IOWA STATE UNIVERSITY
Digital Repository

Retrospective Theses and Dissertations

1954

The vanadium-zirconium alloy system

John Trew Williams
Iowa State College

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Physical Chemistry Commons

Recommended Citation

NOTE TO USERS

Title: **The Vanadium-Zirconium Alloy System**

Author: **John T. Williams**

(Official certification of the classification shown is filed in the

Ames Laboratory Document Library)

Secretary to Declassification
Committee

THE VANADIUM-ZIRCONIUM ALLOY SYSTEM

by

John T. Williams

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

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1954

ii

TABLE OF CONTENTS

INTRODUCTION

The search for more powerful engines and more efficient utilization of fuel in existing types has led almost inevitably to higher operating temperatures. However, the fluids used as working substances in heat engines are likely to be very corrosive at such high temperatures. Frequently, too, the loss of strength which occurs at elevated temperatures in the materials of which the engine is built is an even more serious problem.

The recent upsurge in interest in the refractory metals and their alloys is a result of the corrosion and strength problems encountered in jet engine and nuclear reactor design. The high melting points of many of the less common metals, vanadium and zirconium among them, hold promise that an alloy of good high temperature strength and suitable corrosion resistance may be developed.

Vanadium-zirconium alloys are among those which have been considered at one time or another for use as components of nuclear reactors or jet engines. Knowledge of the equilibrium diagram for the system would be a great aid in understanding the effects of heat treatment on the physical properties of these alloys, since from it one could estimate the phases present and the probable distribution of these phases after the treatment. Therefore, an investigation

of the equilibria existing in the vanadium-zirconium system was undertaken.

REVIEW OF LITERATURE

Little information concerning vanadium-zirconium alloys has been published. Most of that which exists has resulted from surveys of the binary alloy systems of either vanadium or zirconium.

Anderson, Hayes, Roberson and Kroll (1), in a survey of zirconium alloy systems, prepared zirconium alloys containing up to 10 per cent vanadium. The microstructures of these alloys showed the existence of a narrow range of solid solubility and the probable existence of a eutectic reaction between zirconium and a compound.

Wallbaum (2) reported the existence of a compound, V_2Zr, in the vanadium-zirconium system. His alloys were prepared by sintering compacted powder mixtures. Details concerning the purity of the metals used as starting materials and the conditions under which sintering was performed were not given in the note in which the work was reported. Debye-Scherrer X-ray diffraction patterns indicated that the structure of V_2Zr was of the $MgZn_2$ (C 14) type with $a_0 = 5.277$ kX and $c_0 = 8.647$ kX.

P. C. L. Pfeil (3) recently reviewed the existing information on vanadium-zirconium alloys. On the basis of metallographic evidence, he gave the solubility of vanadium

in zirconium as less than 4.7 per cent and probably less than 1.8 per cent.

Rostoker and Yamamoto (4) have presented a probable equilibrium diagram for the vanadium-zirconium system from evidence available in the literature, some incipient melting point determinations, and a few microstructures. The work was a part of a survey of vanadium binary systems. Their diagram indicates the existence of V_2Zr, a peritectic reaction between V_2Zr and a vanadium-rich solid solution at 1740°C, a eutectic reaction between a zirconium-rich solid solution and V_2Zr at about 1360°C, and a limit of solubility of zirconium in vanadium of about three weight per cent. Evidence concerning the equilibria in zirconium-rich alloys was not obtained.

APPARATUS AND EXPERIMENTAL PROCEDURE

Preparation of the Alloys

Materials

The vanadium used in preparing the alloys for this investigation was obtained from the Electro Metallurgical Corporation. A typical manufacturer's analysis of the material is given in Table 1. Rostoker and Yamamoto (4), who used the same type of vanadium, reported the presence of small particles of a second phase dispersed throughout the metal. The behavior of the material during melting also suggests that higher purity is desirable. The metal did not have a sharp melting point, but melted over a range of temperatures.

Table 1

Typical Analysis of Vanadium from the Electro Metallurgical Corporation

Element	Amount Present ppm
Carbon	1,900
Hydrogen	14
Nitrogen	950
Oxygen	360
Other	1,000

Two types of zirconium were used for preparation of these alloys. The first was sponge material made by the U. S. Bureau of Mines by reduction of zirconium tetrachloride with magnesium. The second was zirconium made by thermal decomposition of the tetraiodide at the Westinghouse Atomic Power Development Laboratories.

Alloys made from sponge zirconium were used in the preliminary stages of the investigation for some solidus temperature determinations and for thermal analysis. Alloys made from iodide zirconium were used for all other work. Typical results of spectrographic analysis of the iodide material are shown in Table 2. The purity of this metal is exceptionally good, and the low hafnium content makes it particularly valuable for the study of binary zirconium alloy systems.

Melting

All of the alloys were made by melting pieces of vanadium and zirconium together in a direct-current, electric-arc furnace similar to those of Geach and Summers-Smith (5), Craighead, Simmons, and Eastwood (6), and others. The metals to be alloyed were placed in one of three depressions in a water-cooled copper hearth. Two charges and a zirconium getter were placed in the furnace at one time in normal operation. After evacuation to a pressure less than one

micron of mercury, the water-cooled furnace enclosure was
filled with helium at atmospheric pressure. The zirconium
was melted to remove residual air from the atmosphere prior
to melting either alloy charge. Each alloy charge was
melted, turned over by manipulation of the tungsten elec-
trode which formed the positive pole of the arc, and remelted.
The turning and remelting were repeated at least three times
for each alloy to minimize the inhomogeneity frequently en-
countered in arc-melted alloys.

Table 2

Typical Analysis of Iodide Zirconium

Element	Amount Present ppm
Aluminum	< 30
Calcium	< 10
Chromium	< 130
Copper	50
Hafnium	< 100
Iron	< 200
Magnesium	< 10
Nickel	20
Silicon	< 140
Titanium	< 20

The alloys used in this investigation are listed in Table 3. Compositions calculated from the weights of the furnace charges, the type of zirconium used in preparing the alloy, and available analytical results are given. Melt numbers are listed for convenience in later reference.

Table 3

Alloys Used in Investigation of the
Vanadium-Zirconium Alloy System

Calculated Composition wt. %V	Melt No.	Analysis wt. %V	Type Zirconium Used
0.25	M-805	0.29	iodide
0.5	M-806	0.54	iodide
1	M-807	1.03	iodide
2	M-727	----	sponge
2	M-808	1.97	iodide
3	M-723	----	sponge
3	M-809	3.00	iodide
4	M-812	3.80	iodide
4.5	M-814	4.57	iodide
5	M-811	5.36	iodide
5.5	M-816	5.55	iodide
6	M-815	----	iodide
6.5	M-813	----	iodide
7	M-810	7.02	iodide
10	M-797	----	iodide
10	M-947	----	iodide
15	M-882	----	iodide
20	M-724	----	sponge
30	M-725	----	sponge
40	M-726	----	sponge
45	M-819	----	iodide
47	M-903	45.50	iodide
50	M-590	49.66	sponge
52	M-902	51.68	iodide
53	M-900	53.02	iodide

Table 3 (Continued)

Calculated Composition wt. %V	Melt No.	Analysis wt. %V	Type Zirconium Used
55	M-817	54.10	iodide
60	M-603	57.00	sponge
60	M-873	-----	iodide
65	M-881	-----	iodide
70	M-602	65.52	sponge
75	M-883	-----	iodide
80	M-589	77.16	sponge
85	M-884	-----	iodide
90	M-587	89.05	sponge
92.5	M-886	-----	iodide
95	M-592	-----	sponge
95	M-944	94.33	iodide
97.5	M-899	96.54	iodide
98	M-591	95.01	sponge
99	M-588	98.78	sponge
100	M-818	-----	------

Fabrication

Alloys containing from 10 to 90 weight per cent vanadium were very hard and could not be swaged or rolled. Those containing about 50 per cent vanadium were very brittle.

Pieces of the ingots containing less than 10 per cent vanadium were placed in steel jackets, the jackets were welded shut, and the jacketed alloys were swaged to 1/8 inch diameter rods at about 850°C. The rods were swaged at room temperature after removal from the jackets.

Portions of the alloys containing more than 90 per cent
vanadium were rolled in steel jackets at about 850°C. The
92.5 per cent vanadium alloy cracked badly in rolling and
stuck to the jacket. The sheet was considered unsuitable
for further use.

Analysis of the Alloys

Specimens of some of the alloys were submitted for
either chemical or spectrographic analysis. Qualitative
spectrographic analysis of nine wires swaged from different
ingots showed no contamination by copper, tungsten, or iron.
Geach and Summers-Smith (5), likewise, had found no contami-
nation by the atmosphere, or by copper or tungsten in alloys
made in their furnace. It was assumed that none of the
alloys was contaminated during melting nor during subsequent
swaging in steel jackets in those cases where the latter was
done.

Chemical analyses were supplied by the Analytical
Division of the Institute for Atomic Research. Specimens
were dissolved in dilute hydrofluoric acid. The solution
was partially evaporated to drive off some of the acid, and
zirconium was added to prevent fluoride ion interference
with subsequent operations. The vanadium in the solution
was reduced to the tetravalent state with sulfur dioxide
and was then titrated with potassium permanganate.

The analytical results given in Table 3 for the alloys containing less than 10 per cent vanadium refer to the swaged wires. The results given for alloys containing more than 90 per cent vanadium are for pieces of rolled sheet. The mechanical redistribution of material resulting from rolling or swaging should have made the wires or sheets from which specimens were taken quite homogeneous. It was assumed, in these cases, that the analytical result was representative of the entire wire or sheet.

The amounts of vanadium and zirconium used in making any alloy not rolled or swaged were large enough to permit accurate calculation of the ingot composition. Each component of each charge was weighed to the nearest 0.1 gram for these alloys. Ingots weighed about 90 grams and were weighed to the nearest 0.1 gram. Weight losses were never more than 0.4 gram and were less than 0.1 gram for alloys made from iodide zirconium.

Deviations of analytical results from calculated compositions may have been due to inhomogeneity in the ingot in a few cases. In four cases--the alloys with calculated compositions of 50, 52, 53 and 55 per cent vanadium--the specimen chosen for analysis was cut from a piece of ingot which had previously been annealed for 30 hours at about 1290°C to ensure homogeneity in this portion. The

annealed pieces from these ingots were used for all work
except solidus temperature determinations.

