MASTER**HYDROGEN ABSORPTION IN THE NIOBIUM-VANADIUM SYSTEM**

M. A. Pick and D. O. Welch
Brookhaven National Laboratory
Upton, New York 11973

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Hydrogen Absorption in the Niobium-Vanadium System*

M. A. Pick and D. O. Welch
Brookhaven National Laboratory
Upton, New York 11973

Abstract

The effect of dilute vanadium additions to niobium on hydrogen absorption has been studied by measuring equilibrium pressure-composition-temperature data for a Nb + 6 at.% V alloy and by constructing a theoretical model of the effect of hydrogen trapping on phase equilibria in such systems. The results indicate the H-V binding energy is substantially smaller than thought previously. A depression of the α - α' critical temperature is observed which, if interpreted in terms of trapping, leads to a H-V binding energy of ~ 0.04 eV.

I. Introduction

It is well established that interstitial impurities in niobium can act as traps for dissolved hydrogen. For example, a detailed study of the trapping of hydrogen by interstitial nitrogen in niobium has been published by Pfeiffer and Wipf.⁽¹⁾ It is likely that substitutional impurities can also act as hydrogen traps, and the increased solid solubility of hydrogen in dilute alloys of vanadium in niobium,⁽²⁾ compared with pure niobium, has been attributed to such trapping effects. As evidence that vanadium, and molybdenum as well, acts as a hydrogen trap in niobium, Sasaki et al.⁽²⁻⁴⁾ cite changes of the breadth of x-ray diffraction lines and of the ^{93}Nb NMR absorption curve when hydrogen is added to dilute V-Nb and Mo-Nb alloys. As these effects are somewhat indirectly related to hydrogen trapping, it is desirable to test by other means the effectiveness of vanadium as a hydrogen trap in niobium. Thus, in this paper we report measurements of equilibrium pressure-temperature-composition data for hydrogen in a dilute solid solution of vanadium in niobium and compare the results with expectations based on a simple theoretical model for the effect of trapping on phase equilibria in hydrogen-metal systems. The techniques, both experimental and theoretical, will be described only very briefly, since the details, together with more extensive results, will be published elsewhere.⁽⁵⁾

II. A Theoretical Model

In order to gain insight into the effect of the trapping of hydrogen by substitutional solute atoms on pressure isotherms, the critical tem-

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perature, etc., we have constructed a simple model which incorporates in an approximate manner the essential features of hydrogen-transition metal systems in the α - α' region of the phase diagram, i.e. the "vapor-liquid" region of the lattice gas. In this model, the free-energy of hydrogen solid solutions is calculated with the assumption that, except for short-range "blocking" effects due to H-H repulsions, hydrogen atoms are distributed at random over the available tetrahedral sites of the b.c.c. lattice. The short-range correlations are approximated by requiring that a specified number of interstitial sites adjacent to each interstitial site filled by a hydrogen atom be empty and by requiring that a solute atom may trap at most one hydrogen atom. The configurational entropy is calculated using a modification of the method devised by Lidiard for studying impurity-vacancy binding in metals,^(6,7) approximately corrected by the use of normalizing functions in the spirit of the quasi-chemical approximation.⁽⁸⁾ An elastic interaction between hydrogen atoms is included. The model contains three undetermined parameters: the temperature, T_c° , and hydrogen-to-metal ratio, C_H^* , at the α - α' critical point in pure Nb and the solute-hydrogen binding energy, B . When matched at the critical point, the model yields phase boundaries for the α - α' region of hydrogen in pure Nb within about 10-15% of those measured experimentally by Pryde and Titcomb,⁽⁹⁾ and is in even better agreement with the more recent phase diagram of Welter et al.⁽¹⁰⁾

Requiring that the free-energy resulting from this model be stationary with respect to transfers of hydrogen between the metal solid solution and an ideal gas phase yields the hydrogen partial-pressure, P , versus hydrogen concentration, C_H , isotherm:

$$\left(\frac{P}{P_c^\circ}\right)^{1/2} = \frac{C_H}{(2C_H^* - C_H)} \cdot \frac{C_H^{-\kappa} C_I}{C_H^{-\kappa} C_I} \left(\frac{T}{T_c^\circ}\right)^{7/4} e^{\left\{ \left(g_s + \frac{D}{2}\right) \left(\frac{1}{kT} - \frac{1}{kT_c^\circ}\right) - \frac{2C_H}{C_H^*} \frac{T_c^\circ}{T} \right\}} \quad (1)$$

where g_s is the free-energy of solution (exclusive of configurational entropy) of a hydrogen atom in Nb, D is the dissociation energy of a hydrogen molecule, P_c° is the hydrogen partial pressure at the α - α' critical point in pure Nb, C_I is the fraction of metal atoms that are solute atoms, κ is the fraction of solute atoms which have trapped a hydrogen atom, given by the equilibrium equation:

$$\kappa^2 \left[1 + \frac{e^{-B/kT}}{8C_H^*} \right] - \kappa \left[1 + \frac{e^{-B/kT}}{4C_I} + \frac{C_H}{C_I} \right] + \frac{C_H}{C_I} = 0 \quad (2)$$

and κ_I is the solution of Equation (2) when the binding energy, B , is zero.

