

The V-VO Phase System

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A phase diagram is proposed for the V-VO system based on melting point determinations, differential thermal analyses, metallographic observations, and X-ray parametric measurements. A eutectic reaction occurs at 1640°C and 29 at. pct O. The intermediate phases V_9O and V_2O form peritectoidally at 510° and 1185°C, respectively, while V_4O forms by a peritectic reaction at 1665°C. The VO phase melts congruently at 1790°C. The terminal solubility of oxygen in vanadium increases from 3.2 at. pct at room temperature to a maximum of 17.0 at. pct at the peritectic temperature. There is also extensive solid solubility associated with each of the intermediate phases. Two martensite-like phases form in alloys in the composition range 6 to 9 at. pct O upon quenching from above the 510°C peritectoid horizontal.

THE possible use of vanadium alloys as a structural material in the liquid-metal-cooled fast breeder reactor has brought about a need for a better understanding of the phase relationships between vanadium and oxygen. Vanadium-base alloys are being considered as a cladding material for fast breeder reactors because of the favorable nuclear properties of vanadium in the fast fission range, its fabricability and weldability, good high temperature strength, and relative stability (as compared with stainless steel) toward fast neutron irradiation. A critical factor, however, is the susceptibility of vanadium and vanadium-base alloys to oxygen contamination from either the liquid sodium coolant or the oxide fuel elements and the resulting degradation of their mechanical properties.

The V-O system has been the subject of numerous investigations with contradictory versions of the phase diagram having been proposed. Several discrepancies occur in the literature concerning the number and composition ranges of the phases present. Stringer¹ reviewed the literature up to 1964 and proposed the composite phase diagram shown in Fig. 1. During the course of the present investigation Henry *et al.*² published a substantially different version of the vanadium-rich portion of this system for temperatures below 1200°C. The α solubility limit was found to be much greater than previously reported, increasing from 1.1 wt pct (3.4 at. pct) at 250°C to 3.5 wt pct (10.4 at. pct) at 1200°C. They also identified a new phase, designated V_9O , which forms peritectoidally at 510°C and has a bct structure. The banded microstructure observed by earlier investigators^{3,4} was also studied by Henry who found that a metastable bct phase with a c/a ratio greater than 1.0 was produced in alloys containing from 2.2 to 3 wt pct (6.7 to 9.0 at. pct) oxygen upon quenching in water from 1000°C. However, upon air quenching or furnace cooling the same alloys contain the bct equilibrium phase, V_9O , with a c/a ratio less than 1.0. The purpose of the present study was to clarify the points of disagreement in the earlier work and to determine the phase reactions and boundaries over the entire temperature-composition range of the V-VO system.

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EXPERIMENTAL PROCEDURES

Alloy Preparation and Analysis

The vanadium metal used in this study was prepared at the Ames Laboratory by the aluminothermic reduction of V_2O_5 followed by electron-beam melting.⁵ The major impurities in a typical lot of the metal were as follows: 130 ppm * C, 100 ppm O, 50 ppm N, 60 ppm Ni,

*All values are reported as ppm by weight.

70 ppm Fe, 200 ppm Al, 20 ppm Mg, 300 ppm Si, and <30 ppm Cu.

Alloy buttons weighing 25 to 30 g were prepared by arc melting pieces of vanadium and fused V_2O_5 together in a gettered argon atmosphere. Weight losses were usually less than 0.3 pct. The oxygen concentrations reported throughout this paper were determined by neutron activation analysis and agree very well with the nominal compositions.

Solidus Determination

The solidus or melting points were determined by optically observing the onset of melting in a small hole drilled in the specimen. In this method the specimens are heated by passage of a current through the bar and the melting point is taken as the temperature at which liquid first appears during heating. Because of the difficulty of fabricating bars from the alloys of composition close to VO due to their extremely brittle nature, small pieces of these alloys were heated by radiation from a tantalum tube furnace until melting was observed.

Differential Thermal Analysis

The transformation temperatures were determined by differential thermal analysis (DTA) using vanadium as the standard. Chromel-alumel thermocouples were employed at the lower temperatures, Pt/Pt-13 pct Rh thermocouples up to 1500°C, and W/W-26 pct Re thermocouples at the higher temperatures. Heating and cooling rates of 5° to 30°C per min were maintained throughout the run.