Solidus Temperature Determinations

The temperature at which the first liquid was formed
from a solid alloy was determined by measuring the apparent
temperature of a hole in the specimen with an optical
pyrometer at the first sign of liquid. If the ratio of
depth to diameter of a hole in a solid is great enough,
virtually all thermal radiation entering it will undergo
multiple reflections and be completely absorbed. Such a
hole is, therefore, a good approximation to a black body,
and it will appear to be brighter than any non-black body at
the same temperature. A highly reflecting liquid surface in
the bottom of the hole destroys the approximation to black
body conditions. The apparent temperature of the hole
drops as soon as a small amount of liquid collects in the
bottom. In practice, the liquid usually appears as a black
spot in the bottom of the hole.

Specimens for solidus temperature determinations were
cut from the ingots. Notches were cut into each edge of
the central portion of the specimen to provide a narrow
portion of nearly rectangular cross section. A 0.028 inch
diameter hole was drilled into the center of the rectangular
section to a depth of about 3/16 inch. A few specimens were

annealed for 40 hours at about 1300°C after preparation to ensure a good approach to equilibrium at the solidus.

The specimens were heated to melting in a water-cooled, evacuated furnace by the passage of an electric current (up to 2,000 amperes) through the specimen itself. The furnace was similar to one described by Wilhelm, Carlson and Lunt (7). The ends of the specimen were clamped against heavy copper plates, each of which was clamped to a thick-walled, water-cooled copper cylinder which extended through the furnace shell to act as a current lead. Pressure in the furnace was maintained at or below 10^{-5} millimeters of mercury during heating. The furnace was equipped with a sight glass so that an optical pyrometer could be focused upon the hole in the heated portion of the specimen. The appearance in the bottom of the hole of a black spot which increased in size with increasing temperature was taken as the first indication of melting. The highest reading of the optical pyrometer prior to the appearance of the black spot, corrected by one or both of the methods discussed below, was taken as the solidus temperature. Heating from a few degrees below the solidus temperature to the start of melting required about one-half hour to provide time for establishment of equilibrium conditions in the hot zone.

Since the optical pyrometer had to be sighted upon the hole through a piece of Pyrex glass, corrections for

radiation absorbed by the glass had to be applied to the pyrometer reading. Wien's law was used to calculate corrections because it is simple and is a good approximation to the intensity of thermal radiation emitted by a surface at the temperatures involved here.

The expression for the intensity, $I_{\lambda T}$, of thermal radiation of wave length λ reaching the pyrometer is

$$I_{\lambda T} = A_\lambda\, J_{\lambda T} = A_\lambda\, E_\lambda\, C_1\, \lambda^{-5} e^{-C_2/\lambda T}, \quad (1)$$

where $J_{\lambda T}$ is the Wien's law expression for the intensity of thermal radiation of wave length λ emitted by a surface at the temperature T^o Kelvin, and C_1 and C_2 are constants. E_λ, the emissivity of the surface, is unity for a black body and less than unity for a non-black surface. It is characteristic of the surface but may be a function of temperature. A_λ is the transmission coefficient for the medium or media between the emitting surface and the pyrometer. A_λ and E_λ can be combined into an effective emissivity, E_λ', for the surface.

If the intensity of radiation of wave length λ from a black body at temperature T_A is the same as that from a surface of effective emissivity E_λ' at T, the expression (1) gives

$$\frac{1}{T} - \frac{1}{T_A} = \frac{\lambda\, \log_{10} E_\lambda'}{6210}, \quad (2)$$

where λ is in microns, and the value of C_2, 1.432 cm

degrees Kelvin (8, p. 174), has been inserted. This is the formula used for obtaining the corrected temperature, T, from T_A, the pyrometer reading.

For the pyrometer used, 0.65 microns is the effective wave length at which the brightness of the surface is matched with that of the lamp filament. The lamp current at the matching point is calibrated to give the apparent temperature of the surface.

The second method for correcting optical pyrometer readings was an empirical one. The sight glass was placed between the pyrometer and a standard lamp. The pyrometer was focused upon the lamp filament, and the pyrometer lamp current was set and standardized at the apparent temperature reading. The current through the standard lamp was then varied until the two filaments appeared to be equally bright. The potential drop across a standard resistance in series with the lamp was determined, and the current was calculated from Ohm's law. The corrected temperature was read from a calibration curve of lamp current versus black body temperature. Corrected temperatures obtained by this method were chosen in preference to calculated values when both methods of correction were used. The two methods agreed within ± 10°C.

Thermal Analysis

Heating and cooling curves were run by a modification of the method of C. S. Smith (9). In Smith's method the specimen is placed in a closed refractory crucible. It is assumed that both the heat capacity of the specimen and the thermal conductivity of the refractory are temperature-independent and that heat conduction through the refractory wall is proportional to its thermal conductivity and the temperature gradient across it. If a constant temperature gradient is maintained across such a refractory wall, the rate of heat transfer to or from the enclosure is constant. The rate of change of temperature of a specimen with constant heat capacity is proportional to the rate of heat transfer. Any reaction in the specimen changes its effective heat capacity and alters the rate of change of temperature for a given rate of heat transfer.

In the modified method the specimen was placed in an evacuated silica tube which ran through a hole in the center of a firebrick cylinder. A wire-wound tube furnace surrounded the firebrick. One junction of a differential chromel-alumel thermocouple was placed on the inner surface of the cylinder and the other on the outer surface at the center of the heated zone. A chromel-alumel thermocouple was led into the interior of the silica tube through a seal and its junction was placed in contact with one end of the specimen.

A pressure less than 10^{-6} millimeters of mercury was maintained in the tube during operation of the apparatus.

Since the difference in potential between the hot and cold junctions of a chromel-alumel thermocouple is nearly a linear function of the difference in temperature between the junctions, maintenance of a constant difference of potential between the junctions of the differential thermocouple gave a nearly constant temperature gradient across the firebrick. The constant potential difference was maintained by a Minneapolis-Honeywell strip-chart controlling potentiometer. The specimen temperature was plotted against time by putting the output of the thermocouple in contact with it into the pen drive circuit of a Minneapolis-Honeywell strip-chart potentiometer.

The heated zone in this apparatus was open at each end, so that a temperature-dependent heat loss from the enclosure was to be expected. The ratio of length to diameter of the heated tube was made large to minimize the effect.

Dilatometry

An apparatus designed by Dooley and Atkins (10) was used to measure changes of length in specimens cut from alloy ingots. The specimen rested on a fused-silica seat in a fused-silica tube in which pressures of 10^{-6} millimeters

of mercury or less were maintained. A chromel-alumel thermocouple protruded through the silica seat into a hole in the end of the specimen. A pointed, fused-silica rod bearing the core of a linear differential transformer on its upper end rested in a shallow depression in the upper end of the specimen. The transformer windings were mounted on an adjustable platform attached to the furnace tube.

Six volts at two kilocycles was applied to the primary windings of the differential transformer. The secondary voltage, which varied linearly with core position over a 0.020 inch range, was amplified and rectified and put into the chart drive circuit of a Minneapolis-Honeywell function plotter. The output of the thermocouple in contact with the specimen was put into the pen drive circuit of this instrument. A plot of length change versus temperature was obtained directly, therefore. No attempt was made to calibrate the chart scale, but the pen scale was calibrated with a portable potentiometer. Heating and cooling rates employed were about 5°C per hour and were obtained by use of a Minneapolis-Honeywell program controller.

Electrical Resistance

A potentiometric method was used to measure the electrical resistance of wires from these alloys. Three-eights inch pieces of 1/8 inch diameter tantalum rod were

drilled and swaged onto the ends of four inch lengths of
0.025 inch diameter wire. Two lengths of chromel wire
were crimped into a hole in the end of one of the tantalum
pieces and two lengths of chromel plus one length of alumel
wire were crimped into a hole in the end of the other tan-
talum piece. The lead wires were insulated from one another
with small-bore, fused-silica tubing. The arrangement
provided reasonably low resistance contacts to the wire, but
isolated the leads from direct contact with the alloy.

In two cases, the 3.80 and 5.36 per cent vanadium alloys,
pieces of zirconium rod were used in place of tantalum. The
change to tantalum was made when the method proved sensitive
enough to detect the transformation in the zirconium
connectors.

The assembly was placed in a fused-silica tube in an
18 inch long wire-wound tube furnace. Pressures in the tube
were maintained at or below 10^{-6} millimeters of mercury.
Lead wires were brought out of the tube through wax seals.
The furnace temperature was controlled by a Minneapolis-Honey-
well strip-chart controlling potentiometer.

One chromel wire on each end of the specimen served
as a current lead. Current from storage batteries passed
through a standard resistance, a milliammeter, two rheostats,
the leads, and the specimen in series. The two other chromel
wires were connected to a precision potentiometer so that

the potential drop across the specimen could be determined.
The alumel wire and the chromel potential lead on the same
end of the specimen could also be connected to a second
potentiometer for temperature measurements. A switch was
provided to shift the chromel lead from the potential to the
temperature measuring circuit and back. A second switch
permitted measuring the potential drop across the standard
resistance rather than that across the specimen when so
desired. The former was always adjusted to 50.00 millivolts,
corresponding to a current of 50.00 milliamperes, before
the potential drop across the specimen was measured.
Resistance values were calculated from Ohm's law.

Specimens usually remained at a given temperature for
one hour or longer before a measurement was made. Waiting
periods at temperatures above 900°C were somewhat shorter
to minimize possible reaction of the specimen with the silica
tube.

Metallography

Annealing and quenching methods

Table 4 lists the composition of each alloy investigated
by metallographic methods and the heat treatment given it
prior to quenching. Two heat treatments
were given each specimen of four different alloys, as
indicated. These specimens were pieces cut from the ingots.

Table 4

Heat Treatments for Vanadium-Zirconium Alloys

Composition wt. %V	Heat Treatment before Quenching
49.66	40 hours at 1220°C*, then 46 hours at 1100°C
49.66	40 hours at 1220°C*, then 455 hours at 600°C
51.68	30 hours at 1290°C*, then 46 hours at 1100°C
51.68	30 hours at 1290°C*, then 455 hours at 600°C
53.02	30 hours at 1290°C*, then 46 hours at 1100°C
53.02	30 hours at 1290°C*, then 455 hours at 600°C
54.10	30 hours at 1290°C*, then 46 hours at 1100°C
54.10	30 hours at 1290°C*, then 455 hours at 600°C
94.33	25 hours at 1150°C
94.33	89 hours at 1000°C
94.33	385 hours at 800°C
94.33	455 hours at 600°C
96.54	25 hours at 1150°C
96.54	89 hours at 1000°C
96.54	385 hours at 800°C
96.54	455 hours at 600°C
98.78	22 hours at 1150°C
98.78	24 hours at 1000°C
98.78	100 hours at 800°C
98.78	170 hours at 600°C

*1220°C and 1290°C were the temperatures at the outer wall of the furnace tube. Specimen temperatures must have been slightly lower.

