Depth-concentration profile of hydrogen in niobium

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Hydrogen concentration profiles near the surface of hydrogen-charged Nb samples have been measured by utilizing the $^{1}H(^{15}N, \alpha\gamma)^{12}C$ reaction. The Nb foils were charged under various ambient conditions to concentrations corresponding to the single-phase α' region in the phase diagram. Each sample exhibited a strong H surface peak followed by a sharp dip and a gradual increase in H concentration to a plateau. The rate at which the hydrogen concentration increases towards the bulk as well as the height of the plateau is related to the method of sample preparation, the higher the oxygen content, the lower the hydrogen concentration near the surface. These observations suggest that the H concentration near the surface of α'-Nb-55 at. % H is lower than that in the bulk because of the presence of oxides and dissolved oxygen. They also indicate that samples charged with hydrogen after heating to over $\sim 250\,^\circ$C in a pressure of $> 1 \times 10^{-6}$ Torr will develop an oxygen-enriched and hydrogen-depleted zone near the surface.

I. INTRODUCTION

Hydrogen in niobium has been studied for many years for reasons motivated both from a basic as well as an applied point of view. On the one hand it has generated interest within the theoretical physics community because it is a very close physical realization of the theoretical lattice-gas model. On the other hand, it is also studied as a model substance by those interested in the practical aspects of hydrogen storage and other applications of metal-hydrogen systems.

The numerous experimental and theoretical investigations of the Nb-H system have provided us with detailed information concerning many of the more important physical properties of the system, e.g., phase diagram, structures, diffusion coefficients, heat of solution, etc.[1] More recently work has been published dealing with the hydrogen absorption-desorption kinetics of this system and its related surface properties.[2,3] From this work it is apparent that the rate at which hydrogen can be inserted into and extracted from Nb, and also other metal-hydrogen systems more suitable for practical applications, is strongly influenced by the hydrogen concentration on and near the surface of the material.

Zabel *et al.*[4] have measured the hydrogen concentration near the surface of a Nb single crystal containing hydrogen at a concentration very close to the critical concentration of 31 at. %. They used Cu and Mo$K\alpha$ radiation to measure the lattice parameter at different depths within the crystal. The data indicated that there was a layer at the surface, approximately 1.0-μm thick, in which the hydrogen concentration was appreciably less than that further into the bulk of the crystal. Their interpretation is based on the analogy of the lattice gas/liquid with a two-phase mixture of fluids. Cahn has shown that in such a case one can expect "critical wetting" near the critical points.[5]

Another aspect of the problem can be considered using the following qualitative arguments. Nb is an exothermic occluder of hydrogen. The heat of solution of hydrogen in niobium, as well as any other metal, is governed by the balance of three large contributions to the energy:

(a) The dissociation energy of the hydrogen molecule; this is a constant and, of course, positive contribution.

(b) The "electronic bonding" energy of the interstitial hydrogen; this is a negative contribution.

(c) The energy for expansion of the interstitial hole, and the "compression" of the hydrogen atom, to fit that hole. This is a positive contribution.

The sum of these energies being positive or negative decides whether the solution of hydrogen in the material is endothermic or exothermic. It can be assumed that the energy it costs to expand the lattice is minimized at or near the surface of the metal. This would result in the "effective" heat of solution being more negative at the surface and thus leading to a higher hydrogen concentration at the surface,[6] contrary to the findings of Zabel

et al. It is therefore important, from both a basic and an applied point of view, to measure the depth-concentration profile of hydrogen in niobium by an independent technique. This can be conveniently accomplished by the use of nuclear reaction analysis using the $^1H(^{15}N,\alpha\gamma)^{12}C$ reaction.

II. EXPERIMENTAL

A. Sample preparation

Samples charged with hydrogen using two different methods were investigated. The materials used were thin foils (50 μm, MARZ grade) of niobium, 10×25 mm^2 in size. The two methods produced different surface conditions which were the subject of the present investigation. One method consisted of the following procedures. The samples were outgassed and cleaned by heating them resistively to about 1300 K in 1×10^{-6} Torr oxygen followed by a heat treatment at about 2300 K in a vacuum of approximately 1×10^{-10} Torr. This treatment has been shown to remove virtually all the interstitial impurities from the bulk and surface of the niobium.[7] A thin layer of Pd was then deposited onto the clean surface of the niobium *in situ* in the ultrahigh vacuum (UHV) system by evaporation from a hot Pd filament. Such a layer increases the probability that a hydrogen molecule impinging on the surface will dissociate and enter the bulk of the material.[2,8] Because the Pd does not form a stable oxide, this layer leaves the surface clean and free of an oxide which would otherwise form on the niobium surface as soon as it is removed from the UHV system. Such an oxide is an effective barrier to hydrogen transfer both into and out of niobium.

