

of this system. In particular, the Ti-rich liquidus and solidus and the $\beta/(\alpha + \beta)$ boundary are probably realistic.

The free energy functions of the two compounds, χ and TiTc, however, cannot be calculated in the same way as those of the solution phases. In order to complete the diagram, parameters have been estimated, based on a probable phase diagram. The χ phase has been represented as a line compound with the composition 85 at.% Tc. The parameters of the χ phase were determined by an estimated peritectic temperature, together with the solid solubility of Ti in Tc at 1500 °C. Estimated TiTc phase boundaries were calculated from a Wagner-Schottky free-energy function. The free energy of the compound i is expressed as:

$$G^i = F^i + RT(x_{Ti} \ln x_{Ti} + x_{Tc} \ln x_{Tc} + v \ln v + s \ln s - (1 + v) \ln(1 + v)) + C^i s + D^i v$$

The Wagner-Schottky compound is conceptually resolved into titanium and technetium sublattices; v is the concentration of vacancies on the Ti sublattice; s is the concentration of substitutional Ti atoms on the Tc sublattice; x_{Ti} and x_{Tc} are the concentrations of Ti and Tc on their respective sublattices; and x is the overall composition. All concentrations are referred to the total number of atoms. The concentrations of vacancies and substitutions are determined by minimizing the Wagner-Schottky free energy with respect to the variables s and v .

Ti-Tc evaluation contributed by **Joanne L. Murray**, Center for Materials Research, National Bureau of Standards. Thermodynamic calculations have been made using computer programs generously made available by E. Th. Henig and H. L. Lukas, of the Max-Planck Institute, Stuttgart, Federal Republic of Germany. This work was supported by the Office of Naval Research through the Joint Program on Critical Compilations of Physical and Chemical Data, coordinated through the Office of Standard Reference Data, National Bureau of Standards. Literature searched through 1980. Dr. Murray is the ASM/NBS Data Program Category Editor for binary titanium alloys.

G_{TiTc}^0 was chosen to produce the ordering transformation in the solid state. C^{TiTc} and D^{TiTc} were chosen to produce a reasonably wide single-phase region.

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The Cr-V (Chromium-Vanadium) System

51.996 amu

50.9415 amu

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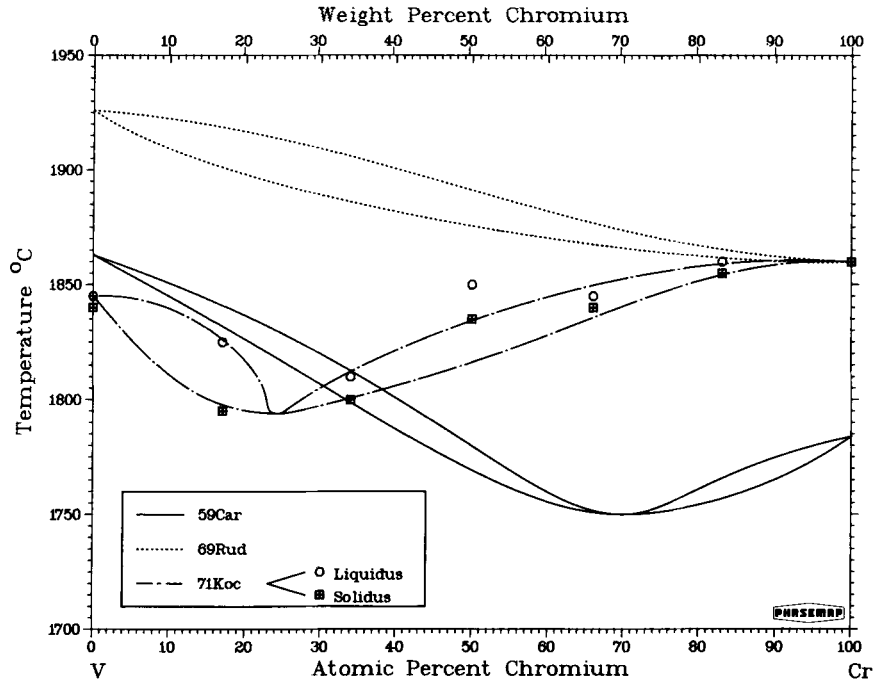
Phase Relationships

