51.4 per cent vanadium alloy was quite adherent.

In the graph of weight gain versus time for the high temperature tests shown in Figure 74, most of the alloys show an initial parabolic increase of weight with time. This is followed by a linear weight-time relation. The slope of the latter portion of the curve gives the rate of oxidation in this range and this quantity or oxidation rate at 775° C has been plotted against composition as a part of Figure 76. While data for the high temperature test do not include alloys in the range between 51.4 per cent vanadium and pure vanadium, it is estimated from the fact that a 69.5 per cent vanadium alloy showed rapid oxidation at 800° C, that the rate of oxidation of the alloys increases rapidly in the composition range

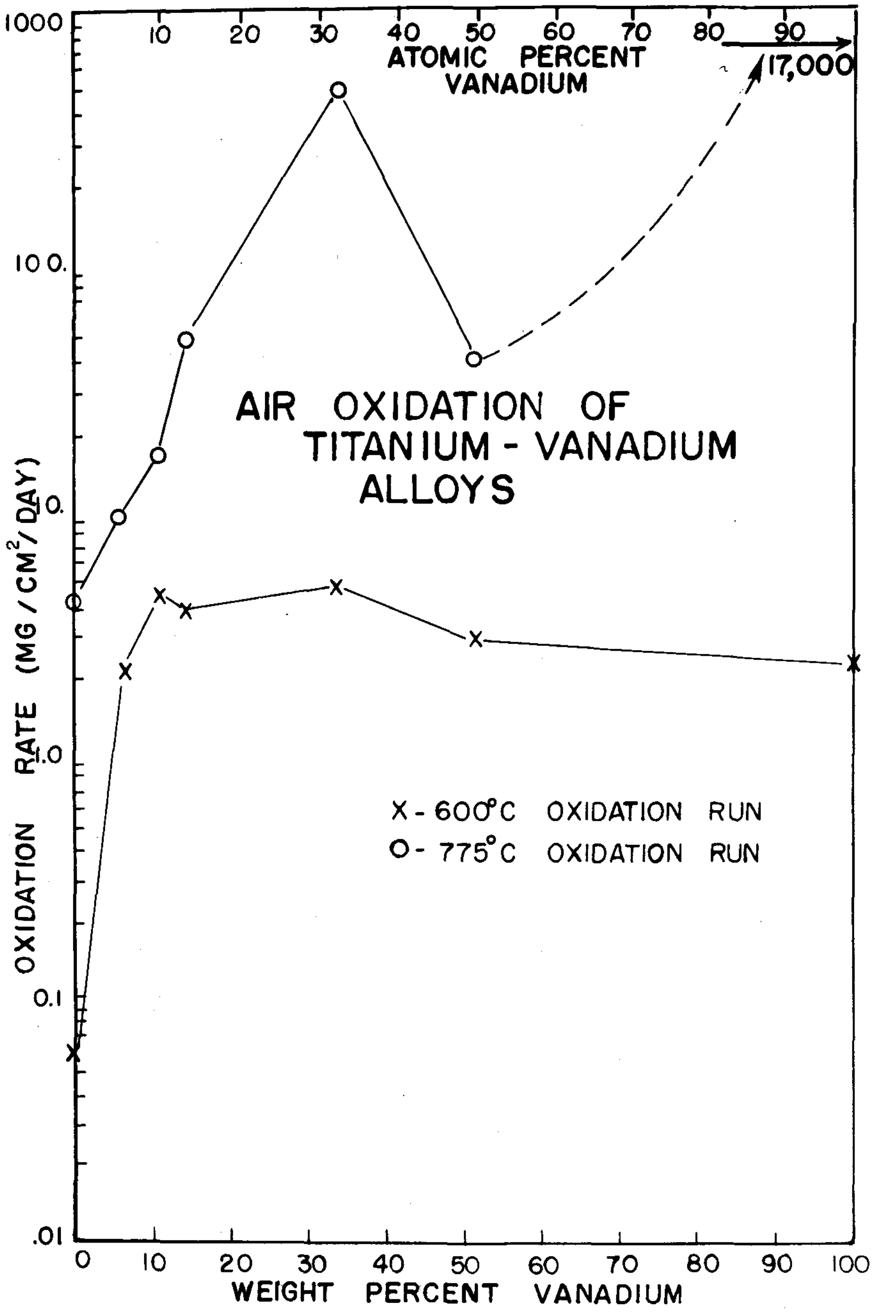


Figure 76. Oxidation Rate vs Composition.

approaching pure vanadium. It is to be noted that the 51.4 per cent vanadium alloy showed comparatively good oxidation resistance at 775° C, giving a definite minimum in the curve.