The other specimens were pieces of sheet material; they were given a single heat treatment before quenching.

The purpose of the preliminary, high-temperature annealing treatment was to remove the non-equilibrium, dendritic type of microstructure exhibited by the ingots. An annealing temperature as near as possible to the solidus was chosen. The succeeding treatment was for the purpose of securing equilibrium conditions at the temperature from which the specimens were quenched.

Annealing at temperatures of 1220°C and 1290°C was done in a Globar furnace. The specimens were placed upon a tantalum boat in a Mullite furnace tube and were heated at a pressure of 3×10^{-6} millimeters of mercury or less. They were cooled to room temperature before being given further treatment.

Heating at temperatures below 1200°C was done in evacuated fused-silica capsules. The specimens were placed in fused-silica tubing and were heated to a temperature slightly above that from which they were to be quenched at a pressure less than 10^{-6} millimeters of mercury. The specimens were then cooled under the high vacuum, and the tube was sealed off on each side of each specimen to form the capsules. The capsules were heated in a tube furnace.

Quenching was accomplished by plunging the fused-silica capsule containing the specimen into a mixture of dry ice and trichloroethylene and crushing the capsule.

Polishing and etching methods

Specimens were ground on a series of abrasive papers of decreasing grit size. A canvas-covered lap loaded with moistened, 400-grit carborundum powder was found to be most satisfactory for a first polishing stage. The same abrasive on a damp Microcloth[1]-covered lap was used as a second stage. Final polishing was done on a Microcloth-covered lap with Grade 1 diamond paste.

Nitric acid was used to etch alloys containing more than 90 per cent vanadium. Hydrofluoric acid was satisfactory in other cases. Quick swabbing followed immediately by rinsing in water was necessary.

X-ray Diffraction

Production of powder specimens for analysis by X-ray diffraction was relatively simple. Pieces of alloys containing from 30 to 70 per cent vanadium were readily crushed in a Plattner mortar. A fine silica fiber coated with a hydrocarbon grease was rolled in the powder to produce the specimen proper.

Powder specimens were exposed to copper radiation filtered by nickel foil in a Debye-Scherrer type camera with Straumanis film mounting. Vanadium fluoresces somewhat

[1]Microcloth is the trade name for a cloth with cotton backing and rayon pile supplied by Buehler, Ltd.

in copper radiation, but exposures to chromium radiation gave no noticeable improvement in the quality of film patterns. No precision techniques were attempted.

RESULTS AND DISCUSSION

The Equilibrium Diagram

Figure 1 shows the equilibrium diagram for the vanadium-zirconium system deduced from the results of this investigation. The existence of the horizontals at 1230°C and 1300°C was shown by solidus temperature measurements. The eutectic nature of the 1230°C horizontal is obvious from its position, but it was confirmed by metallographic evidence. Metallographic evidence, also, showed the peritectic nature of the 1300°C horizontal, the composition limits for the gamma phase, and the probable boundary of the vanadium-rich solid solution. Thermal analysis, dilatometry, and electrical resistance measurements were relied upon to establish the eutectoid horizontal at 777°C and the boundary between the beta and alpha-plus-beta regions. X-ray diffraction data confirmed the existence of V_2Zr, showed that there was no transformation in the compound, and indicated that the composition range for its existence was very small. These lines of evidence are discussed in detail in the following sections.

The Solidus

The results of solidus temperature determinations are shown in Table 5. Calculated compositions rather than
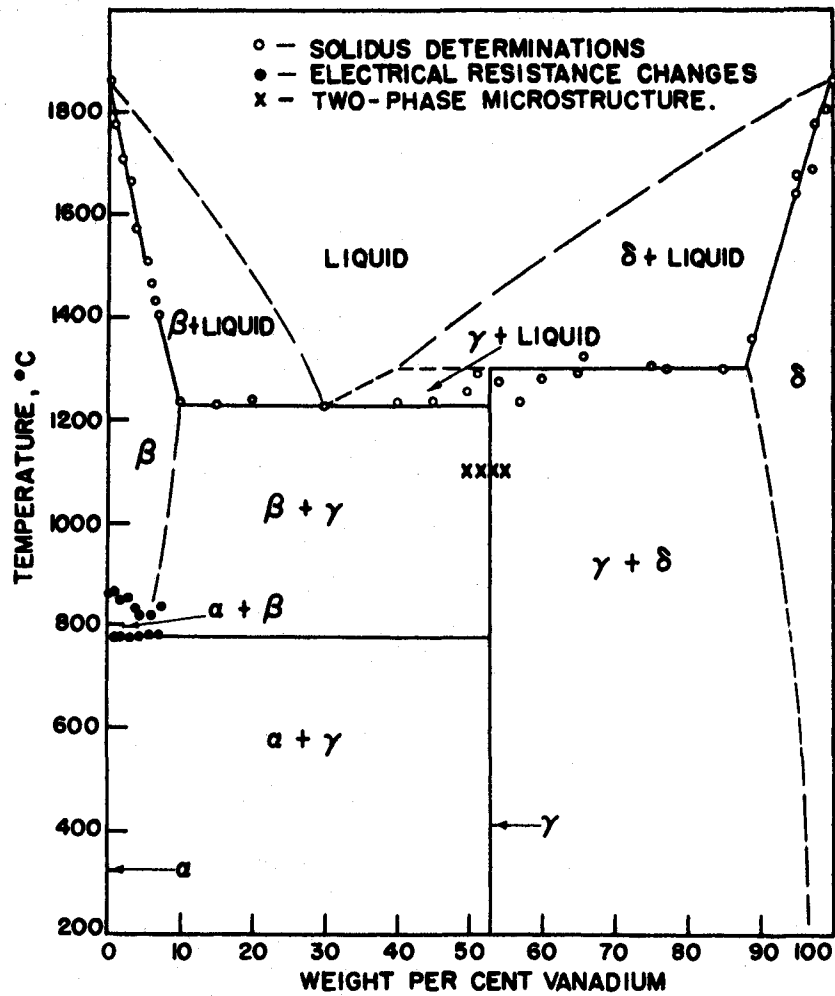
Fig. 1.   The equilibrium diagram for the
vanadium-zirconium alloy system.

Table 5

Solidus Temperatures of Vanadium-Zirconium Alloys

Calculated Composition wt. %V	Melt No.	Solidus Temperature, deg. C					Average
		Spec. 1	Spec. 2	Spec. 3	Spec. 4	Spec. 5	
0	-----	1856	1854	1860	1869	1860	1860
1	M-807	1770	----	----	----	----	1770
2	M-727	1705	----	----	----	----	1705
3	M-723	1665	----	----	----	----	1665
3	M-809	1670	----	----	----	----	1670
4	M-812	1570	1580	----	----	----	1575
5	M-811	1495	1495	1530	----	----	1505
6	M-815	1465	----	----	----	----	1465
6.5	M-813	1430	1435	----	----	----	1430
7	M-810	1420	1390	----	----	----	1405
10	M-797	1315	1175	1370	1315	1250	1285
10	M-947	1235	----	----	----	----	1235
15	M-882	1230	----	----	----	----	1230
20	M-724	1260	1225	1245	----	----	1240
30	M-725	1225	1225	----	----	----	1225
40	M-726	1235	1235	1230	----	----	1235
45	M-819	1235	1235	1235	----	----	1235
47	M-903	1235	----	----	----	----	1235
50	M-590	1280	1240	1240	----	----	1255
52	M-902	1290	----	----	----	----	1290

27

Table 5 (Continued)

Calculated Composition wt. %V	Melt No.	Solidus Temperature, deg. C					
		Spec. 1	Spec. 2	Spec. 3	Spec. 4	Spec. 5	Average
53	M-900	1295	1305*	----	----	----	1300
55	M-817	1265	1275	1280	----	----	1275
60	M-603	1235	----	----	----	----	1235
60	M-873	1275	1275	1285	1285	----	1280
65	M-881	1285	1295	----	----	----	1290
70	M-602	1325	----	----	----	----	1325
75	M-883	1305	1305	1290*	1310*	----	1305
80	M-589	1300	----	----	----	----	1300
85	M-884	1305	1295	1330*	----	----	1310
90	M-587	1360	----	----	----	----	1360
92.5	M-886	1315	1325	----	----	----	1320
95	M-592	1675	----	----	----	----	1675
95	M-944	1640	----	----	----	----	1640
97.5	M-899	1685	----	----	----	----	1685
98	M-591	1775	----	----	----	----	1775
99	M-588	1805	----	----	----	----	1805
100	M-818	1850	1865	----	----	----	1860

*Specimen heated about 40 hours at about 1300°C before determination.

analytical results are given, since the calculated values are probably more reliable than the analytical results for pieces of the ingots. The results of individual determinations and the average value are given for each composition. Temperatures marked with an asterisk were obtained from measurements upon specimens heated for about 40 hours at about 1300°C after preparation. The temperature of the outside wall of the furnace tube in which the heating was done was 1320°C. The specimen temperature must have been slightly lower.

Observed solidus temperatures decreased rapidly with increasing vanadium content from 1860°C at pure zirconium to 1230°C at 10 weight per cent vanadium. From 10 per cent vanadium to 50 per cent vanadium the solidus temperature was 1230°±10°C independent of composition. Between 50 per cent and 90 per cent vanadium the value 1300°±25°C was obtained with one exception--1235°C for one of the 60 per cent vanadium alloys. A rapid increase in solidus temperature with increasing vanadium content was observed from 90 per cent vanadium to pure vanadium. A solidus temperature of 1860°C was found for vanadium. The material exhibited a melting range rather than a melting point.

As Figure 1 indicates, the rapid change in solidus temperature with composition near the ends of the diagram shows that vanadium and zirconium have some mutual solid

solubility at high temperatures. This is roughly 10 per cent by weight of one element in the other at the maximum, as the solidus curve shows.

