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*Indicates key paper.

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The Nb-V (Niobium-Vanadium) System

92.9064

50.9415

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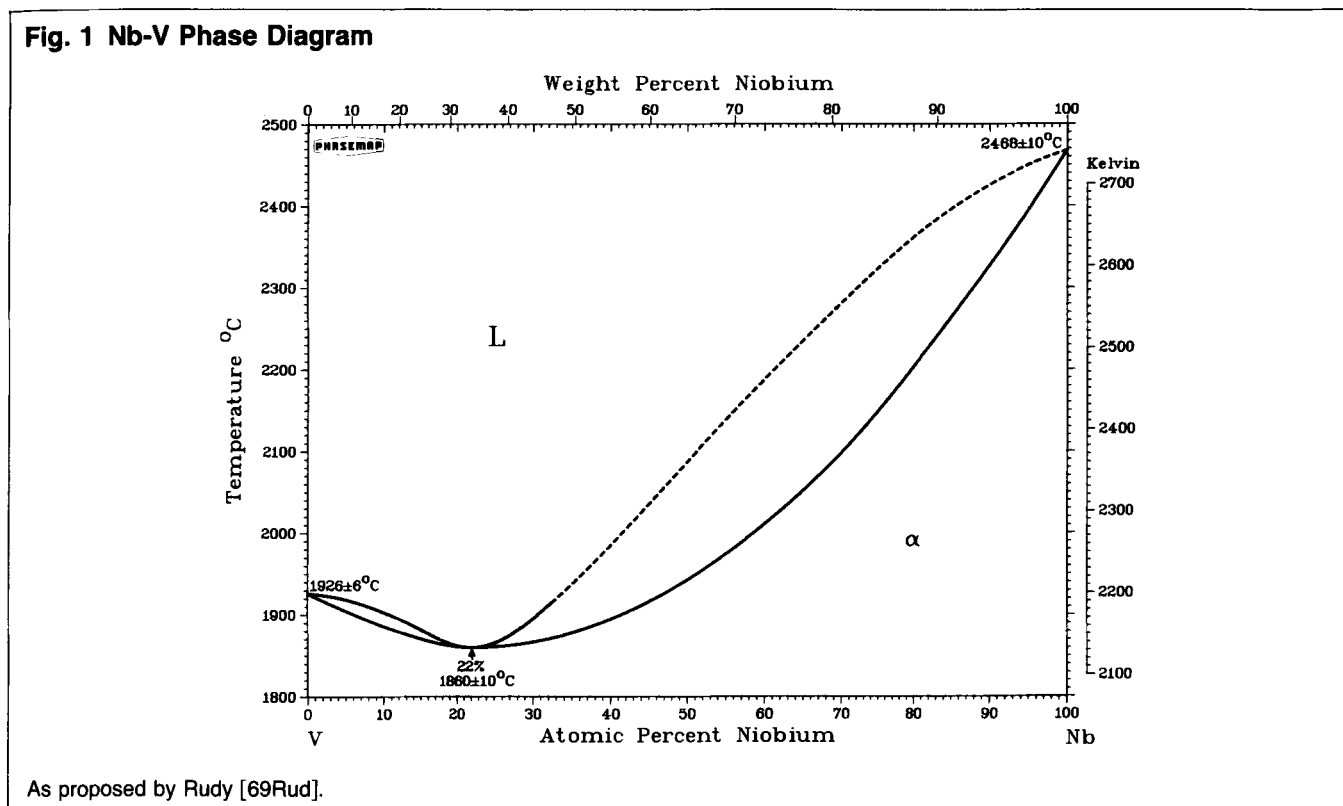
Phase Relationships

Nb and V form a continuous series of solid solutions with a minimum melting point near the V-rich end of the system. This may be seen in Fig. 1, which is the diagram proposed by Rudy [69Rud], with the minimum at 1860 °C and 22 at.% Nb. Other investigations also have reported the existence of a minimum melting point, with Wilhelm *et al.* [54Wil] placing it at 1810 °C and 23 at.% Nb and Baron *et al.* [60Bar] placing it at 1720 °C and 26.8 at.% Nb. The agreement between the composition for the minimum reported by Wilhelm *et al.* and that reported by Rudy is quite good in view of the flatness of the solidus in the region of the minimum. The differences among the values from the three investigations are quite probably attributable to variations in purities of the V and/or Nb that were used. Wilhelm *et al.* indicated the purity of their V as approximately 99.7%, with a melting point of 1860 °C, whereas Baron *et al.* indicated a purity of 99.4% for their V, with a melting point of 1890 °C. For Nb, Wilhelm *et al.* reported a purity of 99.9%, with a melting point of 2420 °C, whereas Baron *et al.* reported a purity of 99.9%, with a melting point of 2415 °C. Although Rudy gave no purity specifications for his base metals, his observed melting points for V (1926 ± 6 °C) and Nb (2468 ± 10 °C) are close

to currently accepted values for these metals [81BAP], which indicates that his metals were relatively pure. On this basis, Rudy's diagram is preferred.