After Pd-plating, the sample is removed from the UHV system and inserted into a hydriding unit. The base pressure in the diffusion-pumped and cold-trapped hydriding unit was typically in the high 10^{-7}-Torr range. The sample is heated in this system to 100−250°C to remove adsorbed water vapor. The sample can then readily absorb a premeasured amount of hydrogen to the desired concentration. Finally, the sample is removed from the hydriding unit and immersed in mercury to remove the Pd coating and restore the impermeable oxide barrier.[9]

The second method of hydrogen-charging used is similar to that employed by most investigators of metal-hydrogen systems. A bare sample, either as provided or precleaned in UHV as described above,

is placed in the hydriding unit. The oxide layer on the surface, which inhibits the hydrogen uptake, is dissolved into the bulk of the material by heating it to approximately 800°C. At this point the premeasured volume of hydrogen is admitted and the sample absorbs the gas as the system cools to room temperature. In order to study the effect of a poor vacuum in the hydriding unit, samples were heated to 800°C in different base pressures prior to the admission of hydrogen. One sample was heated in a vacuum of 1×10^{-6} Torr, one in 6×10^{-6} Torr, and one sample was heated in 1×10^{-5} Torr oxygen.

B. Determination of hydrogen depth profiles with the $^1H(^{15}N,\alpha\gamma)^{12}C$ reaction

The hydrogen concentration depth profiles were measured utilizing the 6.385-MeV (lab) resonance of the $^1H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction ($Q = 4.966$ MeV). The hydrogen-containing target is bombarded with a ^{15}N beam, and the number of 4.43-MeV γ rays from the deexcitation of the residual ^{12}C nuclei is counted.[10] As an ion beam passes through a target, it loses energy continuously within the target. When the target is thick enough, the beam loses all of its energy and becomes implanted in the target. Therefore, when the incident-beam energy, E_B, is greater than the resonance energy, E_R, the beam slows through the resonance at a depth D_x from the surface where

$$D_x \approx \frac{(E_B - E_R)}{dE/dx} \ .$$

This expression is valid when the stopping power, dE/dx, does not change appreciably over the energies of interest. In our case the stopping power (calculated for NbH$_{0.55}$ from the Northcliffe and Schilling tables[11]) can indeed be assumed to be constant, 2.9 keV/nm, between the beam energies 6.385 and 10.0 MeV. The stopping-power values from the Northcliffe and Schilling tables[11] were within 10% of the values given by Ziegler,[12] both of which were based on indirect experimental data.

The 6.385-MeV resonance is the lowest-energy resonance. The cross section at energies below this resonance is 3−4 orders of magnitude lower than the peak value and then falls off rapidly to zero. This is an important feature since all these samples have hydrogen in the bulk, and lower energy excitations would produce γ rays from the bulk of the sample. On the high-energy side of the resonance

the excitation function is 3 orders of magnitude lower than the peak value. Therefore, all of the γ rays can be assumed to be from the single resonance, and measuring the γ-ray production as a function of ^{15}N-beam energy gives a direct measurement of the hydrogen concentration as a function of depth in the target.

The depth resolution δ_x is given by

$$\delta_x \approx \frac{\Gamma_T}{dE/dx},$$

where

$$\Gamma_T = [\Gamma^2 + W^2 + (2.36\alpha)^2]^{1/2}$$

and $\Gamma = 6$ keV, the resonance width of the nuclear reaction, W is the spread in the incident-beam energy, and α is the straggling due to the energy loss of the beam in the sample. The spread in the incident-beam energy W is due to the acceleration process and was approximately 2 keV for this experiment. Since the energy loss of the beam is due to multiple scatterings where the ions lose small fractions of their total energy, a spread about the mean energy of the beam will develop as the beam slows within the sample. Figure 1 shows a plot of Γ_T and δ_x as a function of depth for a ^{15}N beam incident on NbH$_{0.55}$ assuming $\Gamma = 6$ keV and $W = 2$ keV. The straggling parameter α was calculated using the Lindhard and Scharff formulation,[13]

