BNWL-SA-4473

Conf-721111--23

SOLUBILITIES AND DIFFUSIVITIES OF HYDROGEN ISOTOPES IN NIOBIUM, NIOBIUM-ZIRCONIUM ALLOYS, AND VANADIUM AT HIGH TEMPERATURES

by

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DISCLAIMER

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ABSTRACT

Alloying elements having potentially strong interactions with hydrogen isotopes may be present in CTR first wall materials, either due to intentional alloying or because of neutron-induced transmutation. The effect of zirconium (up to 20 wt percent) on the solubility and diffusivity of hydrogen and deuterium in niobium alloys has been investigated at 900°C. Zirconium additions to 20 percent have little effect on hydrogen isotope diffusivity. Hydrogen solubility data is presented for vanadium and niobium-1 zirconium alloy at temperatures of 800, 900, and 1000°C and pressures between 0.05 and 100 Torr. Zirconium addition of one percent has negligible effect on gas solubility. A zirconium addition of 10 percent significantly increases gas solubility. Deuterium exhibits a lower solubility than hydrogen at equal pressures and temperatures for the alloys studied.

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1. INTRODUCTION

Fusion reactor technology is aimed toward first-generation plants fueled by deuterium and tritium, due principally to the relatively low D-T ignition temperature. The lack of natural sources of tritium dictates that tritium breeding will be required to sustain the tritium fuel supply. In present concepts, tritium breeding will occur in large reservoirs of lithium metal or lithium salt. A major challenge in the D-T fusion reactor concept will be to contain the radioactive tritium while at the same time maintaining an extractable tritium concentration in the lithium or lithium salt blanket. The seemingly delicate balance between tritium containment and extraction requires that the diffusivities and solubilities of tritium in CTR structural materials be well defined over the life of the reactor.

The candidate materials for the first wall and blanket include niobium, vanadium, molybdenum and stainless steel. The first two materials have relatively high hydrogen isotope solubilities, while the latter two have relatively low solubilities. Certain proposed alloy additions can also interact strongly with hydrogen, e.g., zirconium in the case of niobium-zirconium alloys and titanium and zirconium in the case of TZM (Mo-0.5 wt % Ti-0.1 wt % Zr).

Over the life of the reactor, changes in alloy composition by transmutations are expected to occur, predominantly from interactions with the high-energy neutrons. Estimates for neutronically-generated species and their concentrations were reported by Martin[1] for niobium and by Wiffen[2] for niobium and vanadium. Martin predicts substantial ingrowth of Zr and Y in niobium, amounting to 0.6 and 10 atomic percent, respectively, after 20 years, based on a flux of 14.1 MeV neutrons of 3.7×10^{4} n/cm^2-sec. Both Zr and Y have the potential to interact strongly with hydrogen isotopes. Wiffen presents transmutation rates of niobium (due to Steiner) of 1.4 percent/year Zr + Mo + Y. The transmutation product is estimated to be 95 percent Zr, initially; at the end of 20 years, it is estimated to be 66 percent Zr, 33 percent Mo. These figures are predicted on a flux of 3.7×10^{15} n/cm^2 sec. For vanadium, the transmutation rate under the same flux conditions is estimated to result in 0.7 percent/year Cr + Ti, with the product consisting of approximately 90 percent chromium.

Because of large uncertainties in CTR fluxes and component lifetimes, it is not clear what the actual values for neutronic impurities will be. However, the consequences of deliberate alloy additions which interact strongly with hydrogen isotopes has generated some concern.[3] To place the consequences of deliberate or neutronic alloy additions to niobium into better perspective, hydrogen solubility and diffusivity measurements were undertaken on alloy compositions containing the strong hydride-formers zirconium and yttrium. Hydrogen and deuterium solubilities in vanadium also were studied to extend the data available in the literature to lower pressures in the temperature range of 800 to 1000°C.