The alloys heated at 600° C showed a somewhat different behavior from that at the higher temperature. Weight increases in the early stages of the tests, see Table 22, are shown in Figure 75. Extended tests on these alloys at 600° C gave data (not shown) that tended to follow a somewhat parabolic curve in most cases. It may be seen that the two commercial grades of titanium did not differ appreciably in rate of oxidation at 600° C after the initial short time oxidation. This initial difference may be due to the fact that the National Lead sponge had been given a high vacuum anneal at 1000° C to remove some impurities, while the duPont sponge had been arc melted directly without benefit of any such clean-up treatment.

Film characteristics of the alloys subjected to the 600° C oxidation run were different in appearance ffom those heated at the higher temperature. Instead of the dark purple film of vanadium pentoxide that had been present in the case of the pure vanadium, this metal in the lower temperature tests showed a brownish-yellow film (V_2O_5) underlaid by a blue film, presumably of V_2O_4

and lower oxides. Colors ranged from this brownish-yellow film on vanadium to the blue-gray one on the 5.96 per cent vanadium alloy, and to the tightly adherent bluish film over pure titanium.

In these experiments at 600° C, vanadium showed an initial oxidation rate comparable to that of the 14.1 and the 33.8 per cent vanadium alloys (Figure 75). Initial oxidation rates were, in decreasing order, 51.4, 14.1, 100, 33.8, 10.7, and 5.96 per cent vanadium, and 100 per cent titanium. This order changed somewhat when the data for the interval between 195 and 4435 minutes (Table 22) was considered. There, the decreasing order of oxidation rate was 33.8, 10.7, 14.1, 51.4, 100, and 5.96 per cent vanadium, and 100 per cent titanium. These rates are plotted in Figure 76, which also shows graphically the slightly greater rates occurring in the 10.7 to 33.8 per cent vanadium alloy range as compared to the pure vanadium.

As a result of these experiments, titanium was seen to be the most resistant to oxidation at the two temperatures employed. In either case, alloying of titanium with vanadium increases the oxidation rate. In the 775° C tests, for example, increasing the vanadium content to 5.96 per cent roughly doubles the oxidation rate while increasing the vanadium content to 10.7 per cent increases oxidation four-fold. In the case of the 600° C test, the effect of alloying is even more pronounced, with the 5.96 per cent vanadium alloy showing over 37 times the oxidation rate of titanium at 600° C. An increase to 10.7 per cent vanadium results in a further increase in rate to 77 times that of the pure titanium. Thus, in the lower temperature range, although the rate of oxidation is comparatively small, the oxidation rate is seen to be relatively very sensitive to variation in composition of the alloys.

The term "oxidation" has been used very loosely in the preceding discussion as synonymous with scaling. However, since the alloys had been heated in air, there was a possibility of forming some nitride as well as the oxide. The principal component of the scale produced at the higher temperature (775° C) was inferred from its physical properties. The liquid film that covered vanadium was obviously vanadium pentoxide and the amount of nitride accompanying it was undoubtedly small. Titanium at the higher temperature was also primarily oxide as could be seen from the milky white color of the scale. While it was difficult to say with certainty what the composition of the scale of the intermediate alloys was, their colors could well be attributed to mixtures of the white of titanium dioxide and the purple of vanadium pentoxide.