$$\alpha^2 = \begin{cases} \alpha_B^2 L(X)/2, & X \leq 3 \\ \alpha_B^2, & X \geq 3 \end{cases}$$

where $\alpha_B^2 = 4\pi Z_1^2 Z_2 e^4 N D_x$,

$$L(X) = \frac{dE}{dx}\left[\frac{m_e}{4Z_1^2 \hbar^2 N}\right]X,$$

$$X = \frac{v^2}{(e^2/\hbar)^2 Z_2},$$

where N = atomic density, and $dE/dx = 2.9$ keV/nm for this experiment.

The 6.385-MeV resonance is narrow, on the order of 6 keV and has a peak cross section of 450 mb.[10] As discussed by Lanford,[10] there exists considerable confusion as to the parameters of this resonance. Using the surface contamination as the target, he measured the resonance width to be 6 keV, a factor of 2 narrower than the 1977 Ajzenberg-Selove[14] compilation. Uncertainties in dE/dx and Γ_T will yield uncertainties in the depth
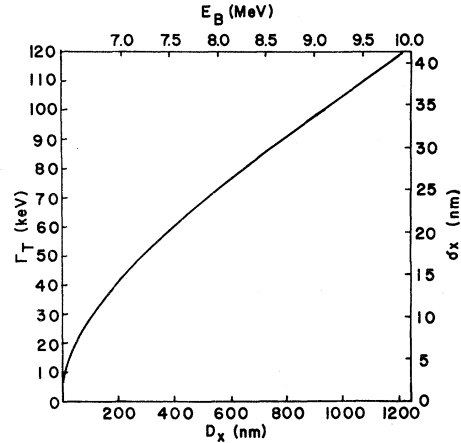

FIG. 1. Total reaction width Γ_T and depth resolution δ_x as a function of the ^{15}N-beam energy and the depth.

resolution δ_x. The major contribution to the uncertainties in Γ_T, arises from Γ and W near the surface and then switches to uncertainties in α as the energy is increased. It is therefore very important to obtain improved values for the resonance width and the cross section of this nuclear reaction as well as the stopping power and straggling.

C. Experimental apparatus

The ^{15}N beams were obtained from one of the Brookhaven National Laboratory MP Tandem van de Graaff accelerators. After momentum analysis the beam was focused with a magnetic quadrupole and then collimated with three 5-mm apertures. The first collimator was placed 1 m from the target to reduce the possibility of background production. It was possible to send the beam through the sample chamber to a dump 2.5 m away. With this configuration the background could be quickly and conveniently assessed. The chamber pressure was usually around 1×10^{-6} Torr when pumped with a cryopump or liquid-nitrogen—trapped turbo pump. At all times during the experiment the background from extraneous hydrogen was negligible and no corrections to the data were necessary.

The target holder was insulated and heated so that the beam current on the samples could be monitored while they were heated to approximately 200 °C. The temperature was monitored with a thermocouple and the uncertainty in the temperature values is ± 5 °C.

The 4.43-MeV ^{12}C γ rays of interest were detected with a 10-cm $\times$ 12.5-cm NaI(Tl) γ-ray detector. The pulses from the detector were sorted in an on-

line computer data-acquisition system. Summed events in the region which included the full-energy and 1-escape peaks were taken as representing the hydrogen concentration. Beam currents around 50 nA of $^{15}N^{2+}$ (1.5×10^{11} particles/s) were high enough to give reasonable rates, but low enough to preclude significant radiation damage. The run time for a single data point was generally around 5−20 min.

For the purposes of the present experiment relative values of the hydrogen content sufficed. Using literature values for the reaction cross section and detector efficiency, it was possible to estimate the absolute concentration of hydrogen. The results were in reasonable agreement with the known concentrations in the bulk.