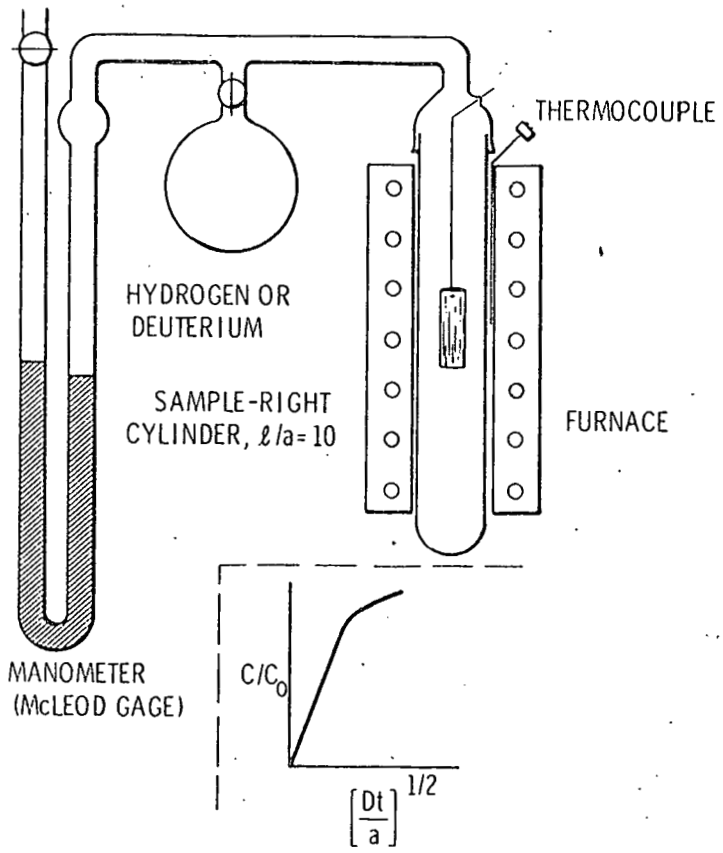
2. EXPERIMENTAL

In the case of equilibrium pressure-temperature-composition (P-T-C) tests, the amount of gas absorbed by the sample at a given gaseous overpressure was determined by pressure decrease in a standard volume. Sufficient time was allowed for the sample to reach a state of equilibrium. The kinetics of absorption of H_2 or D_2 gas was determined by monitoring a pressure decay in the standard volume system; a pressure buildup was monitored in the case of determining desorption kinetics. In this latter case, a mercury diffusion pump extracted the gas from the sample and held it in a standard volume for measurement. Steady-state permeation rates of hydrogen isotopes through a metal thimble were determined by measuring the pressure buildup in a standard volume, where the gas is held for measurement. Figures 1 and 2 show the major features of the experimental apparatus.

2.1 Materials

Two groups of metal alloys were obtained for the hydrogen isotope studies. The four experimental niobium alloys prepared for the 900°C absorption-desorption tests and the commercial alloys obtained for the equilibrium solubility and the steady-state permeation tests are described in Table 1.

Yttrium was included in one of the melts because it is an expected niobium transmutation product; zirconium can also result from transmutation, or it may be intentionally added as an alloying element. The special melts were made up as buttons by standard melting procedure. Cylinders 0.64 cm diameter by 3.18 cm long were machined from the buttons. The samples were vapor blasted to minimize the possibility of a slow surface reaction and degreased prior to testing.

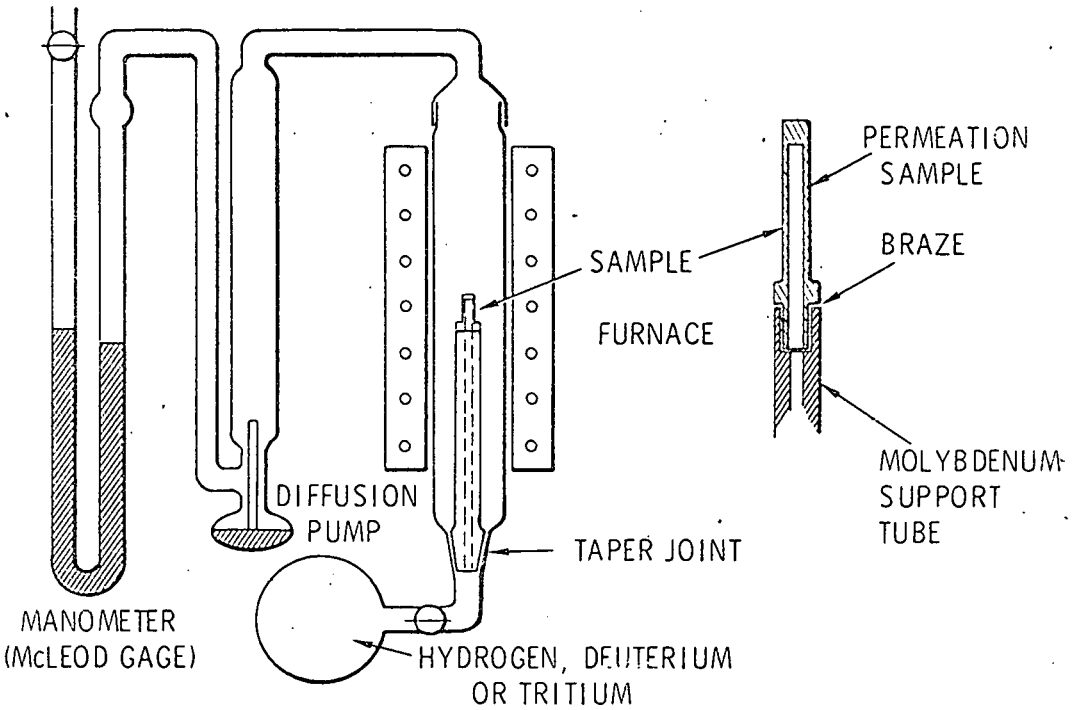


SHAPE OF THE CURVE PREDICTED BY THE DIFFUSION EQUATION:

$$C/C_0 = 1 - \frac{32}{\pi^2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{1}{\beta_m^2 \, (2n+1)^2} \, \mathrm{EXP} \left\{ \left[- \frac{(2n+1)^2 \pi^2}{25} + \beta_m^2 \right] \left[\frac{Dt}{a^2} \right] \right\}$$