Recent work at the Ames Laboratory [82Sch] provides additional corroboration for the existence of the melting minimum. A large single crystal was grown of a 22 at.% Nb-78 at.% V alloy by electron-beam melting. Growth of single crystals by this technique is generally successful only with congruently melting alloys and is usually unsuccessful for alloys with a melting range. Thus, the fact that a single crystal was obtained implies that 22 at.% Nb is at or near the composition of congruent melting.

The general features of the phase diagram in Fig. 1 are additionally supported by the thermodynamic calculations of Molokanov *et al.* [77Mol] and of Balakrishna and Mallik [79Bal]. In both instances, the calculated liquidus and solidus curves meet to form an azeotropic melting minimum near the composition of the melting minimum of Fig. 1. The calculations of Molokanov *et al.* [77Mol] were, however, carried a step further to predict the existence of a miscibility gap in the solid bcc phase field with a critical point of 380 °C and 50 at.% Nb. The significance of this prediction is questionable because a regular solution model was employed which, with a positive interaction



parameter, guarantees a critical point at 50 at.% with the magnitude of the critical temperature being scaled by the magnitude of the interaction parameter. Certainly, the model is an oversimplification, and there is no experimental evidence to indicate the existence of any immiscibility. On the contrary, superconducting studies at very low temperatures [61Hul, 67Sir] show persistence of the continuous bcc solid solution to the vicinity of absolute zero. It must be admitted, however, that diffusion of either atomic species in these Nb-V alloys must be exceedingly slow at temperatures below 380 °C, with equilibrium requiring very long times. Unambiguous evidence that the continuous solid solution at low temperatures is not a "frozen in" metastability would be difficult to obtain. Some additional discussion of the thermodynamic calculations may be found in the "Thermodynamics" section of this review.

Rostoker and Yamamoto [54Ros] reported finding no information in the literature pertaining to the Nb-V system prior to their own report of 1954. Their work with alloys containing up to 56 at.% Nb showed microstructures indicative of continuous solid solution. In exception, after annealing alloys containing 19 and 26 at.% Nb at 900 °C for 170 h, they observed small amounts of a grain boundary precipitate that they speculated might be a σ phase. The failure of later investigators to find this precipitate phase makes it likely that it was due to contaminants. Wilhelm *et al.* [54Wil] performed long term anneals (170 h at 900 °C) on several alloys in the composition range 20 to 55 at.% Nb, and in no instance did they observe a second phase in a microstructure. Likewise, X-ray diffraction patterns of filings from the same alloys after annealing at 650 °C for 113 h failed to show any phase other than the bcc solid solution. Elliott [54Ell], in a third report during the same year as the reports of

Rostoker and Yamamoto and of Wilhelm *et al.*, reported still different results. In an alloy of 33.3 at.% Nb, Elliott observed microstructures characteristic of a solid solution, but with a "peppery precipitate". The term "peppery precipitate" implies an intergranular rather than a grain boundary precipitate, and the results thereby differ from those of Rostoker and Yamamoto [54Ros]. Elliott indicated that X-ray diffraction patterns of his material showed a bcc Nb-V solid solution with weak lines from bcc Nb. Thus, it may be inferred that the "pepper" arose from incomplete mixing because both Wilhelm *et al.* [54Wil] and Rudy [69Rud] found a smooth variation of the bcc lattice parameter as a function of composition across the system.

Though the atomic size ratio of Ta to V is $r_{Ta}/r_V = 1.086$ and that of Nb to V is $r_{Nb}/r_V = 1.093$, and the electronegativities of Ta and V are closely comparable, and in spite of the fact that Carlson *et al.* [59Car] found a cubic TaV₂ Laves phase in the Ta-V system, Elliott's report [54Ell] showed no indication of a Laves phase in his alloy of NbV₂ stoichiometry nor has any other investigation found indication of such a phase.