X-Ray Method

The X-ray parametric method was used extensively to determine the various phase boundaries of this sys-

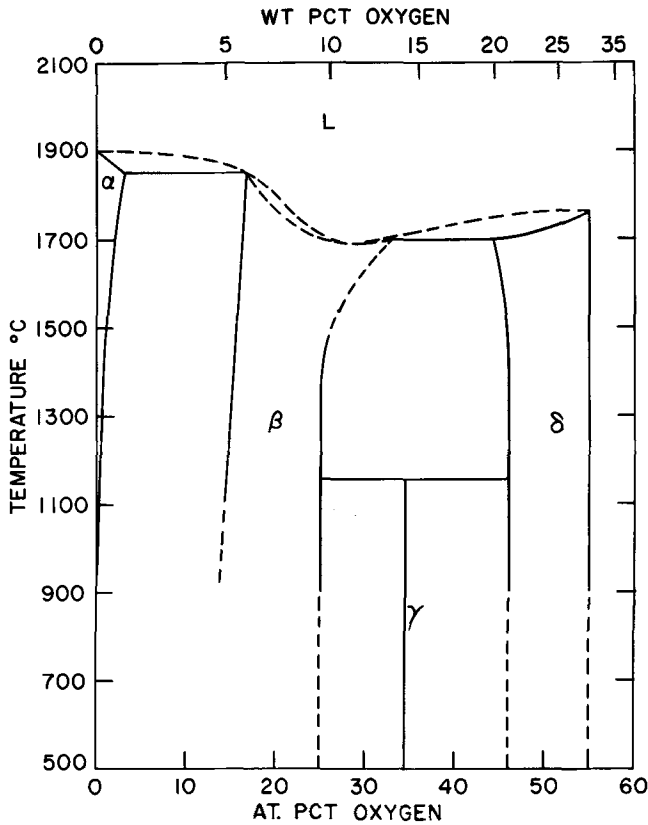


Fig. 1—Tentative V-VO phase diagram proposed by Stringer.¹

tem. Portions of the arc-melted buttons were sealed in outgassed tantalum crucibles under a vacuum of 10^{-5} torr and homogenized at 1200°C for 100 hr. Powders of these alloys, obtained either by filing or crushing, were then sealed in tantalum crucibles under a partial pressure of argon. All specimens were annealed at 1000°C for 18 to 24 hr and then heated or cooled slowly to the desired temperature, held until equilibrium was obtained, and quenched into a brine solution chilled by crushed ice. The room temperature structure was obtained by slow step-wise cooling to 200° to 400°C followed by furnace cooling after a long time anneal in this temperature range. The powders were then sealed in glass capillaries and exposed to $\text{CuK}\alpha$ X-radiation in a 114.59-mm Debye-Scherrer camera. Lattice parameters were calculated by use of the Nelson-Riley extrapolation function with the computer program of Vogel and Kempter.⁶

Metallography

Preparatory to metallographic examination, the alloy specimens were wrapped in tantalum foil and sealed in evacuated quartz tubes. The heat-treated alloys were quenched by breaking the glass tubes in an iced-brine solution. The specimens were mechanically ground through 600 grit papers and electropolished in a 6 pct perchloric acid-methanol solution maintained at -70°C by a dry ice-acetone mixture. They were then etched with a solution of 10 parts HF, 5 HNO₃, 5 H₂SO₄, and 50 H₂O.

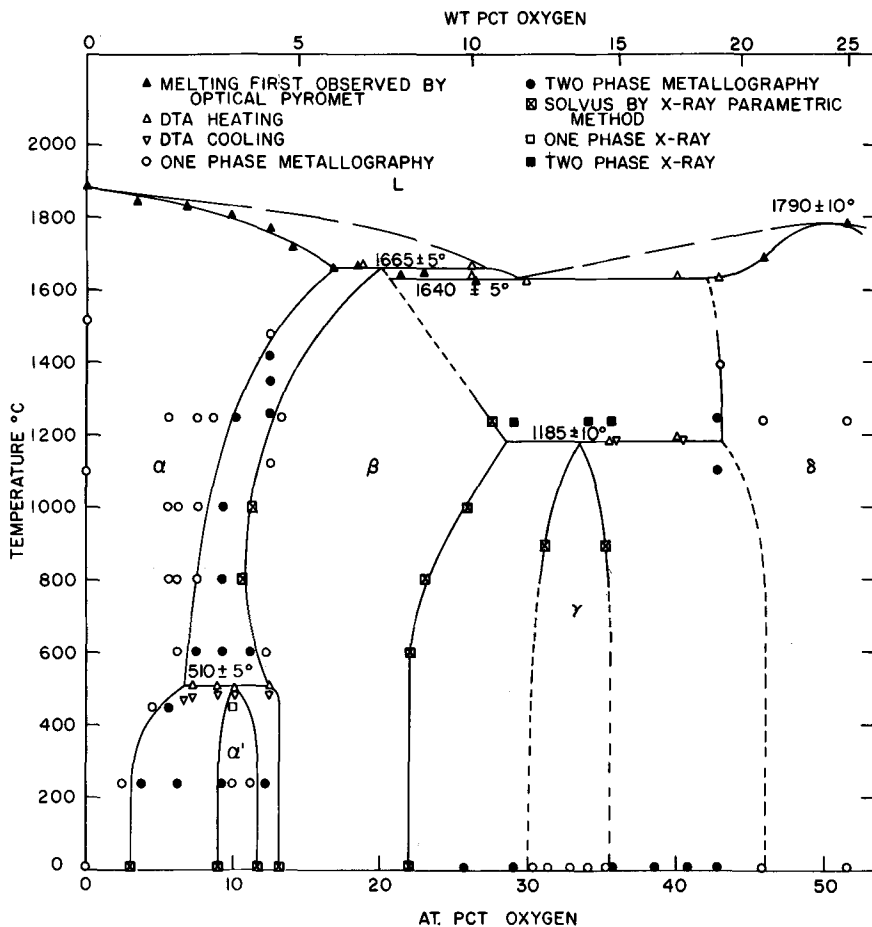


Fig. 2—Proposed V-VO phase diagram and plot of experimental data.