III. RESULTS

Typical results of measurements made simultaneously on several samples prepared by the two methods described above are shown in Fig. 2. The spectra were all taken at a temperature of 120 °C. Plotted on the ordinate is the number of 4.43-MeV photons detected as a function of the incident energy of the ^{15}N ions. The incident-energy scale is indicated on the top abscissa of the graph for curve A. Curves B, C, and D are each shifted in energy by 0.2 MeV so as to facilitate comparisons. The γ-count scale remains the same for all curves. The lower abscissa shows depth scales for each of the
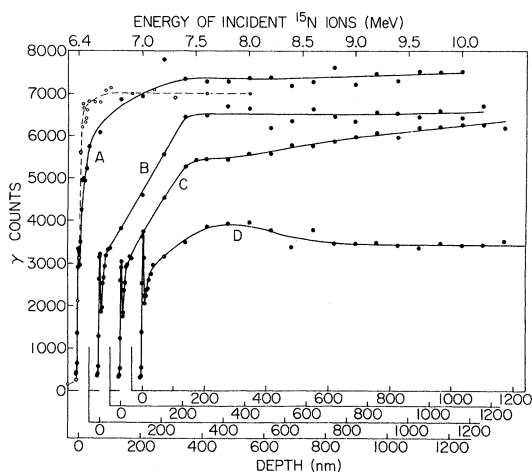

FIG. 2. γ-ray yields as a function of the ^{15}N-beam energy and the depth for five different samples. Samples A, B, and C, as well as the one shown as a dashed line, contained 55 at. % H, sample D contained 50 at. % H. Differences in sample preparation are explained in the text.

curves. The γ count can be taken to be proportional to the local hydrogen concentration.

Samples A, B, and C each contained 55 at. % H ([H]/[Nb] = 0.55). We chose this concentration for most of the samples because at this value the NbH phase diagram indicates that the samples will be in the α' single-phase region at temperatures above ~90 °C.[15] Several samples with a concentration of 33 at.% H, the critical concentration, were also investigated. Sample A was cleaned in UHV, Pd-plated in situ, and hydrided at approximately 230 °C. Samples B and C were cleaned in UHV and then charged in the diffusion-pumped hydriding unit after heating to 800 °C. The only difference between B and C was the pressure in the vacuum system at 800 °C, namely 1×10^{-6} and 6×10^{-6} Torr, respectively. Sample D was treated in the same way as samples B and C but differed in that pure oxygen was admitted into the hydriding unit while the sample was at 800 °C. The oxygen pressure was allowed to reach 1×10^{-5} Torr for 1 min and then pumped out. Hydrogen was then admitted into the system to hydride the sample to 55 at.% H. However, due to the oxidizing procedure, the sample only absorbed to a concentration of 50 at.% H. The results shown as open circles and a dashed line are for a sample prepared in a way almost identical to that of sample A. The only difference was that the hydriding took place at a slightly lower temperature, namely at 160 °C. This sample is shown as a dashed line because it was measured during a different run at the Tandem van de Graaff, and the absolute γ intensities might, therefore, differ slightly. This sample also contained 55 at.% H.

IV. DISCUSSION

The experimental curves show several distinguishable features. They are discussed in the following in the context of Fig. 3 which shows the results of curve B from Fig. 2. The first feature to appear (A) as a function of energy is the sharp surface peak at the resonance energy (6.385 MeV). This peak appears in all samples with roughly the same intensity. It is due to hydrogen-containing gases (water, hydrocarbons) adsorbed to the surface of the samples. This layer cannot be eliminated with the present experimental setup. Under the vacuum condition in the sample chamber of the van de Graaff accelerator, a contamination layer from the residual gas will develop in seconds.
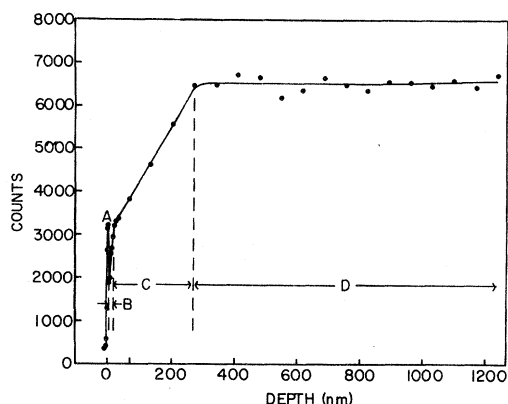
Below the surface peak the samples generally

FIG. 3. Representative hydrogen depth profile showing main characteristics; A: adsorbed hydrogen-containing layer, B: Nb_2O_5 oxide layer, C: layer containing dispersed oxide (Nb_2O_5) particles decreasing first in size and then in number as a function of depth, D: bulk region containing dissolved oxygen.