The composition of the scale on the alloys of the 600° C run in the high titanium range was estimated from the data of Gulbransen and Andrews (36). These investigators studied the kinetics of the reaction of nitrogen and of oxygen with titanium at several temperatures and pressures. They suspended titanium in a furnace heated at the desired temperature and followed the weight gain as a function of time with a microbalance. The highest pressures they used were 7.6 cm for both oxygen and nitrogen.

As an example, their data showed that iodide titanium heated at 600° C in a 7.6 cm of oxygen, gained 39 micrograms/cm^2 over a 20 minute interval or 88 micrograms/cm^2 after 120 minutes. When nitrogen was substituted for oxygen under the same conditions, weight gains of 5 and 8 micrograms/cm^2 were reported for the 20 and 120 minute intervals, respectively. The composition of a thin scale resulting from the heating of the metal in a mixture of equal portions of oxygen and nitrogen, might be expected to show oxide and nitride in amounts proportional to the measured reaction rates of oxygen and nitrogen with titanium, or approximately 90 weight per cent oxide (87.5 atomic per cent), and 10 weight per cent nitride (12.5 atomic per cent). Assuming that the amount of oxide and of nitride scale produced in air is proportional to the partial pressure of each gas, and that the metal is covered with a scale containing no lower oxides or nitrides, the TiN composition in the scale would be roughly $(.79)(.125)/(.79)(.125) + (.21)(.875)$ or 35 mol per cent (30 weight per cent), the rest TiO_2. The assumption that the reaction rate is proportional to the pressure is open to question in the case of nitrogen, which has been found not to show direct proportionality between weight gain and pressure for titanium at low pressures. It was used, however, in lieu of a better assumption. The scale on titanium was blue at the lower temperature, indicating either that some nitride was present besides the white oxide of titanium, or that the metal was incompletely oxidized to TiO_2 at this temperature.

Because of the manner of carrying out the air oxidation tests, as described earlier, by alternately heating the specimens and withdrawing from the furnace for cooling and weighing, other mechanisms can be assumed as effective in offering an explanation for the variation of scaling rate with composition, in addition to that for an isothermal scaling run. Such explanations involve differences in the coefficients of expansion between the surface scale and the underlying metal. Any rupturing of this film on heating or cooling would permit freer access of air to the metal.

B. 315° C Steam Corrosion Rates

A high temperature steam corrosion test was run on a number of titanium-vanadium alloys. Samples of approximately 2 square centimeters area were polished on successively smaller grit wheels and then finished on number 600 paper. Identification was marked on each specimen with a vibrator tool, and the specimens were placed in a stainless steel bomb containing distilled water. There, they were in contact with each other and with the bomb walls. The cap, fitted with a silver sheet gasket, was screwed on tightly and the bomb suspended in a furnace where it was held at 315° C for 125 hours. Five hours were allowed for reaching soaking temperature, eight for cooling. Arc melted Series II alloys were used exclusively for these corrosion tests.

From the results tabulated in Table 24, it is seen that the alloys show good resistance to corrosion under the above conditions. The appearance of all alloys on removal from the bomb was good, with no detectable scale having formed. Because of the short time that the alloys were exposed and the fact that the weighing error (0.2 mg) was of the same order of magnitude as the weight gain, a correlation of these small corrosion rates with composition is open to some question. Maximum corrosion rates observed do not appear to be associated with maximum hardness, which, as a measure of internal stress, might be expected to be associated with increased corrosion. Also, there appears to be no correlation between the microstructures of the arc melted specimens and their corrosion rates.

C. Solubility of the Titanium-Vanadium Alloys in Hydrofluoric Acid

The comparative rates of solution of titanium and its alloys with vanadium in hydrofluoric acid solution were examined briefly. It was hoped that a marked difference in the rates of solution might be observed for the one