EXPERIMENTAL RESULTS AND DISCUSSION

The proposed V-VO phase diagram shown in Fig. 2 summarizes the results of this investigation. The data plotted have been obtained from melting point determinations, differential thermal analyses, X-ray parametric measurements, and microscopic examination of heat-treated alloys.

Solidus

Solidus points obtained by both the melting bar technique and DTA are plotted in Fig. 2. The data establish the presence of one horizontal at 1665°C extending from 17.0 to about 27 at. pct O and a second at 1640°C having the approximate range of 20.5 to 42 at. pct O. Microstructural evidence indicates that the upper horizontal is associated with the peritectic formation of the intermediate phase, β , while the lower horizontal is associated with a eutectic reaction at approximately 29 at. pct. The latter is illustrated by the micrograph of a 29.1 at. pct O alloy in the arc-cast condition, Fig. 3. Repeated heating and cooling DTA curves of a 26.1 at. pct O alloy confirmed the existence of both the peritectic and eutectic horizontals by exhibiting a strong thermal arrest at 1645°C and a weaker, yet distinct, one at 1668°C.

This eutectic reaction has not been reported by any of the previous investigators. Seybolt and Sumsion³ observed similar microstructures which they attributed to a eutectoid reaction although they did not determine the coordinates of the transformation. Although the cast structures exhibit microstructural features characteristic of a eutectoid, the interpretation that this is the result of a eutectic reaction is more consistent with the solidus data which indicate the presence of a minimum in the liquidus between vanadium and VO.

α Solvus

The boundaries of the solid solution regions of this system were determined by a combination of X-ray parametric and metallographic methods. Difficulty was encountered in determining the α solvus at temperatures above the α' horizontal by the X-ray para-

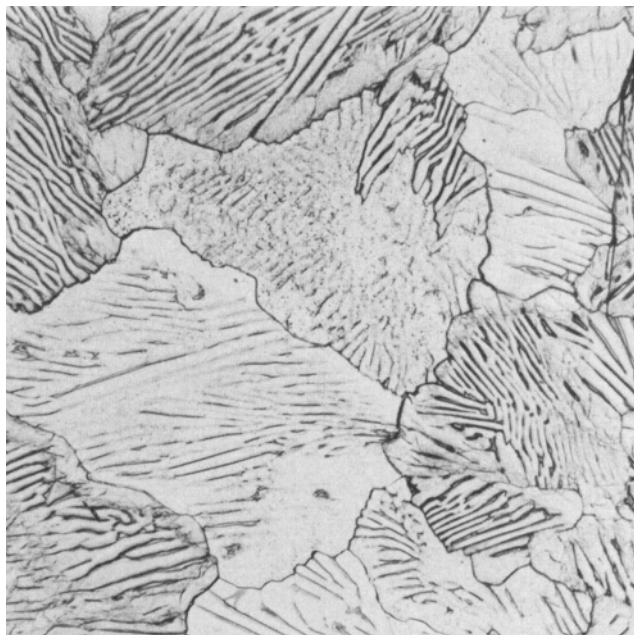


Fig. 3—V-29.1 at. pct O alloy as-cast. Alloy is of eutectic composition. Magnification 289 times.

metric method. The supersaturated α structure could not be retained upon quenching in alloys containing greater than 6 at. pct O and a transformation structure resulted. This, of course, obviated the use of the X-ray parametric method for determining the boundary at the higher temperatures and made reliance on microstructural evidence alone necessary.

The room temperature α solubility limit is placed at 3.2 at. pct O from the lattice parameter-composition data shown in Fig. 4 and is supported by the microstructural data. This value is much greater than that shown in the Stringer diagram;¹ however, it is identical to that of Seybolt and Sumsion³ at 600°C and is close to the solubility reported by Henry *et al.*² of 1.1 wt pct (3.4 at. pct) at 250°C.