Three separate investigations of the V-Cr system have been the bases for proposals of three somewhat different versions of the system. All three versions show a complete series of solid solutions. There is no evidence of ordering or compound formation although attempts [51Pea, 52Mar] have been made specifically, but unsuccessfully, to find a σ phase in the system at lower temperatures. The differences among the three proposed versions of the diagram concern the liquidus-solidus equilibria and are illustrated in Fig. 1. The earliest investigation, by Carlson *et al.* [59Car], was done with comparatively poor quality metal (99.7 wt.% V and 99+ wt.% Cr) and, even though the melting points of that investigation are low because of the low purity, the data indicate a minimum in the melting of V-Cr alloys near 70 at.% Cr and 1750 °C. The second investigation, by Rudy [69Rud], found no minimum or maximum in melting at any composition between pure V and pure Cr. The third investigation, by Kocherzhinskii and

Shishkin [71Koc], again reported a melting minimum, but on the other side of the system near 25 at.% Cr and 1795 °C. Fig. 1 includes the data points from Kocherzhinskii and Shishkin because the liquidus line in the figure has been modified from that of the original report to meet the thermodynamic requirement of tangential contact between liquidus and solidus at the melting minimum. The Kocherzhinskii and Shishkin data were reported in both tabular and graphical form, and these agree. Thus, even though the Kocherzhinskii and Shishkin results are close to being an inverse of the results of Carlson *et al.*, it seems unlikely that this inverse nature arose through a labeling error.

Support for the occurrence of a melting minimum in the system is provided by calculated phase diagrams. One of these has been published by Molokanov *et al.* [77Mol]. These authors used a regular solution model with estimated interaction parameters and an algorithm developed by Kaufman and Bernstein [70Kau]. With melting points of 1907 °C for V and 1877 °C for Cr, the calculated phase

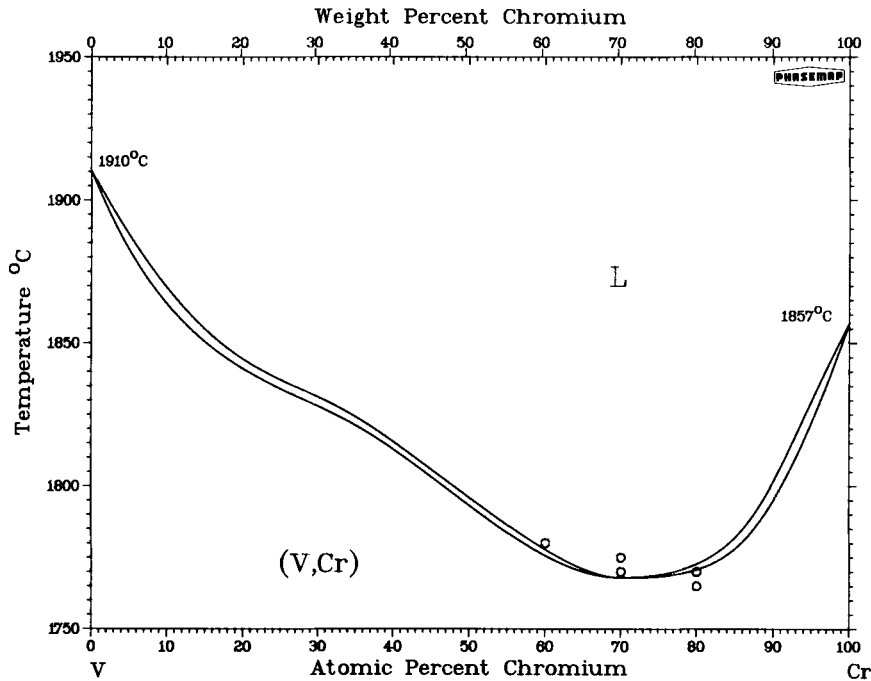
Fig. 1 Cr-V Phase Diagram



Comparison of liquidus-solidus equilibria as proposed by Carlson *et al.* [59Car], Rudy [69Rud], and Kocherzhinskii and Shishkin [71Koc]. The data points of Kocherzhinskii and Shishkin are shown because the liquidus and solidus lines have been modified from those of the original paper in order to meet the thermodynamic requirement of mutual tangency at the melting minimum.