Table 24

315° C Steam Corrosion Test of Titanium-Vanadium Alloys for 125 Hours

Composition (wgt. % V)	Area (cm^2)	Weight gain (mg)	Rate of gain ($mg/cm^2/mo.$)	Hardness Rockwell "A"
0	2.64	0.0	0.0	50.9
1.2	3.34	0.3	0.5	51.4
2.5	3.25	0.1	0.2	63.5
3.1	2.75	0.1	0.2	56.4
4.2	2.70	0.0	0.0	60.2
5.3	2.26	0.1	0.3	65.2
7.6	2.26	0.0	0.0	67.2
10.9	2.28	0.1	0.3	72.2
14.8	1.96	0.0	0.0	72.0
20.0	2.25	0.4	1.0	67.1
21.0	2.21	0.2	0.5	62.4
26.1	2.36	0.9	2.2	61.8
31.0	2.76	0.3	0.6	61.3
51.7	1.55	0.0	0.0	65.3
75.5	1.87	0.5	1.5	60.7

phase alpha titanium, the two phase alpha plus beta alloys, and the one phase beta alloys.

To determine the relative rates of solution, what might be termed the differential dissolving potential was measured. The potential difference was measured between a reference metal and its alloy, standing side by side in a given dissolving medium, in this case hydrofluoric acid solution. The one dissolving the more rapidly would tend to be cathodic as compared to the other.

A single piece of titanium standing in a hydrofluoric acid solution dissolves according to the equation (66)

$$Ti + 3\ HF \rightarrow Ti^{+3} + 3\ F^- + 3/2\ H_2 .$$

In the presence of air, the trivalent titanium is undoubtedly largely converted to the tetra valent state.

$$1/4\ O_2 + 1/2\ H_2O + Ti^{+3} \rightarrow Ti^{+4} + O\ H^-$$

When a reference metal and one of its alloys are placed together in an acid solution, they both tend to dissolve. The alloy may dissolve at a faster or slower rate than the metal. In the case of titanium and an alloy of titanium with vanadium, the titanium probably dissolves in some such manner as indicated by the above equations. The alloy, containing titanium at an activity characteristic of the alloy, may also dissolve in the same manner. With approximately the same submerged area for eachsspecimen, the faster dissolving metal would leave behind the greater number of electrons, so that by connecting the two metal samples together, a difference in potential should be found between them. In the present case, the metal samples were fastened by means of alligator clips to copper wires that led directly to the terminals of a Rubicon potentiometer. The best possible balance was found in view of the fluctuating nature of the potentials. Each specimen, attached directly to the potentiometer, was lowered into a solution of 48 per cent hydrofluoric acid, and both the titanium and the titanium-vanadium alloy began to dissolve, as evidenced by gas evolution. A potential was developed that tended to change with time. In an attempt to stabilize the voltage somewhat, about 6 grams of electrolytic titanium powder was dissolved in 150 cc of the 48 per cent hydrofluoric acid solution. The following approximate potentials (Table 25) were obtained on the Series II as-arc-melted alloys in this hydrofluoric acid solution. These potentials were measured against arc melted titanium as a reference.

Table 25

Relative Dissolving Potentials of Titanium-Vanadium Alloys Against Titanium

Alloy (wgt. % V)	Potential difference (volts)	Alloy (wgt. % V)	Potential difference (volts)
5.3	0.005	51.7	0.151
14.8	-0.049	51.7*	0.266
20.0	-0.029	75.5	0.334
26.1	0.1	84.5	0.438

*Homogenized.

All alloys were in the as-arc-melted state excepting the 51.7 per cent vanadium alloy that had been homogenized. Negative values before the voltage indicate that the alloy dissolves in the hydrofluoric acid more readily than pure titanium, while positive values indicate that the alloy is less soluble in this particular electrolyte than titanium. The results show that generally the alloys exhibit decreasing rates of solution in this acid as the vanadium content is increased, a behavior already anticipated from observation of the etching characteristics of these alloys.

In further experiments, alloys of the Series I 700° C, the 750° C and the 910° C quenches were compared with titanium. Results are shown in Table 26.