The solvus boundary at elevated temperatures is based primarily on microscopic evidence as is illustrated by micrographs of the 7.6 and 9.2 at. pct O alloys, Figs. 5 and 6 respectively, quenched from

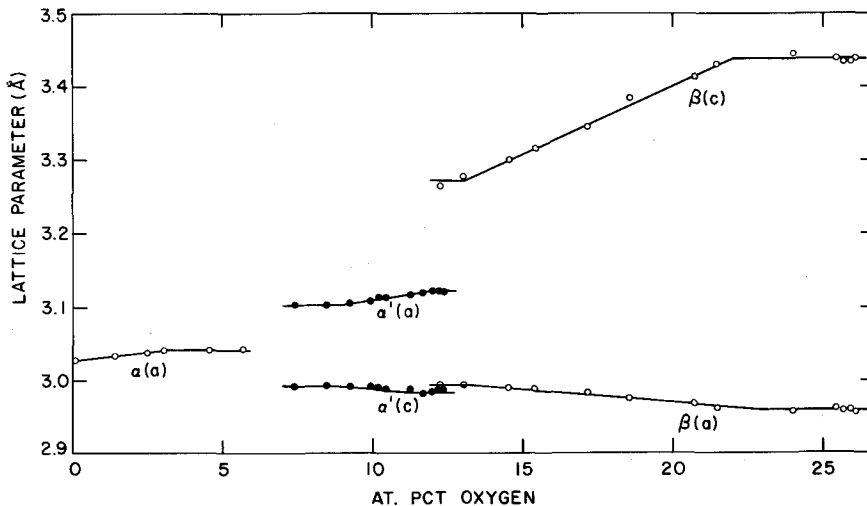


Fig. 4—Lattice parameter-composition data for alloys slow-cooled to room temperature.

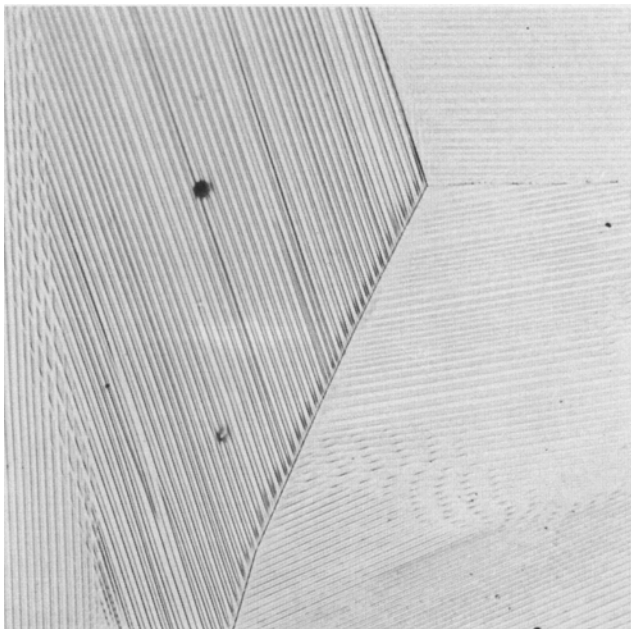


Fig. 5—V-7.6 at. pct O alloy quenched from 800°C. Martensite-like structure of transformed α . Magnification 281 times.



Fig. 7—V-10.1 at. pct O alloy quenched from 240°C. Single-phase α' . Magnification 281 times.

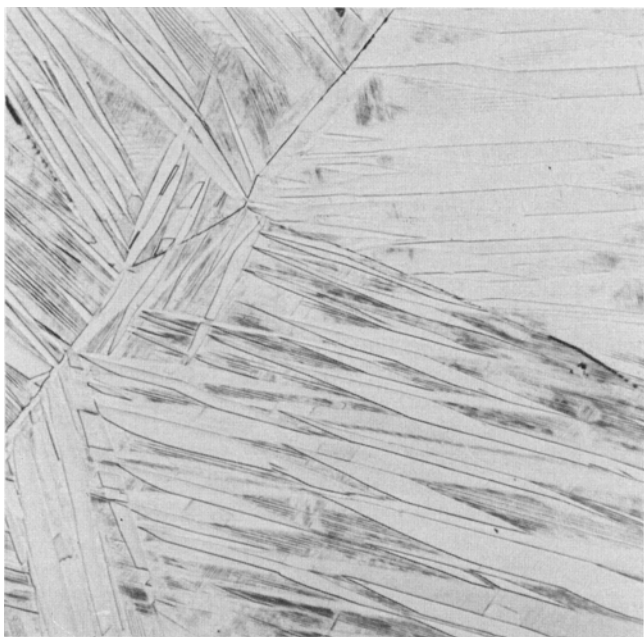


Fig. 6—V-9.2 at. pct O alloy quenched from 800°C. Striated plates of primary β embedded in a matrix of transformed α . Magnification 281 times.

800°C. The 7.6 at. pct alloy is interpreted as having been single phase α at temperature but having transformed to the banded structure of Fig. 5 during quenching. At this same temperature the 9.2 at. pct alloy consisted of plates of β in an α matrix and upon quenching α has transformed as is shown in Fig. 6. The transformation structure, designated martensite by Henry *et al.*,² will be discussed in a later section. Extrapolation of the α solvus boundary to the solidus gives a maximum terminal solubility of 17.0 at. pct O at 1665°C.