J. F. Smith, D. M. Bailey and O. N. Carlson, 1982.

Fig. 2 Calculated Liquidus-Solidus Equilibria



Based on the vapor pressure data of Aldred and Myles [64Ald] and showing representative melting points from the recent determinations of O. N. Carlson.

J. F. Smith, D. M. Bailey and O. N. Carlson, 1982.

diagram of Molokanov *et al.* showed a melting minimum near 55 at.% Cr and 1819 °C. In their book, Kaufman and Bernstein have not included a calculated V-Cr phase diagram, but they have included independent estimates of the interaction parameters for use with a regular solution model. These allow the expression of the excess Gibbs energies of formation of bcc alloys from the bcc elements as

$$\Delta G_{\text{bcc}}^{\text{xs}} = -13\,300 X_{\text{V}}X_{\text{Cr}} \quad \text{J/g-at}$$

and of liquid alloys from the liquid elements as

$$\Delta G_{\text{liq}}^{\text{xs}} = -15\,730 X_{\text{V}}X_{\text{Cr}} \quad \text{J/g-at}$$

with X representing mole fraction. These expressions can be used to generate an independent version of the phase diagram if they are combined with expressions for the Gibbs energies for fusion of the elements in order that formation of both the liquid and solid alloys may be referred to the same standard states. For this purpose, the Gibbs energy of fusion for V was taken as [81Smi]

$$\Delta G_{\text{M,V}} = 21\,500 - 9.9 T \quad \text{J/g-at}$$

and for Cr as [Hultgren, Elements]

$$\Delta G_{\text{M,Cr}} = 16\,900 - 7.9 T \quad \text{J/g-at}$$

With these expressions, calculations show that alloy melting should occur with a broad flat minimum in the vicinity of 60 to 70 at.% Cr and 1812 °C.

With the preponderance of evidence indicating a melting minimum in the system, but with uncertainty as to the composition and temperature of this minimum, it was decided that the effort to make a few additional solidus determinations was warranted. O. N. Carlson made such determinations on a few alloys in the composition range of 60 to 80 at.% Cr. The alloys were prepared with Cr of ~99.99 at.% purity and V of ~99.95 at.% purity; the Cr was obtained from Chromalloy Corp. and the V was prepared at this laboratory. The specimens were heated resistively in an inert gas atmosphere by passage of a high amperage current through a bar of the alloy supported between two water-cooled electrodes. The onset of melting was observed with an optical pyrometer sighted on a small black-body hole in the specimen. The values for the observed melting temperatures were found to be reproducible to within 10 °C. The high volatility of Cr led to the visual observance of metal vapors in the chamber for alloys containing 90 at.% Cr or more. This introduced an error in the temperature measurements and, hence, no solidus determinations are reported in this concentration range. However, no vapors were observed in the vicinity of the minimum temperature. Furthermore, because no crucible is required for this method, the usual crucible contamination problem is obviated. The supplemental solidus determinations are, therefore, believed to be representative of the purest V-Cr alloys that have been measured.

Melting temperatures between 1765 and 1780 °C were found and, because these values are considerably below the melting point of either V or Cr, the new measurements confirm the existence of a melting minimum in the composition range 60 to 80 at.% Cr. A more precise definition of the coordinates of the melting minimum was then achieved by a new calculation of the phase diagram. This calculated phase diagram is shown in Fig. 2; representative data points from the melting point determinations are included in the figure. The calculated melting minimum is

close to 70 at.% Cr and 1768 °C. The Gibbs energy functions for this calculated diagram were based on the vapor pressure data of Aldred and Myles [64Ald], and more details concerning the calculation are given in the "Thermodynamics" section. This calculated diagram is believed to be the best compromise for representing currently available data.