All potentials in the last three columns of Table 26 were made in approximately 8 molar hydrofluoric acid containing 0.1 molar titanium ion. The results represent an average potential value over time intervals of from 5 to 15 minutes. Variations of up to 25 per cent and more from the listed average voltages were frequent. However, the average values given in this table for quenched alloys appear to be fairly constant for a given composition over quite a variety of heat treatments and acid concentrations. The highest readings in the two

Table 26

Relative Dissolving Potentials of As-Quenched Titanium-Vanadium Alloys Against Titanium

Composition (wgt. % V)	Potential in volts at quenching temperatures				
	700° C*	750° C**	750° C	750° C	910° C
5.96	-0.028	-0.056	-0.075	-0.042	-0.031
10.7	-0.10	-0.101	--	-0.122	-0.109
14.1	-0.044	-0.044	-0.075	-0.075	--
33.8	0.1	--	0.048	0.051	--
51.4	--	--	0.21	0.19	--
100.0	--	--	--	0.49	--

*Potential measurements carried out in a 12.5 M HF solution, 0.3 M in titanium ion.

**Potential measurements carried out in 4 M HF, 0.1 M in titanium ion.

phase region appear to occur at about the 10 per cent vanadium alloy, where, in most instances, the alloy hardness is the greatest. This alloy dissolves more rapidly than any in hydrofluoric acid solution. No pronounced change in the differential voltage was found in going from a one to a two phase region. Little significance can be attached to the above results. The method might be used as an optional method for determining which of a series of alloys is the most soluble in a given reagent. If the acid had been nitric acid, the vanadium would have probably been the most cathodic of these specimens.

IX. CONCLUSIONS

1. Satisfactory alloys of titanium with vanadium can be prepared by arc melting together the component metals under argon. No appreciable differences were noted in the as-arc-melted alloys prepared by combining titanium, as sponge from two commercial sources, with vanadium prepared in the laboratory by calcium reduction of vanadium pentoxide.

2. Alloys of titanium and vanadium can be prepared by coreduction of the mixed oxides with calcium with fairly satisfactory results in the high vanadium range. Reductions to give high titanium alloys were not satisfactory either from the standpoint of yield, or quality of metal, which was extremely brittle. Coreduction of the mixed oxides of titanium and vanadium yielded alloys enriched in vanadium, which makes it difficult to control composition by this method. For example, a mixture of oxides, which if completely reduced should have given a 60 per cent vanadium alloy, yielded instead an 80 per cent vanadium alloy.

3. At high temperatures, the body-centered cubic titanium and vanadium are completely miscible in all

proportions to give a complete series of solid solutions, from pure titanium to pure vanadium. The microstructure of the solid solutions does not appear to be entirely single phase, due perhaps to the presence of some impurities in small amounts. The results of x-ray studies clearly indicate, however, that the lattice parameter of the body-centered cubic beta phase of vanadium is increasingly expanded as the larger titanium atoms are added in substitutional solid solution. The most titanium that it was found possible to retain conveniently in the beta form on water quenching to room temperature, corresponded to about an 18.5 per cent vanadium (81.5 per cent titanium) alloy. More titanium than this in solid solution apparently caused the beta solid solution to undergo a martensitic type transformation to give secondary alpha and beta solid solution with a lattice parameter corresponding to the 18.5 per cent vanadium alloy.

4. As the result of metallographic studies, the transition that takes place in pure titanium at 885° C was shown to be progressively lowered by additions of vanadium to titanium. Thus, the beginning of this transition on cooling is lowered to approximately 600° C by an addition of 23 per cent vanadium to the titanium. The presence of about 0.25 per cent oxygen in the

titanium-vanadium alloys was indicated to raise the beta to alpha plus beta transition temperature. This amounted to about 50° C at the 10 per cent vanadium composition, and is in accord with the elevation of the transition temperature of pure titanium by additions of oxygen.

5. The solid solubility of vanadium in the hexagonal form of commercial titanium containing about 0.25 per cent oxygen, was indicated from x-ray and metallographic evidence to be less than one per cent at 700° C.

6. The melting point of pure vanadium produced by calcium reduction of the pentoxide, and employing either iodine or sulfur as booster, was determined as 1860° ± 20° C. This high melting point of vanadium is in line with the theoretical considerations of Pauling. Vanadium, with an intermediate number of cohesion electrons, should have a melting point between that of titanium and chromium. Appreciable amounts of oxygen in vanadium definitely increase its melting point.