Crystallography

Crystal structure data are given in Table 1. Lattice parameters of the continuous bcc solid solution have been determined as functions of composition by both Wilhelm *et al.* [54Wil] and Rudy [69Rud]. Data points are plotted in Fig. 2 and smoothed values are listed in Table 2. It may be noted that there is a slight positive deviation from Vegard's law, which is consistent with positive interaction energies between the two constituent species in the solid solution and thence consistent with the azeotropic melting minimum.

Table 1 Nb-V Crystal Structure Data

Phase	Composition, at.% Nb	Pearson symbol	Strukturbericht designation	Space group	Prototype	Lattice parameter, nm <i>a</i>
α , (Nb), or (V)	0-100	<i>cI2</i>	A2	<i>Im3m</i>	W	0.3026-0.3306

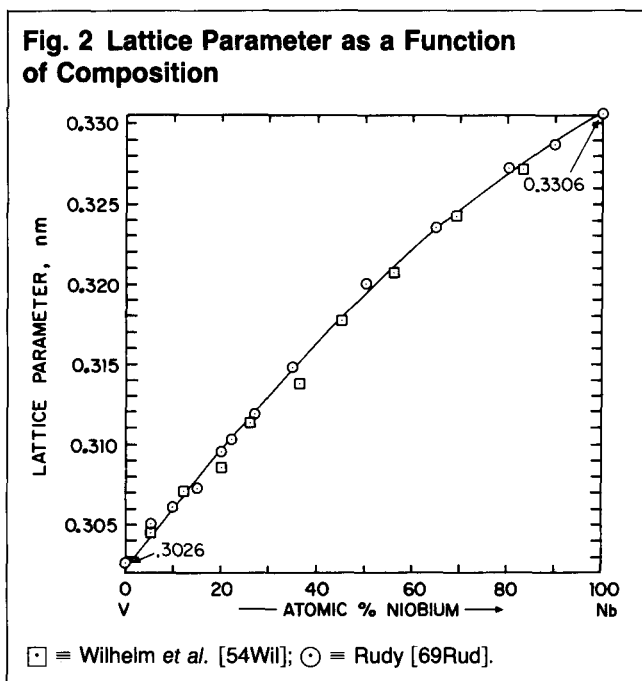


Table 2 Lattice Parameters Representing the Smoothed Values from the Curve of Fig. 2

Composition, at.% Nb	Lattice parameter, nm <i>a</i>
0	0.3026
10	0.3061
20	0.3096
30	0.3130
40	0.3162
50	0.3193
60	0.3221
70	0.3246
80	0.3269
90	0.3288
100	0.3306

Balakrishna and Mallik showed their calculated results only by graph without quoting coordinates for the azeotropic melting, but their graphical comparison of calculated results with the experimental data of Wilhelm *et al.* [54Wil] showed good accord. Balakrishna and Mallik made additional calculations with a quasichemical model and with a surrounded atom model, but the added complexity did not significantly improve agreement between calculated and experimental results. For the present review, a new calculation was made with the regular-solution model; an enthalpy of fusion of 21 500 J/mol with a melting point of 2183 K was used for V [81Smi], an enthalpy of fusion of 26 400 J/mol with a melting point of 2740 K was used for Nb [Hultgren], and the interaction parameters of Balakrishna and Mallik [79Bal] were employed. These interaction parameters are 602 J/mol Nb_xV_{1-x} for liquid alloys and 10 841 J/mol Nb_xV_{1-x} for bcc alloys. This calculation shows the azeotropic melting point to occur at 23 at.% Nb and 2115 K (1841 °C), and calculated liquidus and solidus curves are shown in Fig. 3.

Thermodynamics

Nb-V alloys are superconducting at all compositions [67Sir, 61Hul, 70Cor], with transition temperatures first dropping from ~5.2 K for pure V to a broad minimum of ~4 K between 20 and 50 at.% Nb and then rising to ~9.2 K at pure Nb. Low-temperature heat capacities were measured on a series of alloys at various compositions across the system by Corsan and Cook [70Cor] in the temperature range 2 to 15 K. Heiniger *et al.* [66Hei] also reported low-temperature heat capacity data for an 88 at.% Nb alloy. In both investigations, the normal-state heat capacities were fit to the standard relationship:

$$C = \gamma T + \beta T^3 \quad \text{J/K} \cdot \text{mol Nb}_x\text{V}_{1-x}$$