Seybolt and Sumsion³ observed little temperature

dependence of the solubility between 600° and 1000°C in contrast to the marked dependence found in the present study. Henry *et al.*² also found a pronounced temperature dependence with the solubility increasing to 3.5 wt pct (10.4 at. pct) at 1200°C in good agreement with the results of the present study. Stringer¹ placed the maximum terminal solubility at approximately 3 at. pct at 1850°C.

Upon heating vanadium in air at low pressures Edington and Smallman⁷ obtained evidence for a new bcc suboxide phase with a lattice parameter of 12.2Å. Thomas and Villagrana⁸ have shown that the results of Edington and Smallman can be explained on the basis of a $V_{64}O$ (1.5 at. pct) ordered phase. This superstructure is analogous to $Ta_{64}C$ in which the interstitial atoms occupy preferred sites forming a bct structure.⁹ This ordered structure would exist within the α solid solution region, but since it was not investigated in the present study it has not been included in the phase diagram.

α' Phase

Differential thermal analyses confirmed the presence of the peritectoid reaction associated with the V_9O phase (herein identified as α') as reported by Henry *et al.*² The DTA data plotted in Fig. 2 show a measurable hysteresis in this transformation from an average of 510°C on heating to 480°C on cooling. The metallographic and thermal evidence indicates that the normalized magnitude of the differential breaks attains a maximum at V_9O , the composition shown for the α' phase at the peritectoid temperature.

A plot of the lattice parameter-composition data shown in Fig. 4 places the homogeneity range of the bct α' phase from 9.0 to 11.8 at. pct O at room temperature. Although only the lattice parameter-composition plot is shown, the room temperature solubil-

ity limits of α' are also based on similar plots of c/a and volume-composition data. The microstructure of a 10.1 at. pct alloy held for several days below the peritectoid horizontal shows the characteristic striated structure of the α' phase, Fig. 7.

Cambini *et al.*¹⁰ have reported the occurrence of a vanadium suboxide which they identified as VO_x existing over the composition range $VO_{0.06}$ to $VO_{0.1}$ (5.7 to 9.1 at. pct O). They found that the phase is bct and observed a decrease in the c/a ratio from 0.97 to 0.96 with increasing oxygen content. Specimens prepared to have a 2 wt pct (6.1 at. pct) O content exhibited two-phase characteristics in some regions while other areas were entirely transformed to the tetragonal phase. This was attributed to a compositional inhomogeneity in the specimen. Alloys of 3 wt pct (9.0 at. pct) were completely transformed to a tetragonal structure with $c/a = 0.963 \pm 0.003$. A comparison of the X-ray data of Cambini *et al.* with that of the present study shows that their VO_x phase is identical to our α' phase. In the present work, the c/a ratio of the α' phase in the $\alpha + \alpha'$ two-phase field remains constant at 0.9646 ± 0.0003 from 7.4 to 8.6 at. pct oxygen. Plots of the c/a and lattice parameter-composition data exhibit breaks at 9.0 at. pct O, the vanadium-rich boundary of the α' phase. It would thus appear that Cambini and co-workers were the first to identify this new suboxide phase although they have presented inconclusive evidence for its range of homogeneity.

β Phase

The β phase, which is bct with c/a greater than 1.0, forms peritectically at 1665°C and has a wide range of homogeneity. The solvus boundaries of this phase were determined primarily by the X-ray parametric method. The vanadium-rich boundary is placed at 13.2 at. pct O at room temperature, 10.6 at. pct at 800°C, and 11.4 at. pct at 1000°C from the data of Fig.

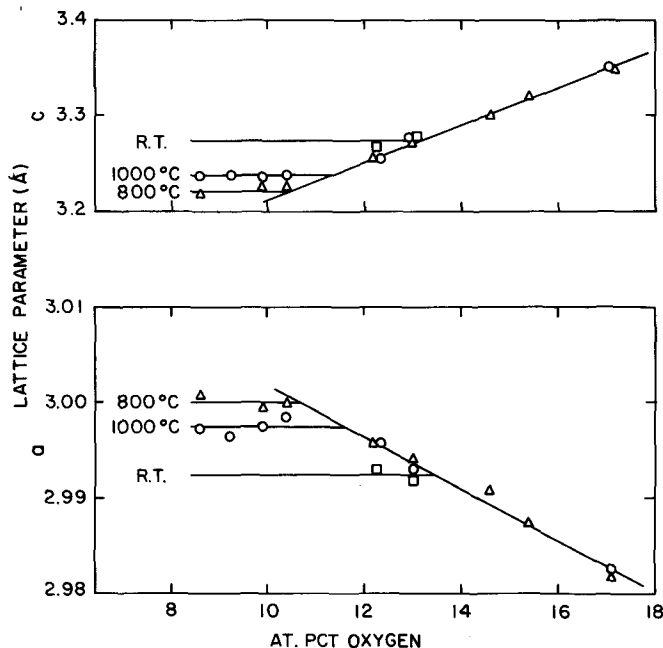


Fig. 8—Lattice parameter-composition data for vanadium-rich boundary of β phase.