The horizontal portion at 1230°C in the solidus curve of Figure 1 must represent a eutectic reaction in the system, since it was the lowest temperature at which any of the vanadium-zirconium alloys started to melt. The rather abrupt rise in solidus temperature obtained at about 50 weight per cent vanadium implies that the reaction by which liquid is formed is one between the beta solid solution and an intermediate phase and not one between the two terminal solid solutions. Figure 2, the microstructure of a 30 per cent vanadium ingot, shows the typical structure resulting from the simultaneous precipitation of two solid phases from a liquid. Apparently, all of the material in this ingot solidified in this way. The eutectic composition must be very near to 30 per cent vanadium by weight, therefore.

Figures 3 and 4 show that the solidus temperature 1300°C obtained over a wide range of compositions is the temperature of a peritectic reaction. Both figures show microstructures of an alloy of 53.02 per cent vanadium. The area of this alloy heated to melting in a solidus temperature determination is shown in Figure 3. Figure 4 shows the material as it was after melting in the arc furnace. The gray areas are the vanadium-rich solid solution formed as the melt

Fig. 2. Eutectic structure
of 30 per cent vanadium
alloy ingot.
Etched with HF.
x 1200

Fig. 3. Peritectic
surrounding in partially
melted zone of 53.02
per cent vanadium alloy
melting point specimen.
Etched with HF.
x 1200
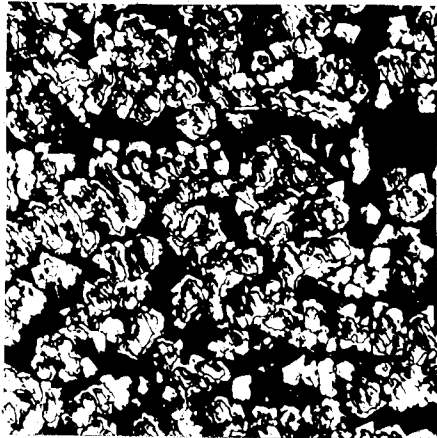
Fig. 4. Peritectic
surrounding in unheated
zone of 53.02 per cent
vanadium alloy melting
point specimen.
Etched with HF.
x 240
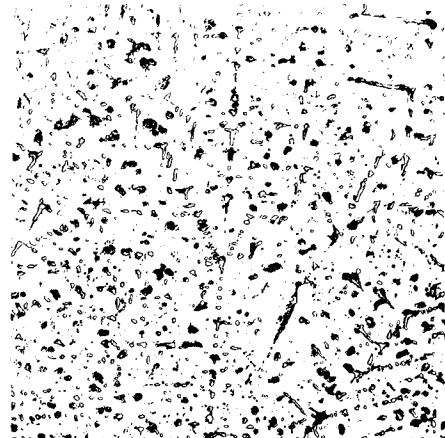
Fig. 5. Delta plus gamma
phases in area adjacent to
hole in 53.02 per cent
vanadium alloy melting
point specimen.
Etched with HF.
x 120

started to cool. White areas surrounding the gray are the intermediate phase formed by reaction of the liquid with the solid solution at the peritectic temperature. The peritectic reaction did not have time to go to completion because of the high rate of cooling in the furnace, so some of the liquid cooled far enough to decompose by the eutectic reaction. Black areas are eutectic--not resolved in these pictures because the eutectic portions were overetched in developing the rest of the structure.

The metallographic evidence alone is enough to establish quite conclusively that a eutectic reaction and a peritectic reaction occur in the vanadium-zirconium system. The temperatures at which these reactions were found to take place, however, might have been subject to a number of errors. The possible errors fall into three classes: the pyrometer readings or corrections may have been erroneous; the conditions for observation of black-body temperatures in the hole may not have been met; the specimen may have been inhomogeneous, or it may not have been in equilibrium at the time liquid appeared.

The uncertainties involved in matching the brightness of the pyrometer filament with that of the hole in the specimen and in obtaining the corrected temperature reading were found to be $\pm 10°C$. This is larger than normal because of the small area of the filament of the standard lamp used to

correct the pyrometer readings. Two pyrometers, each of which had been calibrated against a lamp certified by the National Bureau of Standards, were used throughout the work. The uncertainty in the calibration of these instruments should not have been more than $\pm 5°C$ (8, p. 184). The empirical method employed for correction of pyrometer readings was a safeguard against calibration changes.

Several possible sources of error might have existed if the assumptions upon which the method for solidus temperature determinations was based were not fulfilled. No corrections were applied to temperature readings to account for deviations from black-body conditions in the hole. Therefore, not only must the depth-to-diameter ratio of the hole have been large enough to give an absorptivity of unity, but the region in which the hole was drilled must have been uniform in temperature.

The observed melting point of zirconium was found to be independent of the depth-to-diameter ratio down to a value of four. A value for this ratio of five was assumed to be large enough in the case of the alloys.

Temperature gradients across the region of the hole were measured in several determinations by observing the apparent temperature of the surface at each edge of the hole and at the center. The gradient was found to decrease as the temperature increased. At a corrected temperature of 1260°C, as

determined from observations on the hole, the gradient was
found to be about 30°C. It was never less than 20°C nor more
than 35°C at this temperature. The gradient was from one
edge of the hole to the other in some cases, from the center
to one edge in others. The pyrometer must have indicated
a temperature between the extremes. The error from this
source would have made the temperatures low by no more than
about 15°C.

The necessity for the formation of a visible amount of
liquid in the determination of solidus temperatures leads
to slightly high values, partially compensating for the errors
due to temperature gradients. The error would be largest
for specimens in which the fraction of molten material changed
most slowly with temperature. Good evidence that this error
was not large lies in the close approach of individual values
for the eutectic temperature to the average over quite a wide
range of compositions.

If the general form of the equilibrium diagram shown in
Figure 1 is correct, the first liquid formed from a solid
alloy in this system can only be the result of the melting
of one of the terminal solid solutions, the reaction of
beta with gamma to form liquid, or the decomposition of the
intermediate phase into liquid and delta. The first of these,
the melting of a terminal solid solution, could be observed
only if the hole in the specimen had been drilled into

material consisting of a single phase. For alloys between 10 and 90 per cent vanadium in composition, such extreme inhomogeneity would have been evident upon visual examination. In these cases, the solidus temperature observed must have been either that of the eutectic or of the peritectic reaction in the absence of errors in the temperature measurement proper.

The conditions under which these alloys were cooled were such that some of the eutectic mixture of phases occurred in every ingot with composition between 10 and 90 per cent vanadium. Therefore, the eutectic temperature would have been observed during solidus temperature determinations on any one of these alloys provided that there was enough eutectic mixture to give a visible amount of liquid, and provided that heating did not remove the beta phase at temperatures below the eutectic. The peritectic temperature could have been correctly determined only if there had been enough diffusion in the hot zone of the specimen to remove the beta phase prior to the formation of the first liquid.

Evidence was obtained to show that specimens were effectively annealed during the period of slow heating to the first appearance of liquid. Figures 3, 4, and 5 show different portions of the melting point specimen from the 53.02 per cent vanadium ingot. Figure 3 shows the zone

which had started to melt and Figure 4 shows the unheated portion of the bar, as described previously. Figure 5 shows a portion of the hot zone of the bar adjacent to the hole. Melting had not started in this zone, but the diffusion had been sufficient to remove all traces of the eutectic mixture from it.

Additional evidence that the liquid observed during solidus temperature determinations on specimens of composition between 58 and 90 per cent vanadium was due, in most cases, to the peritectic reaction was provided by the results labeled with an asterisk in Table 5. Each of these results was obtained upon a specimen which had been heated for about 40 hours at a temperature of about 1300°C before the determination was made. The heat treatment made no change in the solidus temperature observed for these compositions.

In one case, that of one 60 per cent vanadium alloy (Table 5), the value for the solidus temperature appears to have been that of the eutectic reaction. This was the only such case encountered.

The data shown in Table 5 and plotted in Figure 1 gave 1230°±10°C for the eutectic temperature and 1300°±25°C for the peritectic temperature. The errors just discussed may have made these values low by as much as 15°C. Certainly, none of them account for the large discrepancy between the

peritectic temperature given here and the value 1740°C indicated by Rostoker and Yamamoto (4).

The Eutectoid Transformation

Thermal analysis, dilatometry, and electrical resistance measurements all gave evidence that the alpha-to-beta transformation temperature is lower in vanadium-zirconium alloys than in unalloyed zirconium. Of the three methods, electrical resistance measurements proved to be the most sensitive and precise for the determination of the temperature of the eutectoid transformation.

Thermal analysis

The results shown in Table 6 were valuable in indicating the range of compositions over which the eutectoid transformation takes place. The thermal analysis curves from which these data were derived are shown in Figures 6 and 7. Figure 6 contains heating curves for several alloys; Figure 7 shows the cooling curves. All compositions indicated on the figures are calculated values except for the two analytical results, 1.03 and 5.36 per cent vanadium. The zero point of the time scale for these curves is arbitrary, but the temperature scale was obtained by calibration of the recording potentiometer on which the curves were made. The temperature range of transformation listed in Table 6 for a particular alloy

Table 6

Transformation Ranges in Some Vanadium-Zirconium Alloys from Thermal Analysis Curves

Composition wt. %V	Temperature[**] Range of Transformation	
	From Heating Curve	From Cooling Curve
1.03	837 - 841	793 - 800
2[*]	832 - 851	800 - 819
3[*]	827 - 837	815 - 829
5.36	824 - 841	795 - 815
10[*]	797 - 819	771 - 802
20[*]	807 - 822	----------
40[*]	854 - 859	----------