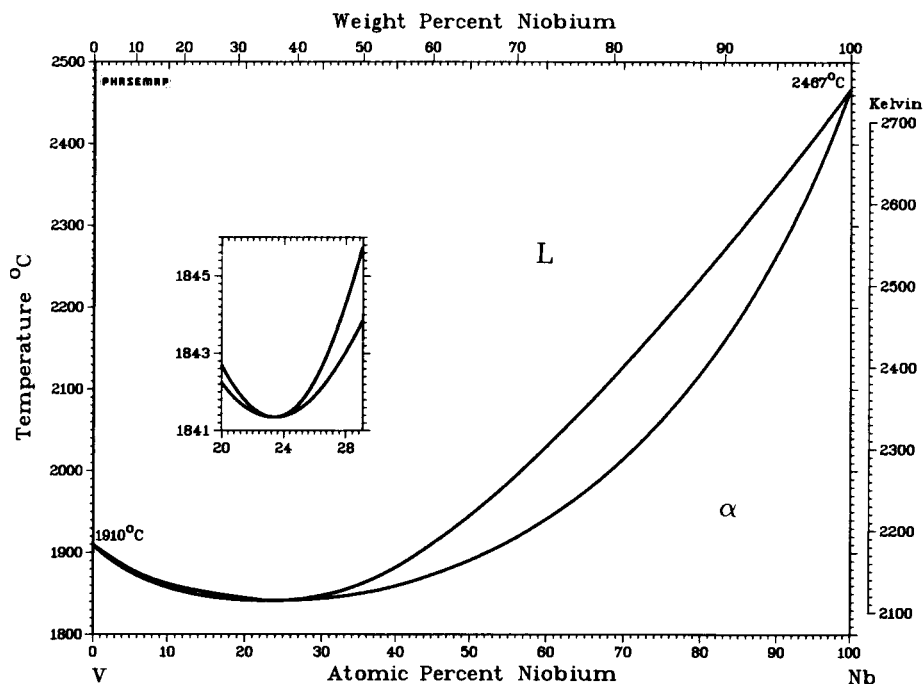
where γ is the electronic specific heat coefficient and $\beta = 1922/\theta_D^3$, with θ_D being the Debye temperature. Values that were reported for γ , β , the superconducting transition temperature T_c , the critical field $H_c(0)$ at 0 K, and the electron-phonon coupling parameter λ are shown in Table 3.

Molokanov *et al.* [77Mol] and Balakrishna and Mallik [79Bal] both calculated liquidus and solidus curves for the Nb-V system with a regular solution model. In both instances, they used the approach of Kaufman and Bernstein [70Kau]. The theoretically generated interaction parameters for both calculations were closely comparable, but the two calculations differed slightly in the values that were used for the melting points and enthalpies of fusion of the constituent elements. Molokanov *et al.* calculated the azeotropic melting at 25 at.% Nb and 1817 °C.

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Fig. 3 Calculated Nb-V Phase Diagram



Calculations are based on a regular-solution model.

J. F. Smith and O. N. Carlson, 1983.

Table 3 Values for Heat Capacities and Superconducting Parameters for Nb-V Alloys at Various Compositions

Composition, at.% Nb	Electronic specific heat coefficient ($\gamma \times 10^3$), J/K·mol Nb _x V _{1-x}	Debye temperature (θ_D), K	Superconducting transition temperature (T_c), K	Critical field(a), $H_c(0)$, 10 ³ A/m	Electron-phonon coupling parameter, λ	Reference
0	9.45	377	5.17	106.3	0.60	[70Cor]
15	9.19	364	4.30	84.7	0.59	[70Cor]
20	8.72	326	4.03	76.3	0.59	[70Cor]
50	8.30	298	4.25	76.2	0.61	[70Cor]
69	7.97	285	4.90	84.4	0.65	[70Cor]
80	7.90	275	5.76	97.0	0.69	[70Cor]
90	7.77	266	6.95	119.1	0.74	[70Cor]
100	7.74	248	9.18	150	0.86	[70Cor]
88	7.05	268	5.7	[66Hei]

(a) At 0 K.

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*Indicates key paper.

#Indicates presence of a phase diagram.

Nb-V evaluation contributed by J. F. Smith 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 1981. Professor Smith is the ASM/NBS Data Program Category Editor for binary vanadium alloys.