8. From a similar plot, Fig. 9, the oxygen-rich boundary was determined as 22.0 at. pct at room temperature and 600°, 23.0 at. pct at 800°, 26.0 at. pct at 1000°, and 27.5 at. pct at 1240°C.

The room-temperature solid solubility limits of the β phase, 13.2 and 22.0 at. pct O, are in fair agreement with Seybolt and Sumsion's³ range of 14.7 to 21.8 at. pct at 600°C. The retrograde solubility observed in the vanadium-rich boundary of the β phase is similar to that reported by Henry *et al.*² although differing somewhat in composition limits. Their data are based on high-temperature X-ray measurements whereas data in the present work are based on X-ray and microstructural evidence from quenched alloys. The exact position of the oxygen-rich boundary of the β phase is still somewhat uncertain. Seybolt and Sumsion observed virtually no solubility change with temperature between 400° and 1400°C, whereas our X-ray and metallographic data show a pronounced change in the solubility over the same temperature range. Henry's results² at 800° and 1000°C tend to support those of the authors.

Metallographic examination of slow-cooled alloys near the oxygen-rich boundary, however, revealed that precipitated γ was not evident until a composition of 25.7 at. pct O was reached. Furthermore, lines corresponding to those of the γ phase did not appear in X-ray powder patterns of slow cooled alloys at lower oxygen compositions. This disparity is probably due to incomplete equilibrium. At 1000°C and above the microstructural and X-ray data are in good agreement.

Martensite Phases

X-ray powder patterns were taken of alloys in the composition range 5.7 to 9.2 at. pct O quenched from various temperatures above the α' peritectoid horizontal. The resulting transformation structures are characterized by highly banded microstructures such as that shown in Fig. 5. Alloys exhibiting completely

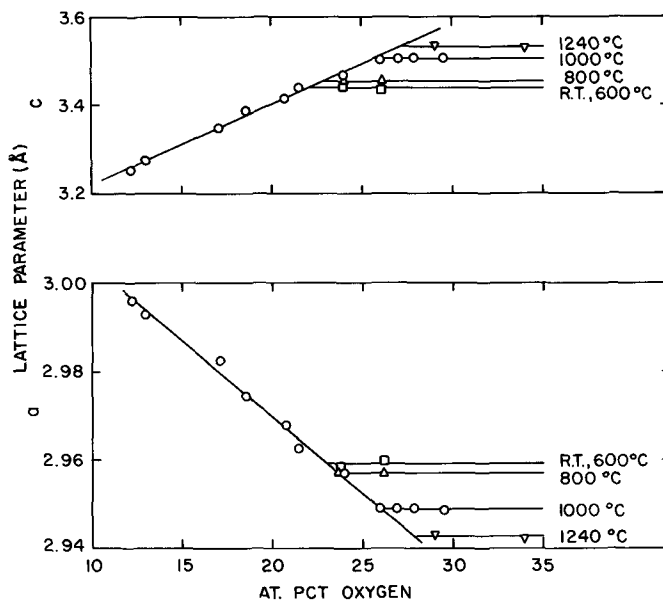


Fig. 9—Lattice parameter-composition data for oxygen-rich boundary of β phase.

Table I. Lattice Parameters of Martensite Phases

Composition, At. Pct O	Quench Temp, °C	a(Å)	c(Å)	c/a
5.7	625	3.0484 (α)		1.0
	1000	3.0490 (α)		1.0
6.3	625	3.0723	3.0152	0.9814
	800	3.0721	3.0152	0.9815
6.6	1000	3.0787	3.0060	0.9764
6.7	1100	3.0700	3.0129	0.9814
7.3	1000	3.0134	3.1495	1.0452
7.6	800	3.0176	3.1374	1.0397
	1000	3.0169	3.1377	1.0400
8.6	625	3.0039	3.1961	1.0640
	800	3.0177	3.1537	1.0450
	1000	3.0089	3.1714	1.0540
9.2	1000	2.9964 (β)	3.2390	1.0810

banded microstructures were interpreted as having been quenched from the single phase α field. The results of these quenching experiments are listed in Table I. The parameters of alloys with a c/a ratio greater than 1.0 have also been plotted in Fig. 10 along with the data of Henry *et al.*² It is interesting to note from the table that the 6.3, 6.6, and 6.7 at. pct O alloys all have c/a ratios less than one while those of the higher compositions have ratios greater than one. The intensity and spacing of lines of the different powder patterns clearly show that two metastable phases exist. One phase, with a c/a ratio less than unity, is structurally related to α' while the other, with a c/a greater than unity, is related to β . The compositional dividing line between the two forms of martensite appears to coincide with the vanadium-rich terminus of the α' horizontal, *i.e.* 6.7 at. pct O.