[*]Calculated composition

[**]Values given are temperatures in degrees Centigrade.
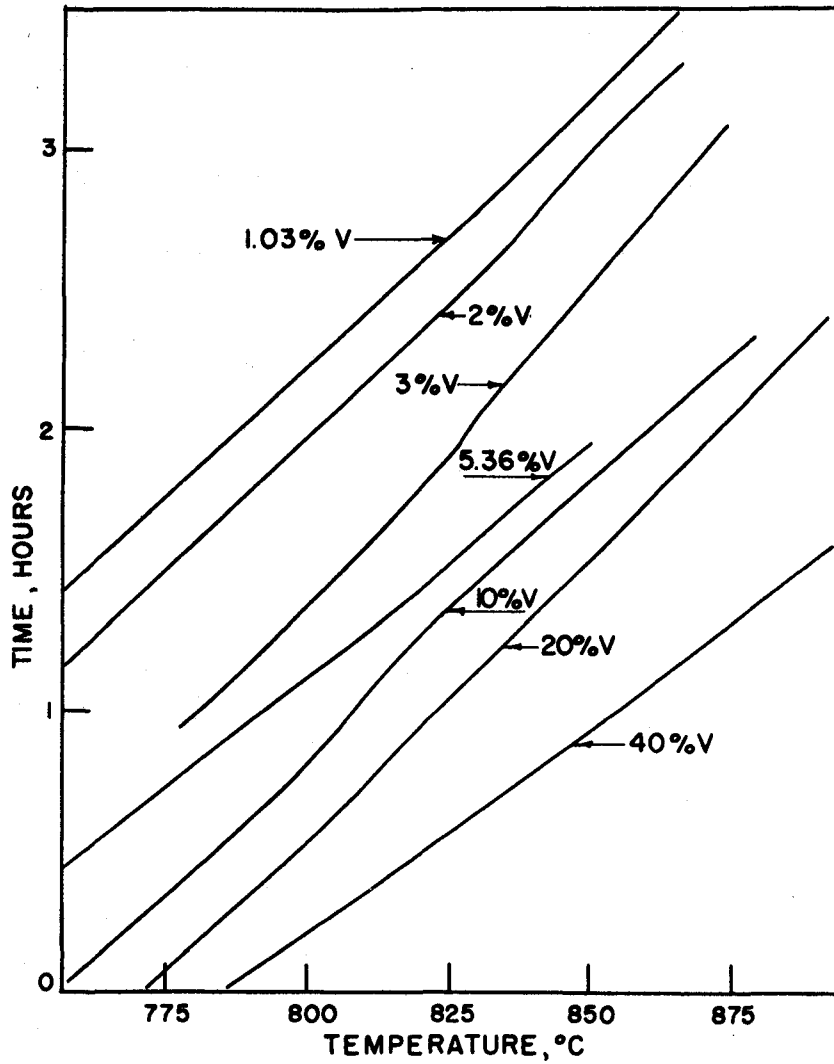
Fig. 6. Heating curves from thermal analysis
         of some vanadium-zirconium alloys.
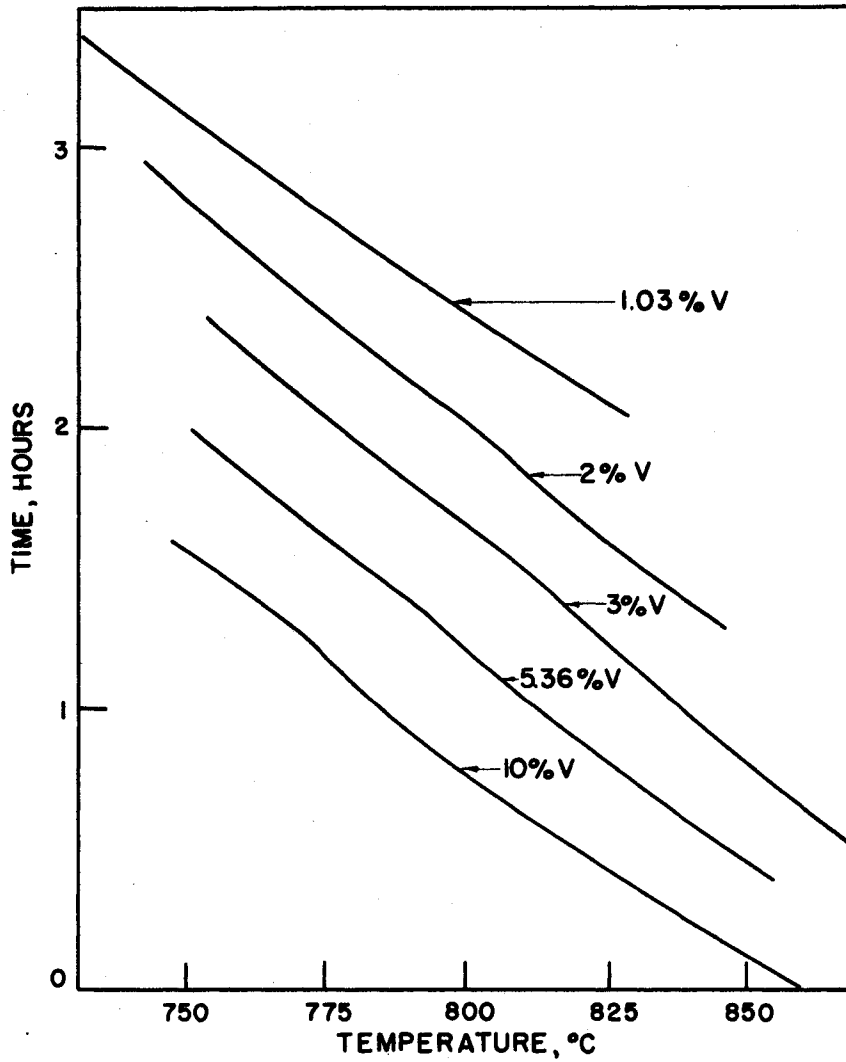
Fig. 7.   Cooling curves from thermal analysis
         of some vanadium-zirconium alloys.

represents the short interval on the corresponding curve of Figures 5 or 6 over which the slope differs from the nearly constant value characteristic of the remainder of the curve.

The results in Table 6 show that a transformation occurred in alloys from 1.03 to 40 per cent vanadium by weight in a temperature range from 770°C to 850°C. The value of Smith's method is illustrated by these results. The specimens were small—about five grams—and yet thermal effects were observed quite readily.

The small effect observed at 40 per cent vanadium suggested that the reaction occurring during heating was one between the alpha phase and an intermediate phase to give the beta phase, rather than one between the two terminal solid solutions.

Dilatometry

The dilatometric curves shown in Figures 8, 9, and 10 confirm the existence of the eutectoid transformation. The temperature ranges over which the curves show a negative slope are listed in Table 7 for 12 alloys. The 6 and 6.5 per cent vanadium values are calculated compositions: others are analytical values. The length scale for the curves is arbitrary. The calibration was approximately the same for each, but the zero point differs from case to case. The
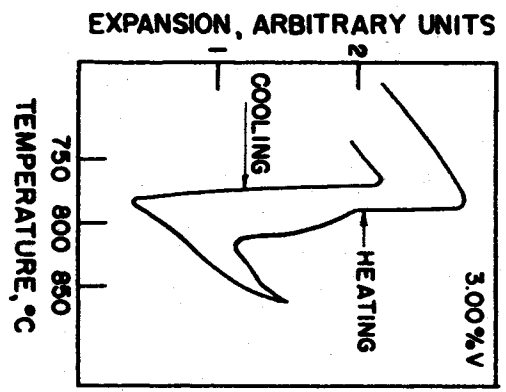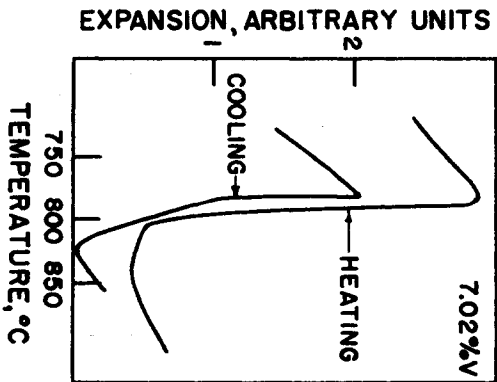
Fig. 8. Dilatometric curves for some vanadium-zirconium alloys.