Pure Cr is antiferromagnetic with a Néel temperature near 310 K [63Bol, 61Bac]. This ordering temperature is sensitive to impurities and tends to be lowered quite appreciably by rather small solute concentrations. Heiniger [60Hei] has made specific heat measurements on V-Cr alloys at liquid helium temperatures. He plotted his data together with that of Cheng *et al.* [60Che] and noted that the composition dependence of the electronic specific heat coefficient showed a pronounced slope discontinuity near 95 at.% Cr. Heiniger has inferred that this discontinuity denotes the boundary between antiferromagnetic and paramagnetic material in the low temperature limit. This interpretation implies that V additions to Cr steeply lower the Néel temperature from 310 K at 100 at.% Cr to 0 K at 95 at.% Cr.

Crystallography

V, Cr, and their alloys crystallize with the bcc structure, of which W is the prototype. The Pearson symbol is $cI2$, and a plot of room-temperature lattice parameter as a function of alloy composition is shown in Fig. 3, which indicates a smooth monotonic increase in lattice parameter from pure Cr to pure V. Data for this plot are from several sources [52Mar, 59Car, 69Rud, 59Sve].

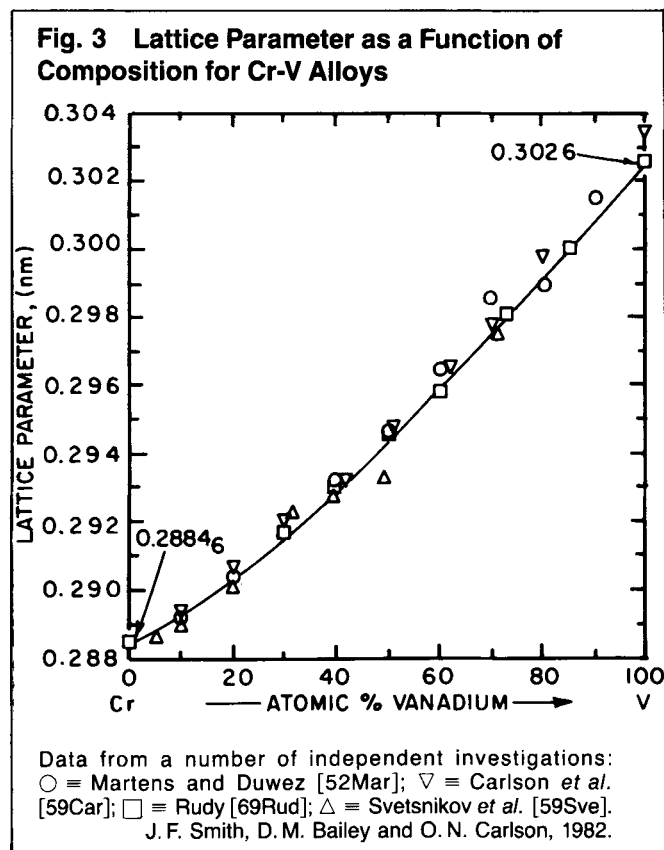


Table 1 Heat Capacities and Entropies for V-Cr Alloys

Composition, at.% Cr	$C_p = a + bT + cT^{-2}$ J/g-at K (a)			Heat capacity, $C_p, 298$ (J/g-at K)	Entropy (b), S'_{298} (J/g-at K)
	a	$b \times 10^3$	$-c \times 10^{-5}$		
23	24.85	7.957	1.855	25.13	30.6
50	25.34	6.796	2.566	24.48	26.7
74	23.75	7.786	2.418	23.35	24.1
80	24.33	8.726	2.990	23.56	23.3
90'	22.84	10.074	2.424	23.11	21.8
95	26.82	3.734	3.867	23.58	24.5

(a) $\pm 3\%$ in temperature range 298 to 625 K. (b) $S'_{298} = S_{298} - S_0$.