The extrapolated lattice parameter-composition plot for the phase with c/a greater than 1.0 converges at a point corresponding to the parameter of the cubic α

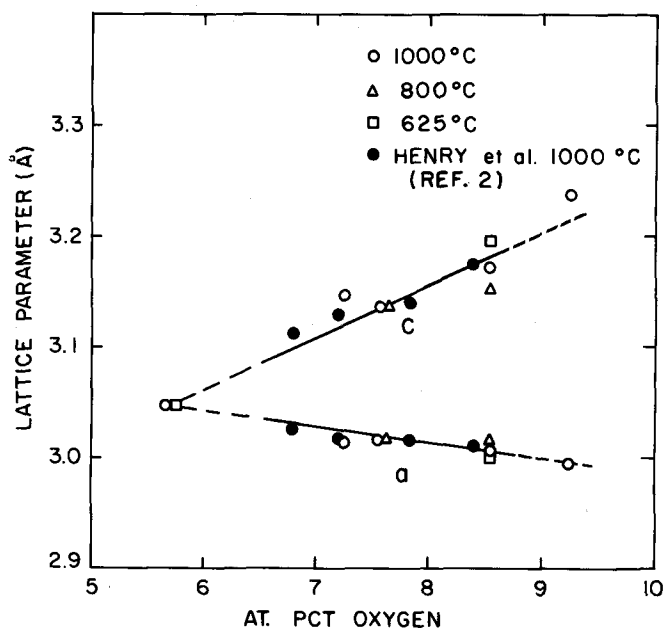


Fig. 10—Lattice parameter-composition data for martensite phase with c/a ratio greater than 1.0. Parameters extrapolated to those of the α and β phases.

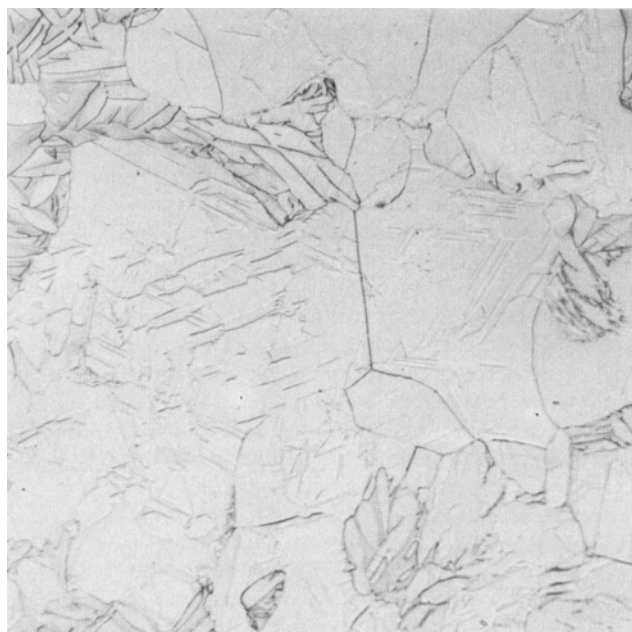


Fig. 11—V-33.1 at. pct O alloy annealed at 1100°C and slow-cooled. Single phase γ . Magnification 281 times.

phase of the 5.7 at. pct alloy quenched from the same temperature range. It is interesting to note that the lattice parameters of the transformed phase also appear to approach the parameters of the 9.2 at. pct β phase alloy quenched from 1000°C. Henry *et al.*² observed that the higher oxygen martensite phase transforms to α' upon heating at 210° to 253°C.

γ Phase

Thermal arrests were observed at 1185°C in heating and cooling curves of the 35.6 and 39.8 at. pct O alloys

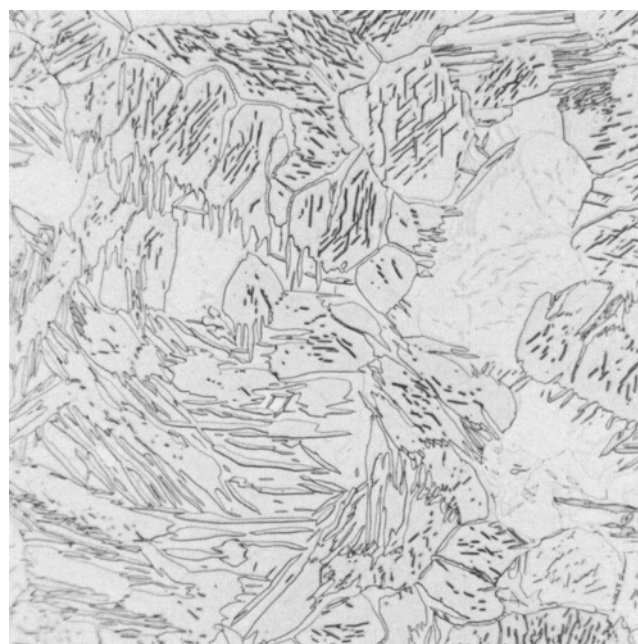


Fig. 12—V-33.1 at. pct O alloy annealed at 1100°C followed by quenching from 1260°C. β and δ phases formed by peritectoid decomposition. Magnification 281 times.