EXPANSION, ARBITRARY UNITS

EXPANSION, ARBITRARY UNITS

EXPANSION, ARBITRARY UNITS
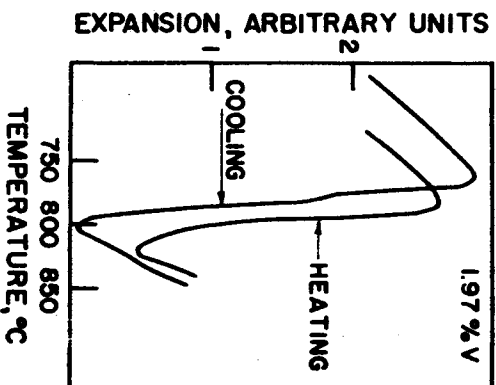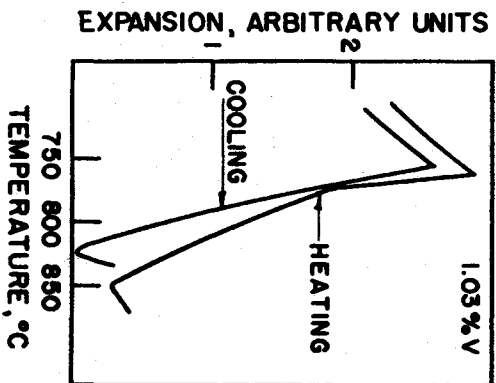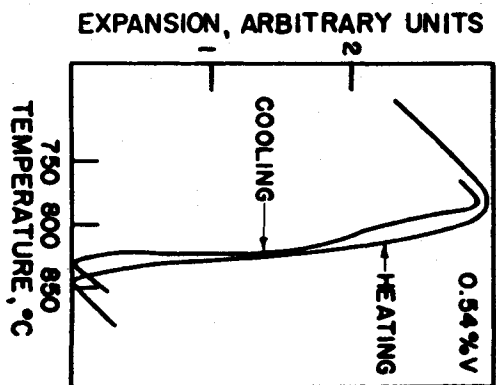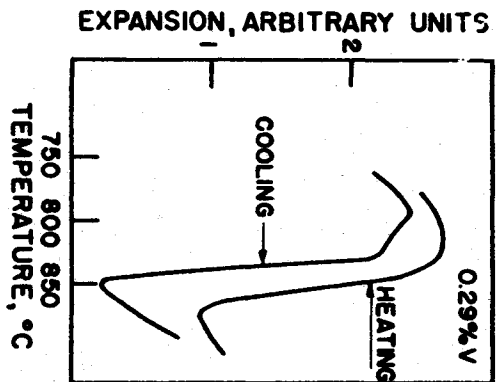
EXPANSION, ARBITRARY UNITS
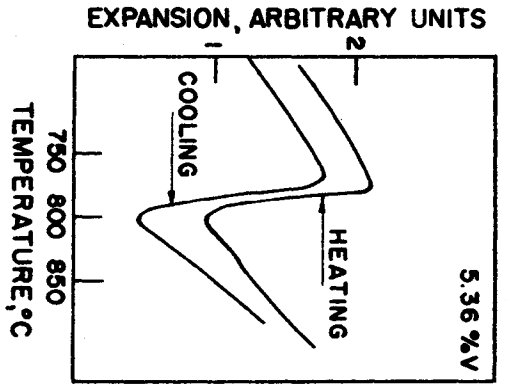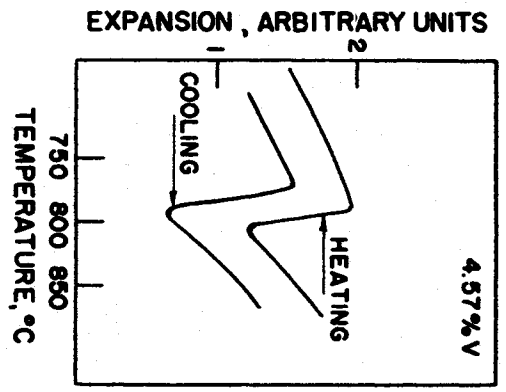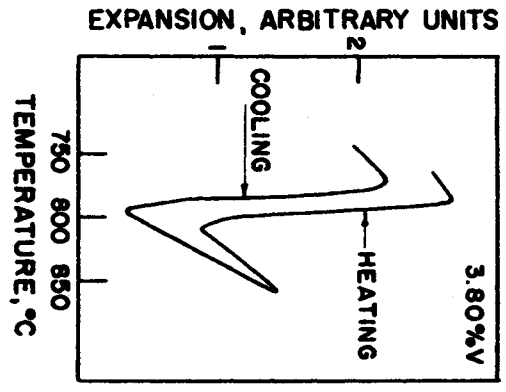
Fig. 9. Dilatometric curves for some
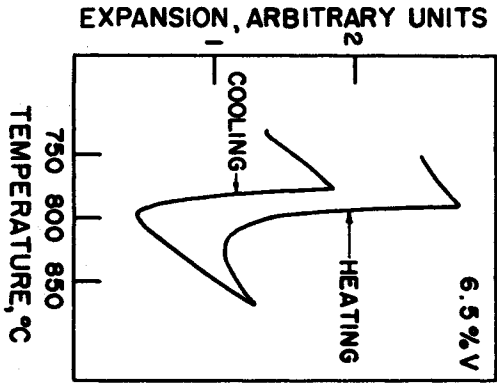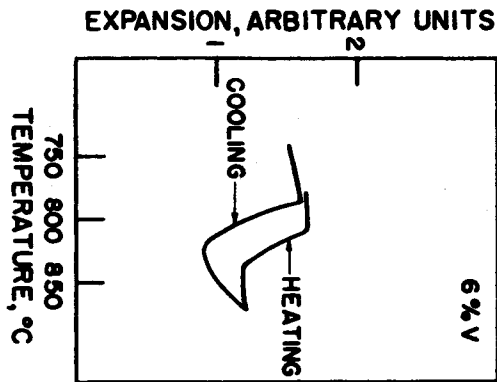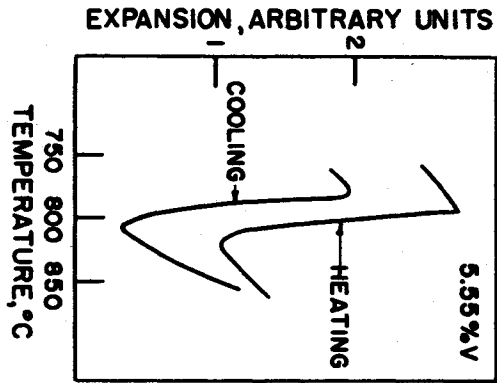   vanadium-zirconium alloys.

43

Fig. 10. Dilatometric curves for some vanadium-zirconium alloys.

44

Table 7

Transformation Ranges in Some Vanadium-Zirconium
Alloys from Dilatometric Curves

Composition wt. %V	Temperature** Range of Transformation	
	From Heating Curve	From Cooling Curve
0.29	812 - 871	793 - 849
0.54	785 - 841	780 - 829
1.03	761 - 849	756 - 824
1.97	788 - 824	766 - 802
3.00	783 - 815	766 - 785
3.80	785 - 810	771 - 795
4.57	790 - 808	760 - 786
5.36	778 - 800	773 - 800
5.55	795 - 824	776 - 805
6*	807 - 834	785 - 822
6.5*	785 - 839	773 - 797
7.02	783 - 849	783 - 822

* Calculated composition

**Values given are temperatures in degrees Centigrade.

temperature scale was determined by calibration of the pen
scale of the function plotter on which these curves were
made.

There are two significant things to be noted about the
dilatometric data. One of these is that the lower tempera-
ture limit of transformation in most of the cases listed in
Table 7 was close to the average value for this limit, 782°C.
The other is that the upper temperature limit decreased with
increasing vanadium content from 0.29 to about five per cent
vanadium. The lower limit was probably the temperature of
the eutectoid transformation. The upper limit probably
represented the boundary between the alpha-plus-beta and beta
regions. If this interpretation is correct, the results
indicate a eutectoid composition of about 5 per cent vanadium
by weight.

The dilatometric curves were not representative of
equilibrium conditions since the temperature ranges of
transformation during heating and cooling were not the same.
The approximation to equilibrium conditions was not as bad
as for thermal analysis, however. The heating curves are
probably more reliable than cooling curves, since they tended
to change less with heating rate than cooling curves changed
with cooling rate. Both heating and cooling rates were
about 5°C per hour for the curves shown in Figures 8, 9, and
10.

Electrical resistance measurements

Table 8 summarizes the electrical resistance data shown in Figures 11, 12, and 13. An arbitrary constant, different for each case, was subtracted from the specimen resistance in plotting the results. This was done to facilitate comparison of the curves. All compositions given are analytical results.

With the exception of the 0.29 and 0.54 per cent vanadium alloys, which have to be discussed separately, the electrical resistance started to decrease rapidly at 777° ±5°C in all of the alloys studied by this method. The temperature at which the resistance again began to rise decreased steadily from 1.03 to 4.57 per cent vanadium, then increased slightly at 5.55 per cent vanadium. None of these alloys exhibited an isothermal decrease in resistance, but in most cases the drop in resistance from 777°C to 785°C was very sharp.

The decrease in electrical resistance shown in these curves was interpreted as being caused by both the eutectoid reaction and the transformation of the alpha to the beta solid solution at temperatures above the eutectoid. The upper limit of resistance decrease for any case was taken as the boundary between the alpha-plus-beta and beta regions for the alloy to which the curve referred. The latter interpretation can hardly be valid for the 5.55 and 7.02 per cent

Table 8

Transformation Ranges in Some Vanadium-Zirconium Alloys from Electrical Resistance Changes

Composition wt. %V	Temperature Range of Transformation deg., C
0.29	802 - 900
0.54	790 - 890
1.03	775 - 865
1.97	777 - 845
3.00	777 - 852
3.80	772 - 830
4.57	777 - 822
5.36	780 - 822
5.55	780 - 830
7.02	782 - 835
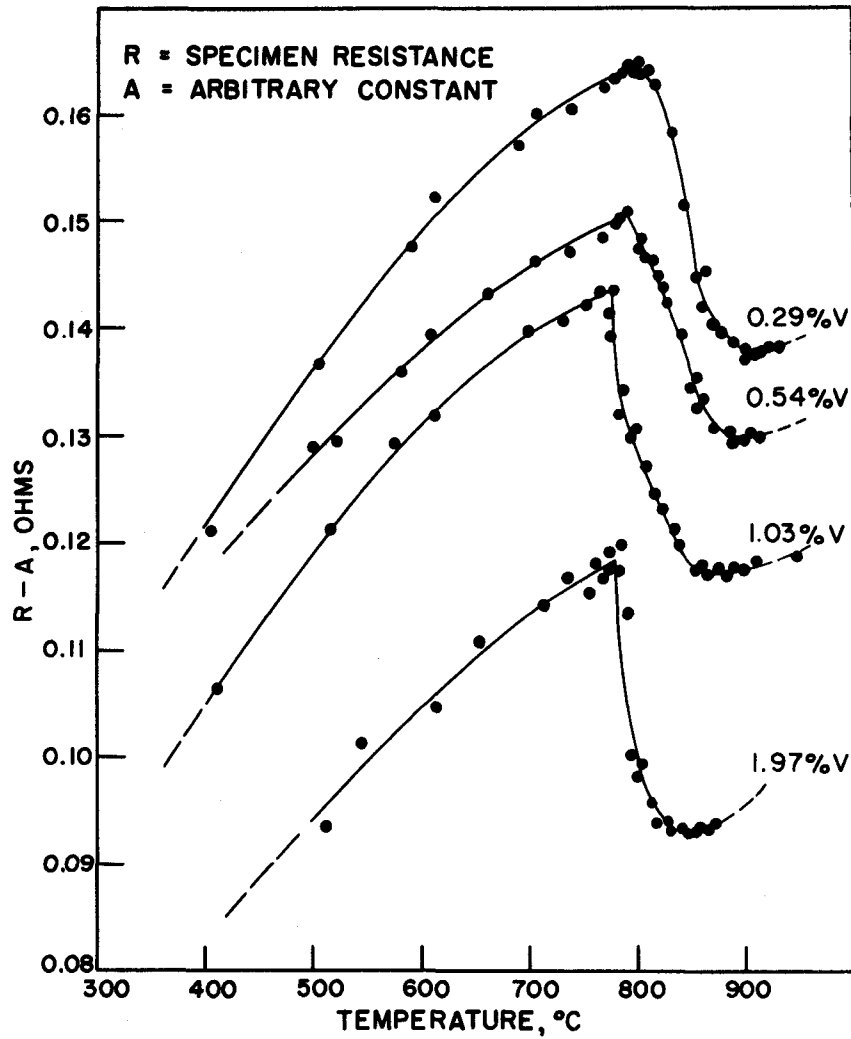
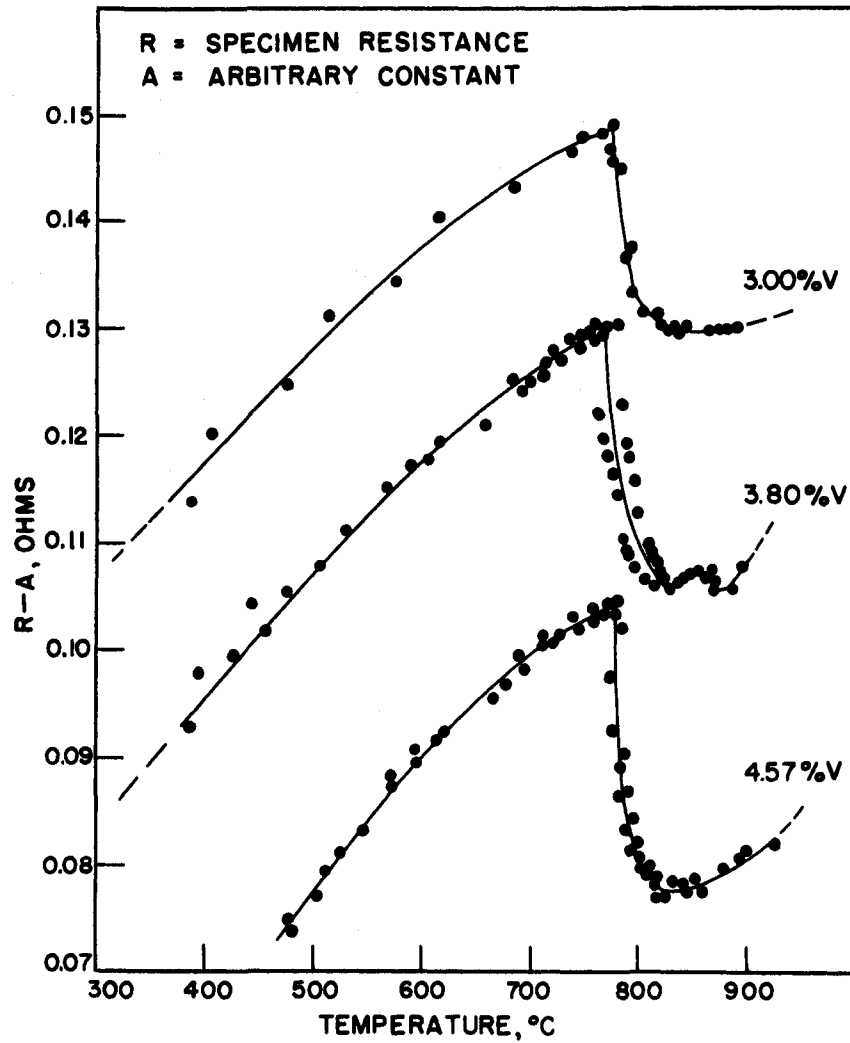Fig. 11. Electrical resistance vs. temperature curves for some vanadium-zirconium alloys.