7. The melting point of crystal bar titanium was determined as 1680° C under a 0.03 to 0.08 micron vacuum by the same method as employed for vanadium. This melting point is lower than literature values for titanium metal. Slight amounts of oxygen in titanium produce a decrease in its melting point.

8. The solidus curve and the approximate liquidus curve were determined for this alloy system. A minimum of about 1570° C occurs in the liquidus at the 30 per cent vanadium composition. Reaction of the high vanadium alloys with appreciable amounts of oxygen, nitrogen, or both, caused by heating the alloys in a 1.1 micron vacuum, resulted in a marked increase in melting temperature and hardness of these alloys.

9. The emissivities of the metals and alloys in a 0.1 micron vacuum follow the progress of surface oxidation during the heating to the melting temperatures. The alteration of the emissivities of each metal or alloy as the temperature is increased, is assumed to be due to the progressive superficial absorption of oxygen or nitrogen. An initial increase in emissivity was observed for vanadium. This may be explained by the effect of low impurity level on this property, and the eventual decrease observed under conditions of continued oxidation may be attributed to the loss of free electrons by the metal. Melting temperatures, as estimated from the highest observed surface temperature (related to emissivities), and reference to a plot of surface temperature against true temperature, were found to be comparable to those determined by the method of hole closure, in most cases.

10. The approximate surface tensions of the metals as determined by the method of sessile drops on the solidified arc melted buttons, gave lower values than the absolute values from the literature. For the titanium-vanadium alloys, the surface tensions, and the estimated surface enthalpies as determined on approximately constant volume drops, appear to parallel the liquidus curve, and correspondingly, exhibit a minimum at about the 30 per cent vanadium composition. The equation of Stefan, suitably modified, appears to be a satisfactory relationship between surface tension and melting temperature for the titanium-vanadium alloys. It should be possible to modify the sessile drop method and thus obtain absolute values of the surface tension of metals and alloys.

11. The alloy densities were measured. The curve of density against composition for the titanium-vanadium alloys may be interpreted as indicating some slight incompatibility of the two metals.

12. Electrical resistivities of the annealed metals and alloys in the beta solid solution region show an almost linear increase from vanadium to a maximum at about the 20 per cent vanadium (80 per cent titanium) alloy, which apparently represents the maximum amount of titanium that can be conveniently retained in the beta

solid solution. From this composition, the alloy resistivity decreases regularly to the limiting value for commercial titanium.

13. From the measured resistivity change of a sample subjected to an annealing treatment at lower temperatures, ordering was at first suspected for the 50 atomic per cent composition. The observed drop in resistivity for this alloy may be equally well explained by the existence of a two phase region that is slow to attain equilibrium at the low temperature (500° C). The latter explanation is probably the more nearly correct.

14. The titanium-vanadium system shows a maximum hardness and tensile strength in the high titanium region, and another small maximum towards the center of the beta solid solution. A hardness maximum was also observed for an alloy containing 2.5 per cent vanadium. The hardness of this latter alloy decreases as it is quenched from successively lower temperatures.

15. The air oxidation rates of all titanium-vanadium alloys treated in air at both 775° C and 600° C, were considerably greater than that of titanium alone. At both temperatures, a peak in the oxidation rate occurs at about the 30 per cent vanadium composition. For the

775° C tests, alloys containing more than 70 per cent vanadium, oxidize very rapidly, exhibiting a liquid oxide film over the sample.

16. Representative titanium-vanadium alloys covering the entire system showed excellent corrosion resistance in 315° C steam for the duration of a 125 hour test.

17. Differential dissolving potentials of the titanium-vanadium alloys against titanium were roughly reproducibly constant for each alloy, when quenched from a given temperature. The magnitude of the voltage difference is an approximate measure of the relative rates of solution of the two specimens in a given solvent. A marked change in the potential in passing from the single phase beta, to the two phase alpha plus beta region was not observed for this alloy system. The maximum rate of solution in hydrofluoric acid was shown by the hardest alloy of the 700° C quench, i.e., the 10.9 per cent vanadium alloy, which is two phase at that temperature.

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