The experiments of Sasaki et al.⁽²⁻⁴⁾ suggest that the binding energy of hydrogen to vanadium in niobium is ~ 0.2 eV. A typical isotherm for a

Nb + 6% V alloy calculated with Eqs. (1) and (2) using this value of B, together with $C_H^* = 0.3^{(10)}$ and $T_c^0 = 465K^{(11)}$ is shown in Figure 1. For comparison, the calculated isotherm for pure Nb is also shown, as the dashed line, in Figure 1. Note that while pure Nb shows Sievert's law behavior, i.e. $(P)^{1/2} \propto C_H$, as C_H approaches zero and exhibits negative deviations ($\partial^2 P^{1/2} / \partial C_H^2 < 0$) from Sievert's law, the V-Nb alloy shows substantial positive deviations ($\partial^2 P^{1/2} / \partial C_H^2 > 0$) from Sieverts law for $C_H \lesssim C_I$, followed by negative deviations, due to the elastic interaction between hydrogen atoms, at higher concentrations. The existence of the positive deviations from Sievert's law is a consequence of strong trapping and will be a feature of any trapping model, not just the particular one used here; thus the observation of such positive deviations in an experimental isotherm would be good evidence in favor of trapping.

The location of the incoherent spinodal points is revealed in calculated isotherms as points where $\partial P^{1/2} / \partial C_H = 0$; the two spinodal points are indicated by arrows in Figure 1. Their location may be found by differentiation of Equations (1) and (2), and finding the temperature at which the two spinodal points coalesce yields the α - α' critical temperature. For the example shown in Figure 1, $T_c / T_c^0 = 0.923$; thus a binding energy of 0.2 eV leads to a depression of the critical temperature of about 35K for Nb-6% V. Such a depression is consistent with the substantial increase in hydrogen solubility observed^(2,3) to accompany alloying Nb with small amounts of V.

Upper and lower bounds for the effect of short-range hydrogen-solute interactions on the α - α' critical temperature can be obtained by treating the solute atom as a perfect trap ($B = +\infty$) or as a perfect center of repulsion ($B = -\infty$) and solving for T_c as described above. The results of such a calculation are shown in Figure 2. These results show that a concentration of "perfect traps" of only about 15% in Nb is required to depress the α - α' critical temperature below the α - α' - β triple point of pure Nb, $\sim 360K$.⁽¹¹⁾ If the critical temperature were depressed below the triple point, then the phase diagram of such a solid solution for $C_H < .5$ would be topologically similar to that of V-H rather than that of Nb-H.

III. Experimental Results

Samples of dilute solid solutions of V in Nb were prepared by arc-melting MARZ-grade niobium and vanadium in UHP-argon. Metallographic examination of the samples revealed no inhomogeneities. Equilibrium hydrogen partial pressure data were obtained in an all-steel high-vacuum system (pressures $< 10^{-7}$ torr). Known volumes of pure hydrogen, obtained by the decomposition of FeTi hydride, were introduced stepwise, equilibrated for

about 30 minutes, and the equilibrium pressure measured using calibrated diaphragm gauges.⁽⁵⁾ Figure 3 shows isotherms obtained in this manner for a Nb-6 at.%V alloy, a composition close to that for which Sasaki et al.^(3,4) claim to have evidence for hydrogen trapping. Isotherms measured over a much wider range of hydrogen content on the same alloy are shown in Figure 4. The isotherms are plotted in Figure 3 as $P^{1/2}$ versus C_H . Although the theoretical development in Section II (Figure 1) indicated that trapping in the degree suggested by Sasaki et al. would produce clear positive deviations from Sievert's law, Figure 3 shows no such deviations. At the higher concentrations shown in Figure 4, negative deviations due to the hydrogen-hydrogen interaction ultimately leading to phase separation can be seen. These isotherms do not exhibit a truly horizontal plateau, even at 418K, although the data in the figure suggest that the α - α' critical temperature for this alloy is only slightly less than 418K. This is substantially depressed below the recently obtained value for pure Nb,⁽¹⁰⁾ 443K, (which is somewhat lower than the older values of 465K⁽¹¹⁾ and 484K.⁽⁹⁾)

IV. Discussion

It is clear from a comparison of Figures 1 and 3 that there is no experimentally detectable positive deviation from Sievert's law and thus that the binding energy between hydrogen and vanadium is appreciably less than the value of 0.2 eV suggested by the experiments of Sasaki et al.⁽²⁻⁴⁾ The magnitude of the depression of the critical temperature is also compatible with a smaller binding energy. If we take $T_c = 418K$ and $T_c^0 = 443K$, the methods described in Section II lead to a binding energy of $\sim .04$ eV. This value of the binding energy contributes so little to the deviation from Sieverts law that it would be undetectable by measurements of the precision of those shown in Figure 3.

In the discussion thus far we have ascribed the entire depression to a "local" effect, trapping. There are also "global" effects, i.e. changes in the average lattice, which act to depress T_c . If we disregard local effects entirely, the theory of Section II, together with an approximate expression for the elastic interaction energy,⁽¹²⁾ indicates that T_c is proportional to $P^2/B\Omega$, where P is the elastic dipole tensor for hydrogen, B the bulk modulus, and Ω the atomic volume. We may obtain a rough estimate by linearly interpolating this "coupling constant" between values for the pure metals, computed from the data of references 13-15. This procedure leads to $T_c/T_c^0 \cong .97$ (compared with the actual value of $\sim .94$), with the depression being attributable to a decrease in P on alloying since changes in both B and Ω act to raise T_c . If such a "global" effect does play a role in de-

pressing T_c , the value of the H-V binding energy would, of course, be less than ~ 0.04 eV.

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Fig. 1. Theoretical hydrogen partial pressure isotherm for Nb + 6% trapping centers of binding energy ~ 0.2 eV. Isotherm for pure Nb is also shown.

Fig. 2. Upper and lower bounds for the change in the α - α' critical temperature which can result from short-range hydrogen-impurity interactions.

Fig. 3. Equilibrium hydrogen partial pressure, plotted as the square-root, versus hydrogen concentration for Nb + 6 at.% V.

Fig. 4. Equilibrium hydrogen partial pressure versus hydrogen concentration for a Nb + 6 at.% V alloy.

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