Fig. 12. Electrical resistance vs. temperature curves for some vanadium-zirconium alloys.
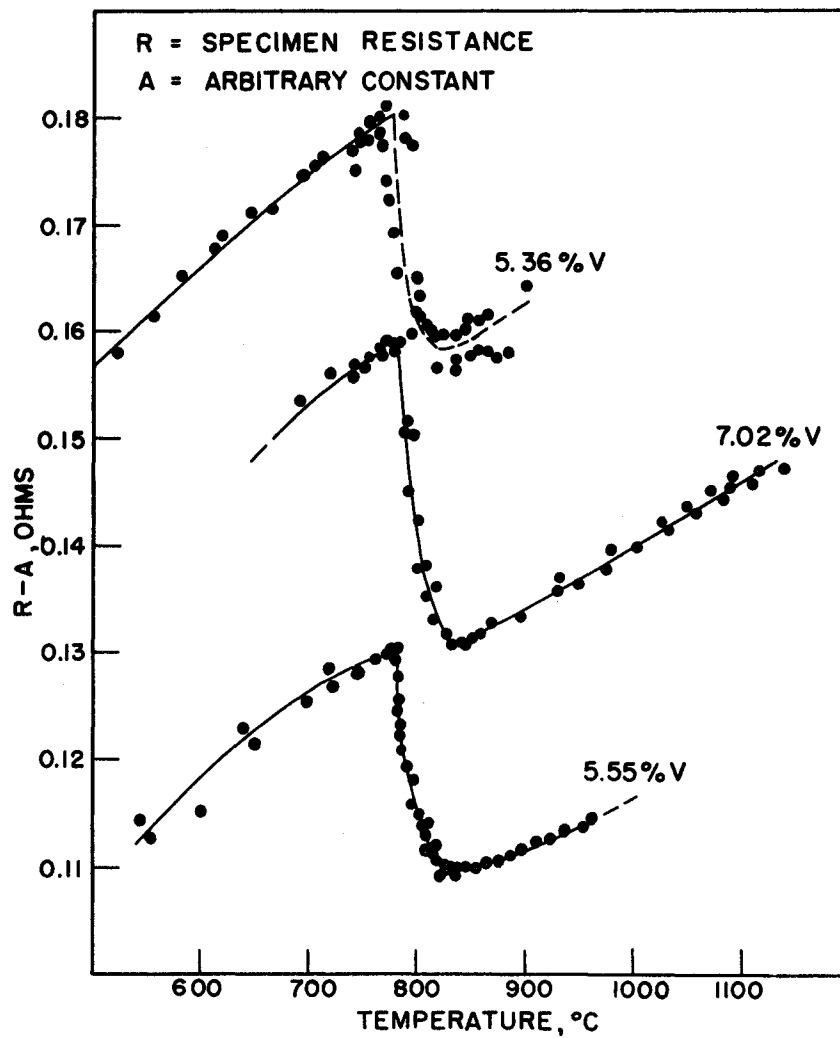
Fig. 13. Electrical resistance vs. temperature
curves for some vanadium-zirconium
alloys.

vanadium alloys, however. Presumably, these alloys should show the eutectoid reaction and a transformation from the beta-plus-gamma to beta regions. The upper limits listed are much too low to be the boundary between these regions; but, even up to 1140°C, the 7.02 per cent vanadium alloy showed no other resistance anomalies. Probably, the amount of material transforming in a large temperature range was so small for the 7.02 per cent alloy that it produced no observable effect on the resistance.

The lower temperature limit of transformation, 777° ±5°C, was taken as the temperature of the eutectoid reaction in the system. The trend in the upper temperature limits established the eutectoid composition at 5 per cent ±0.5 per cent vanadium by weight.

There are some other points in connection with the electrical resistance results which require comment. Points taken during both heating and cooling cycles were plotted on the curves. Points representing cooling cycles generally are somewhat to the left of the curves in Figures 11, 12, and 13; those representing heating are slightly to the right. Most of the curves indicated a good approach to equilibrium conditions. For the 3.80 and 5.36 per cent alloys, however, either the specimens became contaminated during the measurements or waiting periods were too short. In these cases, also, a second decrease in the resistance of the assembly

was observed at 860°C. This was caused by the transformation occurring in the zirconium used to connect leads to the specimen.

The results obtained on the 0.29 and 0.54 per cent alloys are more difficult to explain. If the alloys were truly binary, and if vanadium lowers the alpha-to-beta transformation temperature, the higher temperature limit of transformation for these alloys should have been less than 860°C, the transformation temperature observed for unalloyed zirconium. The observed limit was higher than 860°C in both cases, as it was for the dilatometric results on the 0.29 per cent alloy. The most likely explanation for this behavior is that some impurity (perhaps oxygen) in these alloys raised the transformation temperature above what it would have been in the binary alloys. The presence of such an impurity would also explain the temperature range of transformation observed for the eutectoid proper. The possibility of contamination in these alloys introduces some uncertainty into the values given for the eutectoid temperature and composition.

The rate of transformation

The eutectoid transformation occurs at a very high rate in the vanadium-zirconium alloys. Even at cooling rates of 200°C per minute an increase in electrical resistance was

observed in these alloys at a temperature of approximately
700°C. Moreover, the X-ray diffraction pattern from powder
made by crushing a lump of 47 per cent vanadium alloy quenched
from 1100°C showed alpha lines, not beta. The pattern is
shown in Figure 14.

The Gamma Phase

The composition range of the gamma phase was determined
by metallographic methods. Two heat treatments were given
the specimens used for microscopic examination, as indicated
in Table 4. The first of these treatments at just a few
degrees below the solidus temperature was to eliminate the
dendritic character of the alloys illustrated by Figures 3
and 4. The second was to produce equilibrium conditions at
1100°C before quenching. The effectiveness of the treatment
is shown by Figures 15, 16, 17, and 18. The 51.68 and
53.02 per cent vanadium alloys were nearly single phase.
Most of the black patches shown in Figures 16 and 17 are the
start of cracks in the specimens resulting from mounting in
plastic for polishing and etching. Small oval-shaped parti-
cles of a second phase are visible, however. The 49.66 per
cent vanadium alloy shown in Figure 15 and the 54.10 per cent
alloy shown in Figure 18 contained larger amounts of second
phases. The microstructures show rather well that the gamma
phase must have a very small composition range differing

Fig. 14. X-ray Diffraction Patterns from Some Vanadium-Zirconium Alloy Powders.