Figure 1

Diffusivity Determination by Hydrogen Absorption



PERMEATION EQUATION: $\Phi = -DS \frac{\sqrt{P_o} - \sqrt{P_i}}{\Delta X}$

Figure 2

Determination of Diffusivity by Thimble Permeation

Table 1

ALLOYS USED IN STUDY

SPECIAL MELTS - EXPERIMENTAL BUTTONS

A. Niobium

B. Niobium - 10 wt percent Zirconium

C. Niobium - 10 wt percent Zirconium - 0.1 wt percent Yttrium

D. Niobium - 20 wt percent Zirconium

COMMERCIAL ALLOYS

A. Niobium

B. Niobium - 1 wt percent Zirconium

C. Vanadium

The commercial alloys were obtained in the form of 1.25 cm diameter rod, 75 percent reduced from as-cast condition by hot extrusion. For the equilibrium P-T-C study, right cylinders 0.76 cm diameter by 1.91 cm long were used. For the permeation study, thimbles were machined from the rod stock having cylindrical "window" areas of 9.11 cm^2 and wall thicknesses of 0.20 cm.

2.2 Equilibrium P-T-C and Absorption Studies

P-T-C data were obtained by admitting a measured amount of hydrogen (or deuterium) to the reaction tube containing an outgassed sample of the alloy. The sample weighed approximately 6 grams. At the test temperature, the system was allowed to come to a constant pressure. The equilibrium composition was calculated from the equilibrium pressure, sample weight, volume of gas addition and the volume of the reaction system. In the case of the equilibrium studies conducted on the commercial purity alloys, the same sample was used at each test temperature.

All of the absorption rate studies were conducted at 900°C. In this case, a known quantity of H_2 or D_2 was admitted to the reaction tube, containing a cylindrical sample of the experimental alloy. The rate of absorption was determined by monitoring the pressure decay on an oil manometer.

Albrecht et al.[4] developed an analytical expression relating fractional uptake of gas to a function (their equation is given on Figure 1) of diffusivity D, time t, and cylinder radius a; they found that a plot of C/C_0 vs $(Dt/a^2)^{1/2}$ was linear up to about 40 percent saturation (the approximation to linearity is fairly good even to 70 percent). Such a plot then leads to an easy determination of diffusivity. Albrecht et al. used an

expression specifically developed for a finite specimen having a length/radius (l/a) ratio of 5. Crank[5] presents a plot of the same relationship for a cylindrical sample having an l/a ratio of infinity; the two plots are indistinguishable in the region of interest indicating the applicability of the overall approach to the present study where the sample l/a ratio is 10. It is important to note, however, that the diffusivities obtained by this method in the present study must be considered approximate values only, as the analysis discussed in the foregoing is not strictly applicable when a steady diminution in the surface concentration (C_0 by definition is also the final sample concentration) takes place during the absorption reaction. This consideration is not important in the case of niobium or lightly alloyed niobium, as the initial and final gas pressures, hence initial and final surface solute concentrations, are quite close. In the case of a Nb-20 wt percent Zr alloy, however, the initial and final pressures are markedly different, so that the surface solute concentration can vary substantially during the experiment. This will lead to an artificially high apparent diffusivity for the Nb-20 wt percent Zr alloy, estimated to be of the order of a factor of two in the present study. It was felt that this inherent error was acceptable within the modest scope of the present effort. Also, the pressure decay method is especially well suited to the study of rapid absorption rates, such as those encountered in the present study, where the reaction was commonly 40 percent complete within 30 sec.

2.3 Desorption Studies at 900°C

After a given absorption study had been completed, the sample was quickly withdrawn from the reaction chamber and allowed to cool. During cooling more gas was absorbed; this was measured and "added" to the

sample's inventory for the desorption study. The sample was then dropped back into the furnace tube held at 900 ± 5 °C and a mercury diffusion pump was used to transfer the gas from the sample into a standard volume for measurement. Outgassing and gas collection began before the sample reached 900°C. The outgassing was generally continued until more than 99 percent of the gas inventoried in the sample was recovered.