Thermodynamics

Heat Capacities. In addition to the low-temperature heat-capacity measurements which have already been mentioned in connection with antiferromagnetism, Schröder and Shabel [66Sch] have made heat-capacity measurements on six alloys in the composition range 23 to 95 at.% Cr and over the temperature range 125 to 625 K. The results are summarized in Table 1. In the table, S'_{298} is not an absolute entropy, but is $S_{298} - S_0$, with S_0 being the 'frozen in' configurational entropy of the solid solution at 0 K. Also, the equations for C_p are for the range 298 to 625 K and should not be used for extrapolation to much higher temperatures because the equations yield unreasonably high values for C_p at higher temperatures. Rather, any extrapolation above 625 K should be done with a weak, probably linear, temperature dependence because, at such temperatures, magnetic order does not exist and all vibrational modes are excited to some degree above ground state. Without a magnetic contribution and with the vibrational contribution arising from the degree of excitation and not the energization of new modes, it seems reasonable to apply to these solid solution alloys an upper limit for C_p of 30 to 31 J/g-at K in the vicinity of the melting point. This limit is the same as has been proposed by Kubaschewskii and Ünal [77Kub] as the norm for compounds. Application of this limit to solid solution alloys assumes that short-range configurational order is negligibly temperature dependent, so that no contribution is made to the heat capacity.

Gibbs Energies. Vapor pressures over V-Cr-Ti ternary alloys have been measured by Rolinski *et al.* [72Rol] at temperatures between 1400 and 1700 °C, using the Knudsen effusion method in combination with a mass spectrometer. The Ti content of the alloys which were measured was in no instance less than 10 at.% Ti; binary V-Cr data can, therefore, only be inferred by extrapolation to 0 at.% Ti. Aldred and Myles [64Ald], however, have made vapor pressure measurements by the torsion-effusion method directly on binary V-Cr alloys over the temperature range 1177 to 1377 °C. These latter data indicate somewhat more negative Gibbs energies of alloy formation than the former, but in neither instance are the Gibbs energies of alloy formation large. The experimental values for the excess Gibbs energies of alloy formation from the data of Aldred and Myles show an asymmetry with minimum values occurring in the Cr-rich region. In contrast, the regular solution approximation which was used by Rolinski *et al.* requires symmetry with the minimum excess Gibbs energy of alloy formation occurring at 50 at.% Cr. Because the recent melting data of O.N. Carlson indicate a minimum on the Cr-rich side and, be-

cause the compositional dependence of the heat capacity data above the Néel temperature also show a minimum on the Cr-rich side, the data of Aldred and Myles seem more compatible and were therefore chosen for the development of a set of functions for the calculation of a phase diagram.

A polynomial fit to the Aldred-Myles data generated the following excess Gibbs free energy function for the formation of solid bcc alloys from pure bcc V and pure bcc Cr:

$$\begin{aligned} \Delta G_{\text{sol}}^{\text{xs}} = & X_{\text{Cr}}X_{\text{V}} \{-9590 - 18220(X_{\text{Cr}} - X_{\text{V}}) \\ & - 3874(X_{\text{Cr}} - X_{\text{V}})^2 + 10800(X_{\text{Cr}} - X_{\text{V}})^3 \\ & - T [3.094 - 7.933(X_{\text{Cr}} - X_{\text{V}}) \\ & - 3.412(X_{\text{Cr}} - X_{\text{V}})^2 + 6.188(X_{\text{Cr}} - X_{\text{V}})^3]\} \end{aligned}$$

in J/g-at. A melting point of 1910 °C [81Smi] with

$$\Delta G_{M,V} = 21500 - 9.9 T$$

and a melting point of 1857 °C [Hultgren, Elements] with

$$\Delta G_{M,Cr} = 16900 - 7.9 T$$

were used in units of J/g-at, respectively, for V and Cr for conversion of both liquid and solid alloy formation to common standard states. To develop an expression for the formation of liquid alloys and because of the melting minimum near 70 at.% Cr, parameters for the Gibbs energy of formation of liquid alloys were initially set to force equality of the Gibbs energy of formation of both liquid and solid alloys at 70 at.% Cr and 1760 °C. The resultant parameters for the liquid alloys were then refined without further compositional or temperature constraint to produce the requisite tangency between liquidus and solidus lines at a melting minimum. The phase diagram that was obtained is shown in Fig. 2, and the refined excess Gibbs energy of formation of liquid alloys from the pure liquid elements was found to be:

$$\Delta G_{\text{liq}}^{\text{xs}} = X_{\text{Cr}}X_{\text{V}} [-19250 - 3598(X_{\text{Cr}} - X_{\text{V}})] \text{ J/g-at}$$

It should be noted that this expression contains no explicit temperature dependence, so its validity is restricted to the temperature range of melting of the alloys.

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V-Cr evaluation contributed by J. F. Smith, D. M. Bailey and O. N. Carlson, Ames Laboratory-USDOE and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011. Work was done at the Ames Laboratory, which is operated for the U. S. Department of Energy, under contract No. W-7405-Eng-82. That portion of the work dealing with assessment of phase relationships and crystallography was supported by the Office of Basic Energy Sciences, Division of Materials Sciences (AK-01-02). That portion of the work dealing with thermodynamic assessment was supported by the Department of Energy through the Joint Program on Critical Compilation of Physical and Chemical Data coordinated through the Office of Standard Reference Data, National Bureau of Standards. Literature searched through 1980. Prof. Smith is the ASM/NBS Data Program's Category Editor for binary vanadium alloys.

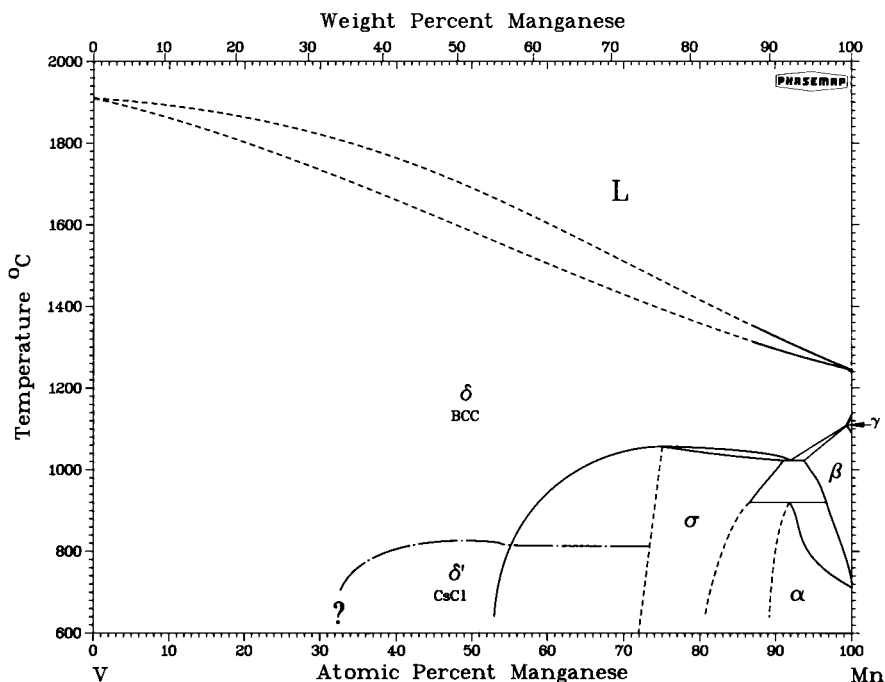
The Mn-V (Manganese-Vanadium) System

54.9380 amu

50.9415 amu

By J. F. Smith and O. N. Carlson
Iowa State University

Fig. 1 V-Mn Phase Diagram



Composite phase diagram based on the Waterstrat [62Wat] investigation, including high-temperature data from Hellawell and Hume-Rothery [57Hel] and the order-disorder boundary (dash-dot line) as determined by Suzuki and Hagiwara [75Suz1].

J. F. Smith and O. N. Carlson, 1982.