Top pattern: 45.50 per cent vanadium quenched from 1100°C

Second pattern: 45.50 per cent vanadium quenched from 600°C

Third pattern: 54.10 per cent vanadium quenched from 1100°C

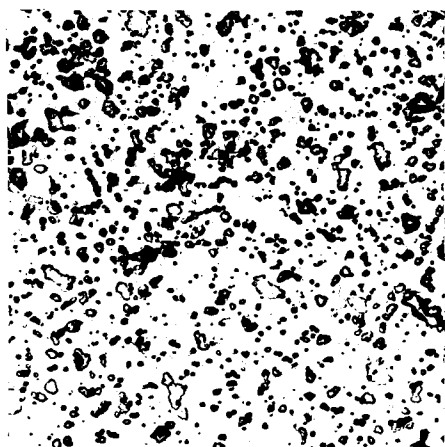Bottom pattern: 54.10 per cent vanadium quenched from 600°C

Fig. 15. Microstructure of
49.66 per cent vanadium
alloy quenched from 1100°C.
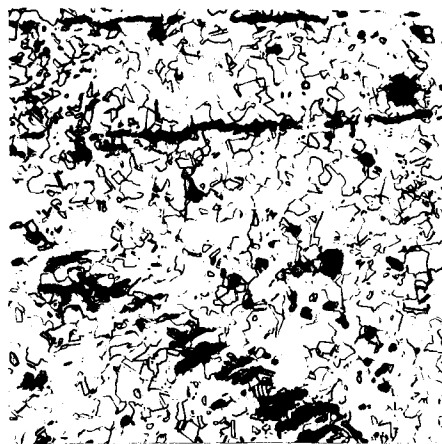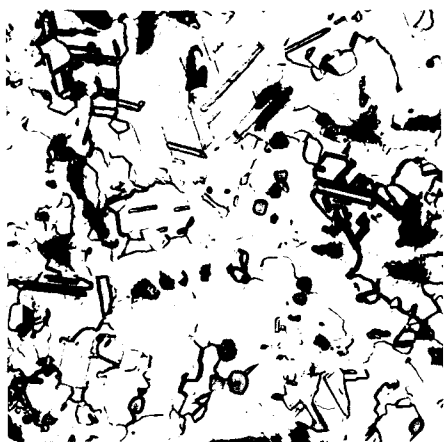Etched with HF.
x 190

Fig. 16. Microstructure of
51.68 per cent vanadium
alloy quenched from 1100°C.
Etched with HF.
x 180

Fig. 17. Microstructure of
53.02 per cent vanadium
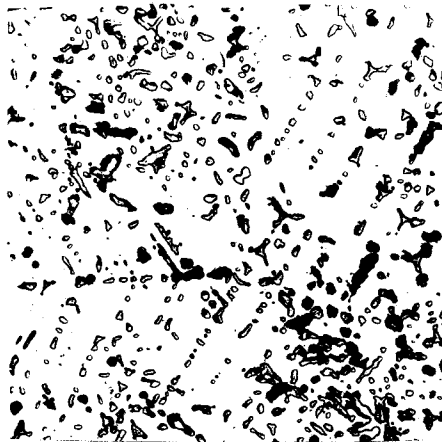alloy quenched from 1100°C.
Etched with HF.
x 240

Fig. 18. Microstructure of
54.10 per cent vanadium
alloy quenched from 1100°C
Etched with HF.
x 180

very little from the stoichiometric proportions for V_2Zr, 52.8 per cent vanadium by weight.

The four X-ray diffraction patterns shown in Figure 14 were made by exposing powders crushed from heated and quenched pieces of alloys to copper radiation filtered by nickel foil in a Debye-Scherrer type camera. The vertical marks on the patterns represent the centers of the exit and entrance slits of the camera. The marks representing the position of the entrance slit in the back-reflection regions do not line up because film shrinkage varied from pattern to pattern.

The heat treatment, prior to quenching, given each of the pieces from which the powder specimens were made is listed in Table 4. The top pattern represents the 45.50 per cent vanadium alloy quenched from 1100°C, and the next pattern is from the same alloy quenched from 600°C. The third pattern is one from the 54.10 per cent alloy quenched from 1100°C; the bottom one represents this alloy quenched from 600°C.

The top two patterns in Figure 14 show weak alpha phase lines and the bottom two show weak delta phase lines; otherwise, the four patterns appear to be the same. This is good evidence that V_2Zr undergoes no transformation and exists only over a narrow range of composition. The occurrence of the alpha and delta phase lines in these patterns is good

evidence, too, that the alpha, beta, gamma, and delta phases are the only solid phases formed in the system.

The evidence obtained from these patterns would be stronger if the patterns were better. Line intensities are weak relative to the background, and resolution in the back-reflection region is poor. These difficulties may have been caused by the method of sample preparation, although it was not expected that crushing alloys as brittle as these would have produced much distortion in the powder grains.

The existence of the compound ZrV_2 established by these results is in agreement with the work of Wallbaum (2). The lines in the patterns shown in Figure 14 could not all be accounted for by the two terminal solid solutions or the structure assigned to ZrV_2 by Wallbaum, however. The patterns were not successfully indexed.

The Delta Region

The only evidence obtained to indicate the limit of solubility of zirconium in vanadium is illustrated by Figures 19 through 22. These are pictures of pieces of sheet rolled from a 94.33 per cent vanadium alloy and quenched from various temperatures. The microstructures of pieces of sheet rolled from the 96.54 per cent vanadium alloy and quenched after the heat treatment described in Table 4 were quite similar to those shown in Figures 19 through 22.
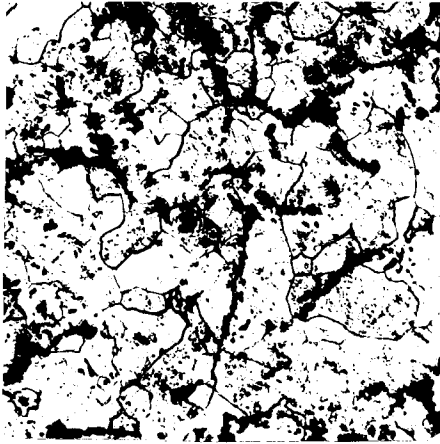
Fig. 19. Microstructure of
94.33 per cent vanadium
alloy quenched from 1150°C.
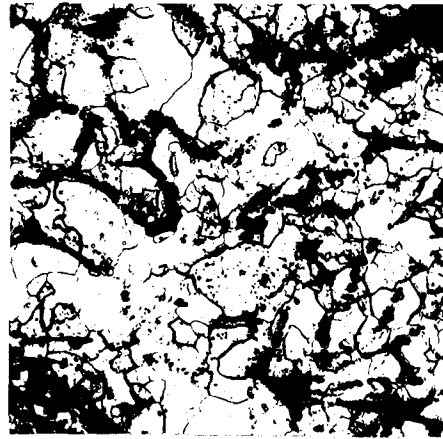Etched with HNO_3.
x 190

Fig. 20. Microstructure of
94.33 per cent vanadium
alloy quenched from 1000°C.
Etched with HNO_3.
x 190

Fig. 21. Microstructure of
94.33 per cent vanadium
alloy quenched from 800°C.
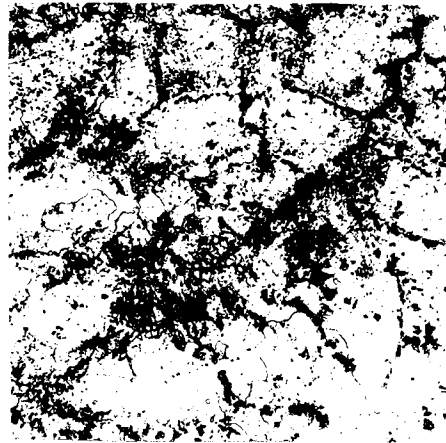Etched with HNO_3.
x 190

Fig. 22. Microstructure of
94.33 per cent vanadium
alloy quenched from 600°C.
Etched with HNO_3.
x 180

Pieces of the 98.78 per cent vanadium alloy quenched after
heating as described in Table 4 showed small particles of
a second phase distributed throughout large grains. The dis-
persed material was apparently the impurity found by Rostoker
and Yamamoto (4).

The black material shown in Figures 19 through 22 is
probably not the gamma phase. The gamma phase reacted much
more readily with hydrofluoric acid and much less readily
with nitric acid than the material in these alloys. There
is a very small amount of a white phase visible in Figure 22
which is probably the gamma phase. The material did not
react readily with the nitric acid used to etch these speci-
mens.

The most that can be said concerning the solubility of
zirconium in vanadium from the evidence contained in Figures
19 through 22 is that the limit is probably slightly less
than five per cent at 600°C and probably greater than five
per cent at temperatures above 800°C. If the interpretation
of the microstructures given above is correct, these alloys
contain quite a bit of material foreign to the vanadium-
zirconium system. In this case, solubility limits may have
been altered from those characteristic of the binary system.

SUMMARY

This investigation of the vanadium-zirconium alloy system produced evidence on several points concerning the equilibrium diagram. It was shown that a eutectic reaction between an intermediate phase and a zirconium-rich solid solution occurs at a temperature of $1230°\pm10°C$, and that the intermediate phase decomposes in a peritectic reaction at $1300°\pm25°C$ to give liquid and a vanadium-rich solid solution. The eutectic composition was found to be near 30 per cent vanadium. The intermediate phase was determined to exist over only a very narrow range of composition near 52.8 per cent vanadium, the stoichiometric composition for V_2Zr. V_2Zr was shown to undergo no solid state transformations.

The lattice type for V_2Zr was not determined. It did not appear to be that reported by Wallbaum (2), however.

A eutectoid reaction was found to take place at $777°\pm5°C$. The reaction could not be completely suppressed by quenching. The eutectoid composition was found to be 5 per cent ±0.5 per cent vanadium. The temperature and composition of the eutectoid may have been influenced by an impurity (perhaps oxygen) in the alloys, however.

Some evidence was obtained to show that vanadium dissolves zirconium to the extent of less than five per cent

at 600°C and slightly more than five per cent at temperatures
above 800°C. The evidence was poor.

BIBLIOGRAPHY

(1) C. T. Anderson, E. T. Hayes, A. H. Roberson and W. Kroll. A Preliminary Survey of Zirconium Alloys. U. S. Bur. Mines, Rept. Invest. No. 4658, 48 pp. (1950)

(2) H. J. Wallbaum. Über Weitere Zirkoniumverbindungen mit Übergangselementen. Naturwiss. 30, 149 (1942)

(3) P. C. L. Pfeil. A Critical Review of the Alloying Behavior of Zirconium. AERE M/TN 11; May, 1952 (unclassified)

(4) W. Rostoker and A. Yamamoto. A Survey of Vanadium Binary Systems. Trans. Am. Soc. Metals 46, 1136-1163 (1954)

(5) G. A. Geach and D. Summers-Smith. A Laboratory Arc-Furnace for Melting Alloys Containing the Refractory Transition Metals. Metallurgia 42, 153-156 (1950)

(6) C. M. Craighead, O. W. Simmons, and L. W. Eastwood. Titanium Binary Alloys. Trans. Am. Inst. Min. Met. Engr. 188, 485-513 (1950)

(7) H. A. Wilhelm, O. N. Carlson, and H. E. Lunt. Thorium-Titanium Alloy System. AECD-3603; June, 1953 (declassified with deletions Dec. 2, 1953)

(8) Am. Inst. Min. Met. Engr. Metals Handbook. 1948 ed. Cleveland, Am. Soc. Metals

(9) C. S. Smith. A Simple Method of Thermal Analysis Permitting Quantitative Measurements of Specific and Latent Heats. Trans. Am. Inst. Min. Met. Engr. 137, 236-244 (1940)

(10) M. E. Dooley and D. F. Atkins. A New Electronic Vacuum Dilatometer. ISC-482; 1954 (unclassified)

ACKNOWLEDGMENTS