2.4 Permeation Studies

The permeation sample consists of a metal thimble brazed to a molybdenum support tube. This assembly is placed in a quartz reaction tube and outgassed. A hydrogen, deuterium or tritium pressure is then imposed on one side of the thimble while the other side is maintained under high vacuum by a mercury diffusion pump exhausting to a standard volume. The rate of gas permeation through the thimble is determined by collecting and measuring the gas passing hrough the thimble in a calibrated volume over a definite time period.

At a constant temperature, the flux or permeation of gas per unit thimble area is related to the pressure by

$$\phi = - DS \frac{\sqrt{P_o} - \sqrt{P_i}}{\Delta x} \qquad (1)$$

where ϕ = flux, D = diffusivity, S = solubility, P_o = pressure on one side of the thimble, P_i = pressure of the other side of the thimble, and Δx = thimble thickness. The flux or permeability is therefore related to both solubility and diffusivity.

3. RESULTS

3.1 P-T-C Data

The concentration of hydrogen and deuterium in the experimental alloys in equilibrium with the final pressures of H_2 or D_2 at 900 ± 5 °C

is shown in Table 2. Note that concentrations are given in both weight units and in terms of atomic ratios.

As expected, solubilities of deuterium are slightly less than hydrogen on an atomic basis. The strong affinity of zirconium for hydrogen and deuterium relative to niobium is evident.

Equilibrium data was obtained on each of the three commercial alloys within the range 800 to 1000°C, 0.03 to 80 mm of Hg pressure (Torr) and about 1 to greater than 100 ppm by weight hydrogen. Figures 3, 4, and 5 are logarithmic plots of equilibrium pressure against composition for the commercial alloys at three test temperatures. Figure 3, the plot for niobium, shows the hydrogen solubility in weight units; the hydrogen and deuterium solubilities are also both shown as atomic ratios. The figure also shows the 800 and 900°C niobium-hydrogen data of Albrecht et al. and two sets of calculated P-C data (at 10 and 100 ppm) obtained from the semiempirical equation of Edwards and Veleckis:[6]

$$\ln p^{1/2} = 10.212 + 0.984 \ln\left(\frac{r}{0.89 - r}\right) + \frac{1}{T} \qquad (2)$$

$$(-4244.7 - 4000.4r + 8872.7r^2 - 19{,}338.0r^3 + 16{,}230.3\, r^4)$$

where r is the hydrogen to metal atomic ratio, p is the pressure of hydrogen gas in mm Hg, and T is the absolute temperature. The results obtained by means of this expression are in good agreement with the experimental data. A similar plot, shown in Figure 4, for hydrogen and deuterium solubility in a Nb-1Zr alloy presents data that can essentially be superimposed on Figure 3. At the temperatures and pressures considered in this study, the one percent addition of zirconium to niobium does not significantly affect the hydrogen (or deuterium) solubility. Figure 5 shows solubility data for vanadium. A comparison of the calculated solubility to experimental

Table 2

Pressure-Composition Equilibria at 900°C

For the Experimental Alloys

Alloy	P_{H_2}	P_{D_2}	Conc., ppm by Wt.	Atom Ratio H(D)/Nb
Nb	67.36		73	0.0068
		64.02	123	0.0057
		63.83	123	0.0057
Nb-10 Zr	5.58		54	0.0050
		5.55	102	0.0047
		5.56	100	0.0046
Nb-10 Zr - 0.1 Y	1.25		24	0.0022
		1.30	45	0.0021
		1.48	43	0.0020
Nb-20 Zr	2.15		111	0.0103
		2.28	200	0.0093

