16 Vanadium

Phase Diagram

The sparse literature on the W–V phase diagram has been reviewed by "Hansen" (1958), p. 1253, "Elliott" (1965), pp. 859/60, "Shunk" (1969), p. 708, and "Vol", Vol. 2 (1962), p. 7; also see [13]. The phase diagram given in "Massalski" (1986), p. 2152, is redrawn from [14].

Samples in the system have been prepared at 10 wt% V increments. Pressed powder mixtures were sintered at 10^{-5} Torr and 1600°C for 20 h, and finally arc-melted. The quenched and annealed samples were investigated metallographically and by X-ray diffraction. The observation of W-rich dendrites indicates a wide separation of liquidus and solidus, but no second phase was found. The unrestricted mutual solid solubility of V and W is confirmed by X-ray diffraction, which was performed also on alloys annealed at 1000°C [1]; see also [2 to 6].

The solidus has no minimum and starts at 1926 ± 3°C on the V side with a slope of ~8.75 K/at% W and ascends more steeply at ≳60 at% W reaching the W side at 3423 ± 10°C [13]. The diagram in "Massalski" gives 1910 and 3422°C as the melting points of V and W, respectively. The minimum in the solidus and liquidus near the V-rich end of the system, reported, e.g., in [3 to 5], appears to be spurious and due to impurities, especially in the V used. According to thermal analysis, metallographic investigation, and property vs. composition plots, there is no minimum either on the liquidus or on the solidus. The following solidus temperatures (± 40 K) are given for the range ≤36 wt% W [7]:

wt% W	0	5	8	14	20	25	36
solidus in °C ..	1890	1910	1940	1960	2010	2050	2100

Impurities are also held responsible for the deviations from Vegard's rule on the V-rich side of the W–V system [8]. Close obeyance of Vegard's rule is observed in pure alloys by [3, 4].

No intermediate phase was observed in the V–W system at 1700 ± 15°C [7] (see also [8]). The indications of a two-phase region at ≳50 wt% W [9] have never been confirmed by later work.

Surface Reactions

An FEM probe-hole technique was used to measure the work function changes ΔΦ upon V adsorption onto W(110), W(211), W(111), W(210), and W(320) surfaces. During the V deposition the pressure was at $\lesssim 10^{-10}$ Torr and the tip was held at room temperature, much below the onset of surface migration at ≳600 K. The Φ vs. coverage (Θ) plots show a monotonous decrease with increasing Θ for the W(110) and W(211) surfaces. On the latter the decrease in Φ at first is weak, then steeper, and finally Φ approaches a saturation value. For W(111), W(210), and W(320), on the other hand, Φ first passes a maximum, then a minimum, and finally saturates. These nonmonotonous ΔΦ vs. Θ curves are explained by an initial smoothing of these rough surfaces. Continued V deposition seems to restore approximately the initial roughness since Φ(max) − Φ(clean) ≈ Φ(sat) − Φ(min) for these surfaces; see the following table of work function values (Φ ± 0.06 eV) [12]:

face	Φ(clean)	Φ(sat)	Φ(max)	Φ(min)	Θ(max)/Θ(sat)	Θ(min)/Θ(sat)
(110)	5.54	4.42	—	—	—	—
(211)	4.82	4.01	—	—	—	—
(111)	4.40	3.88	4.46	3.79	0.82	0.21
(210)	4.35	3.81	4.62	3.57	0.75	0.20
(320)	4.29	3.86	4.77	3.41	0.7	0.1

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