indicating the presence of a horizontal at this temperature. Microscopic examination of a series of alloys quenched from just above and below this temperature has shown that it is associated with the peritectoid reaction, $\beta + \delta \rightarrow \gamma$. This horizontal has been previously reported to exist between 1100° and 1200°C by Rostoker and Yamamoto.⁴

The presence of the γ phase, which has the stoichiometry V_2O , was confirmed by metallographic and X-ray diffraction data. The microstructure of a 33.1 at. pct O alloy, annealed for 24 hr at 1100°C and slow cooled, Fig. 11, is interpreted as consisting of single phase γ and is typical of alloys in that composition range. Upon heating to above the 1185°C horizontal, γ decomposes into two phases as is shown for the same 33.1 at. pct alloy quenched from 1260°C, Fig. 12. The identification of these phases as β and δ was confirmed by X-ray diffraction studies.

Due to the complexity of Debye-Scherrer powder patterns of the γ phase, a Guinier X-ray pattern was taken of a slow-cooled 35.6 at. pct alloy. This pattern could be indexed on the basis of the monoclinic cell reported by Westman.¹¹ His values for the homogeneity range of γ at 900°C have been used in the diagram of the present study.

δ Phase

The δ phase has the stoichiometry VO and crystallizes in the cubic NaCl-type structure. The melting point of VO is placed at 1790°C which compares quite well with the value of 1760°C shown in the diagram by Stringer.¹ The compound is known to exist over a wide range of compositions.¹²⁻¹⁴ The vanadium-rich boundary is placed at 46.0 at. pct O extending from room temperature up to 700°C based on the X-ray data of Gel'd *et al.*¹⁴ Comparison of the microstructures of alloys quenched from 1110°, 1260°, and 1400°C with those in the slow-cooled condition shows a pronounced temperature dependence of the vanadium-rich δ boundary. The boundary recedes from 46.0 at. pct O at room temperature to 43 at. pct at the peritectoid temperature and to 42 at. pct at the eutectic temperature. This temperature dependence is seen from the micrograph of a 40.8 at. pct alloy quenched from just above the peritectoid horizontal, Fig. 13, in which needles of β precipitate appear in the δ regions containing islands of primary β .

SUMMARY

The phase diagram proposed in this paper contains several features that differ from the results of previous investigators.

a) A eutectic reaction occurs at 29 at. pct O and 1640°C.

b) The terminal solubility of oxygen in vanadium is much greater than reported previously, increasing from 3.2 at. pct at room temperature to 17.0 at. pct at the peritectic temperature.

c) There are four intermediate phases, α' , β , γ , and δ , all of which exhibit extensive solid solubility; α' and γ form peritectoidally at 510° and 1185°C, respectively, β forms peritectically at 1665°C, and δ melts congruently at 1790°C.

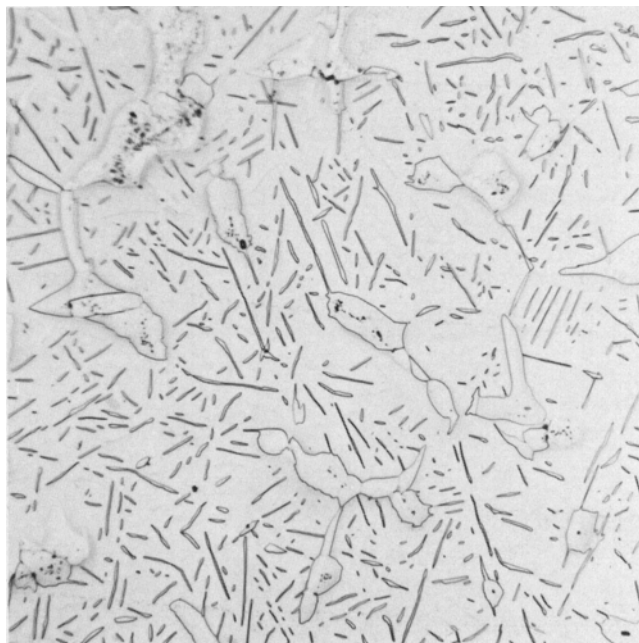


Fig. 13—V-40.8 at. pct O alloy quenched from 1260°C. Primary β surrounding δ matrix containing precipitated β . Magnification 281 times.

d) Two martensite-like phases form in alloys in the composition range 6 to 9 at. pct O when quenched from above the 510°C peritectoid horizontal. One phase, with a c/a ratio less than one, is structurally related to α' , while the other, with c/a greater than one, is related to β .

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