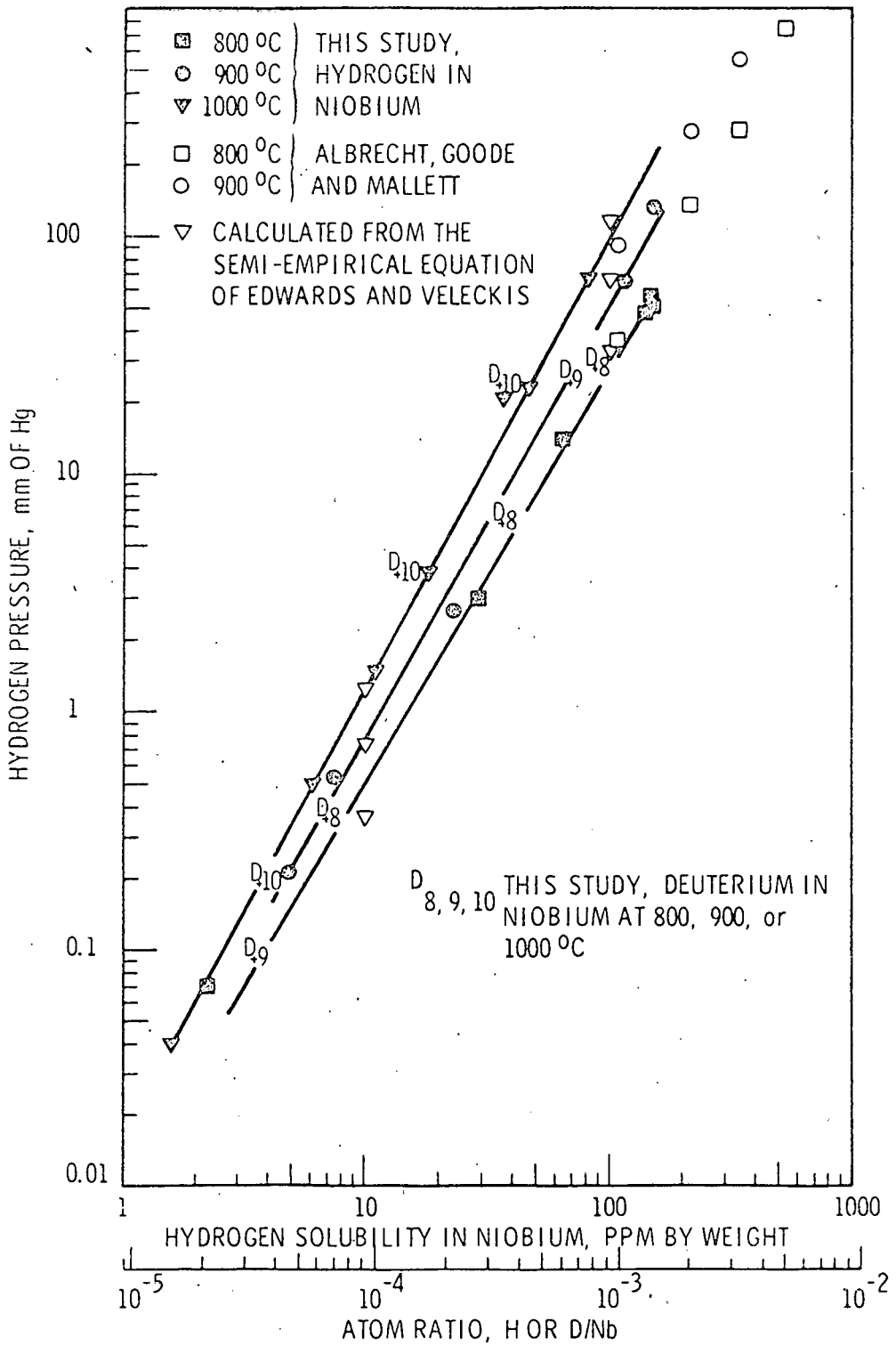


Figure 3

Solubility of Hydrogen and Deuterium in Niobium

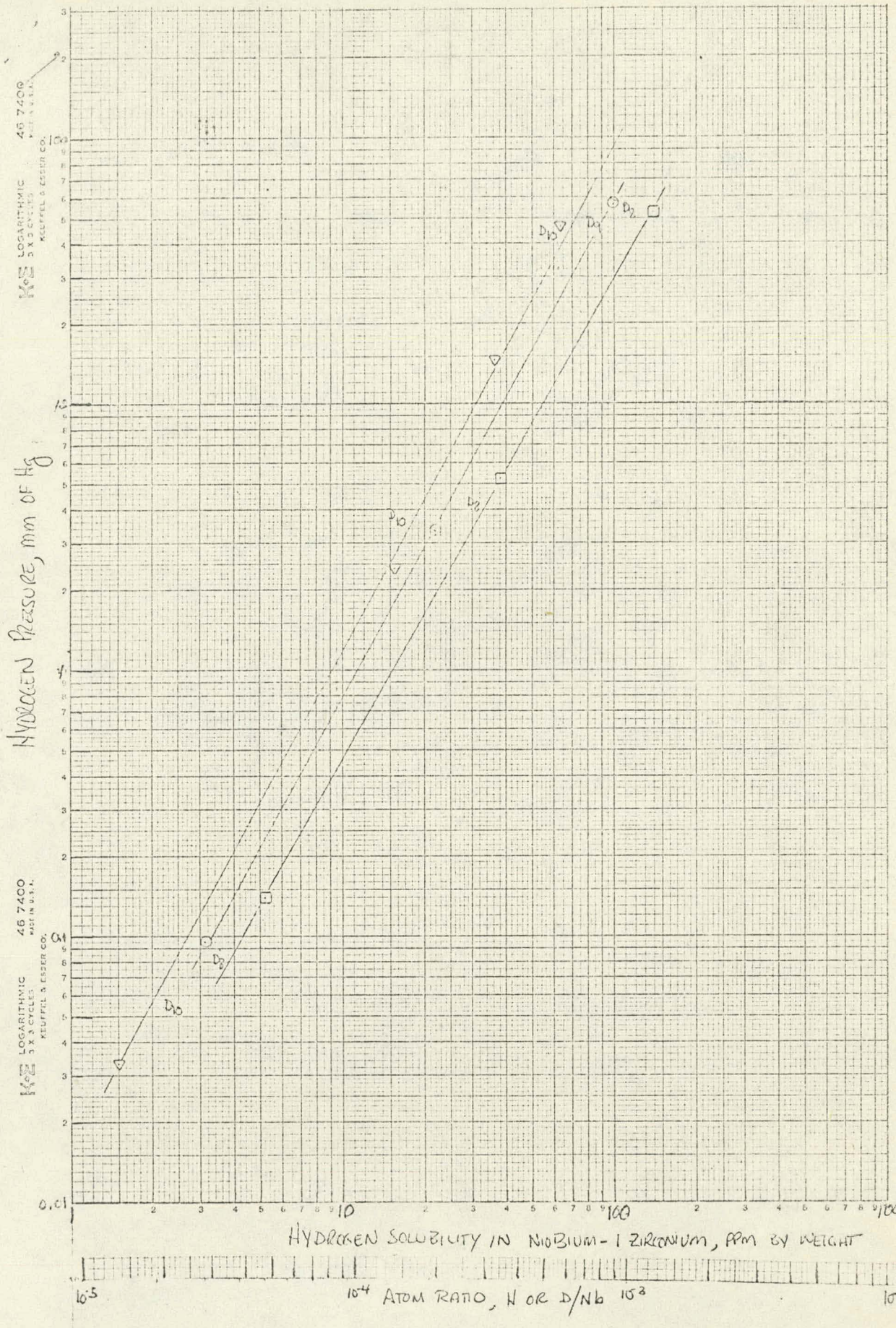


Figure 4
Solubility of Hydrogen and Deuterium in Niobium-1 Zirconium Alloy

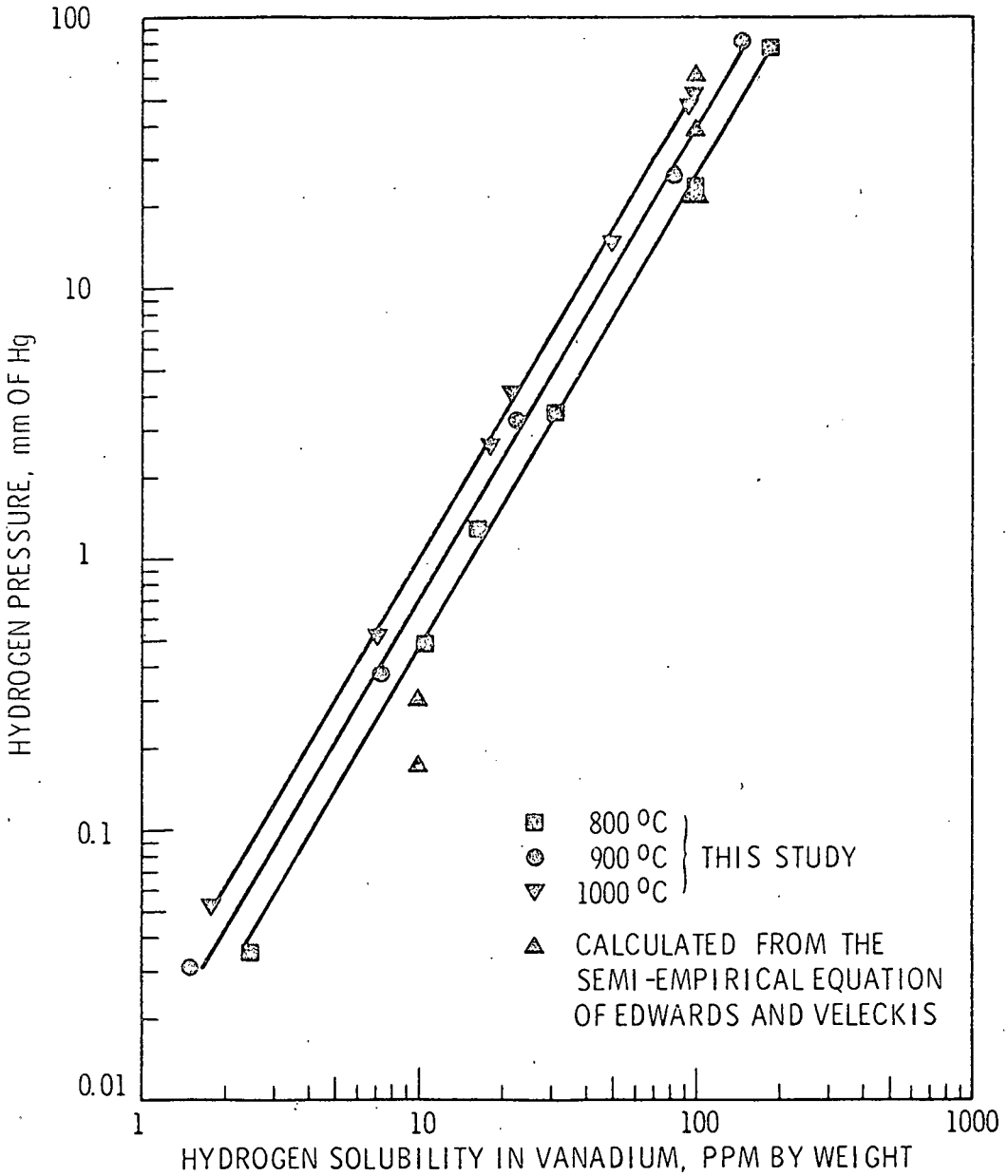


Figure 5

Solubility of Hydrogen in Vanadium

solubility is made using the equation suggested by Edwards and Keveckis for the vanadium-hydrogen system:

$$\ln p^{1/2} = 10.283 + 1.0598 \ln\left(\frac{r}{0.89 - r}\right) + \frac{1}{T}(-3489.2 - 3269.0r + 2563.0r^2 - 762.39r^3 + 4818.3r^4) \quad (3)$$

As can be seen in Figure 5, good agreement is evident at 100 ppm concentration; but at 10 ppm concentration the experimental data indicate lower solubility than predicted.

3.2 Absorption Kinetics at 900°C

The gas absorption kinetics are shown graphically in Figure 6. All absorption curves fit within the boundaries shown. Duplicate trials on a given specimen showed good reproducibility. The diffusivity values calculated for hydrogen fall within the boundaries $D = 1.6 \times 10^{-4}$ cm^2/sec and $D = 2.7 \times 10^{-4}$ cm^2/sec; the values for deuterium fall within the boundaries $D = 1.1 \times 10^{-4}$ cm^2/sec and $D = 2.6 \times 10^{-4}$ cm^2/sec. An extrapolation to 900°C of the data of Albrecht et al.[4] for hydrogen diffusion in niobium yields a value $D = 3.9 \times 10^{-4}$ cm^2/sec.

3.3 Desorption Kinetics at 900°C

Desorption kinetics as determined in the present study are not readily amenable to mathematical analysis, because the tests are non-isothermal and because the solute gradient in the sample is not well defined prior to gas extraction. However, inter-sample comparisons may be expected to yield data on the relative case of recovery of gas from the individual alloys. The boundaries shown in Figure 7 contained all of the data obtained for desorption of deuterium and hydrogen from all of the alloys. The curves were normalized such that t = 0 corresponds

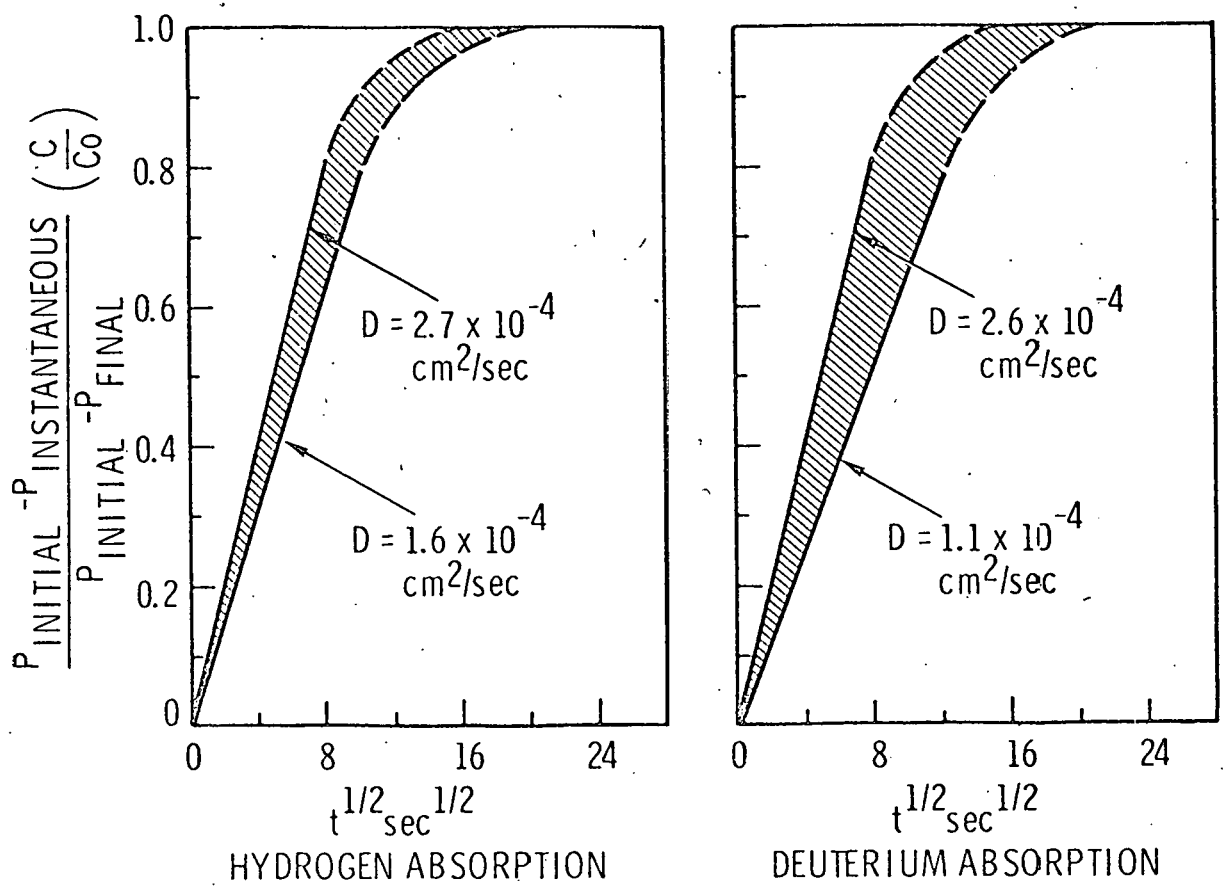


Figure 6

Absorption of Hydrogen and Deuterium by All Alloys at 900°C

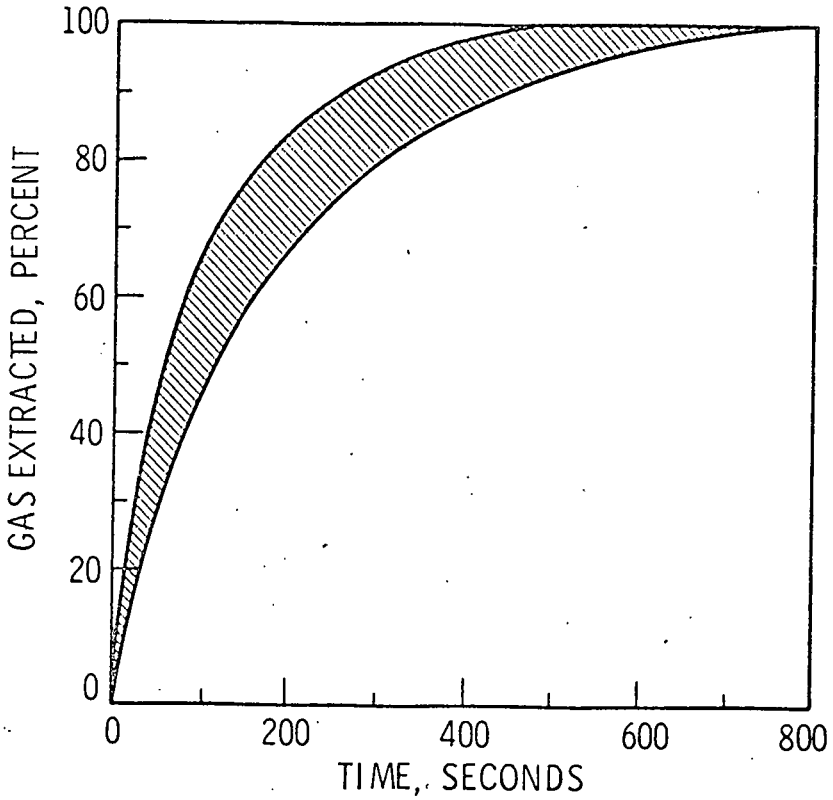


Figure 7

Hydrogen/Deuterium Outgassing Kinetics, All Alloys
Outgassing First Sensed at t = 0

with the first appearance of outgassing, which generally began within two minutes of the sample introduction into the furnace tube.

The data band of Figure 7 indicates that the outgassing kinetics of all systems studied follow the same general pattern, with no unusual gas retention exhibited by any given alloy.

4. CONCLUSIONS

On the basis of the absorption studies reported in the present work, we may conclude that no unusual high temperature absorption or desorption kinetics of hydrogen or deuterium by niobium alloys are caused by the presence of zirconium. It is felt that the experimental techniques employed in the present study based on absorption kinetics were not able to discriminate between individual alloys, or, for that matter, between hydrogen or deuterium, hence the exclusive use of data boundaries instead of data points. It is certain that differences in reaction kinetics will be caused by the presence of alloy elements such as zirconium and yttrium; however, it remains for a more detailed, extensive study to identify and quantify these differences.

Deuterium shows a lower solubility than hydrogen in the alloys studied under the same pressure-temperature conditions. The presence of 1 percent zirconium in niobium does not significantly alter the pure niobium P-T-C curves.

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