show an intensity minimum (B). This minimum is more pronounced in those samples heated to 800 °C prior to hydriding, and is associated with an oxide layer at the surface. A study of the low-temperature oxidation of niobium by Halbritter[16] has shown that the oxidation in this temperature range consists mainly in the growth of a 4- to 10-nm-thick layer of compact and amorphous Nb_2O_5. The Nb_2O_5 was found to be an insulator with a high dielectric constant. The presence of oxygen

vacancies in Nb_2O_5 creates interface states which cause a gradual transition from the insulating to the metallic state. Beneath the Nb_2O_5 is a thin ($\sim$0.4-nm) layer of NbO_x ($x \leq 1$). This layer was shown to be metallic. Further into the material, beneath the interface oxide NbO_x, a region with substantial oxygen enrichment was found. The minimum in the hydrogen concentration, caused by the oxide layer, is followed by an increase in hydrogen concentration (C), which is more or less rapid and depends on the sample, to a value which reflects the bulk concentration, region D.

The results shown as curve A and those shown as a dashed line in Fig. 2, which are qualitatively somewhat different than the rest of the curves, are conveniently discussed together. Both of these samples represent material which was outgassed in UHV and then Pd-plated, therefore containing virtually no interstitial impurities such as oxygen, carbon, or nitrogen. The only difference between the two samples is the temperature to which they were heated prior to hydriding. Sample A was heated to 230 °C for 1 h, while the other sample was heated to only 160 °C for 1 h. We can explain the different results obtained for these two samples by the fact that oxygen, carbon, and maybe nitrogen, which are invariably present on the surface of the sample and in the residual gas of the hydriding unit, will diffuse into the sample at elevated temperatures. The diffusion coefficients for the interstitials in Nb are[17]:

$$D = \begin{cases} 1.5 \times 10^{-2} \exp(-27.6/RT) \text{ cm}^2/\text{s for oxygen} \\ 1.0 \times 10^{-2} \exp(-33.92/RT) \text{ cm}^2/\text{s for carbon} \\ 9.8 \times 10^{-2} \exp(-38.6/RT) \text{ cm}^2/\text{s for nitrogen} . \end{cases}$$

The activation energy is in units of kcal/mole.

The resulting diffusion lengths, $l = \sqrt{2Dt}$, for $t = 1$ h, are $l = 96.4$, 3.26, and 3.10 nm at 230 °C and 11.2, 0.2, and 0.05 nm at 160 °C for oxygen, carbon, and nitrogen, respectively. By comparing the shape of the experimental curves for both temperatures and taking into account the above diffusion lengths, we conclude that a penetration of the Nb surface by an appreciable amount of oxygen (from the oxide surface and from water vapor in the vacuum system) is consistent with the experiment findings. The penetration depth of both carbon and nitrogen is insufficient to explain the hydrogen concentration gradient near the surface. This is in agreement with the study of Halbritter

mentioned above.[16] It remains, however, to be shown that high concentrations of oxygen in niobium tend to displace hydrogen. It is known that very low concentrations (< 1 at. %) of oxygen and nitrogen in niobium can act as hydrogen traps.[18,19]

Samples B and C as well as D were heated to approximately 800 °C for 1 h prior to charging. The diffusion length for all three interstitials is so great at this temperature that the concentration of dissolved gases should be virtually uniform throughout the sample. The fact that the hydrogen concentration is not constant throughout the sample indicates that in these samples a different effect must predominate, namely the precipitation of oxides in the near-surface region. Electron-

microscopic investigations by Hurlen[20] have shown that there is a nucleation-type oxide-formation stage with the formation of dispersed oxide particles under conditions similar to those occurring in our experiments. In this stage the oxide particles increase first in number and later in size. The oxide being formed in this stage is also the pentoxide, Nb_2O_5. Hydrogen is almost certainly insoluble in this Nb oxide because it is a very thin layer of this oxide on the surface which inhibits the desorption of hydrogen from NbH_x samples. The hydrogen concentration in samples B and C increases therefore as the volume fraction of the Nb oxides decreases. This region is then followed by a region from 200 to well over 1200 nm in which the hydrogen concentration is depressed below the bulk value due to the solution of oxygen and the presence of suboxides in the Nb.[21] In the case where oxygen was deliberately added to the residual gas in the vacuum system at 800 °C (sample D), the hydrogen concentration in the region investigated is depressed far below the bulk value. In this case then, due to the availability of sufficient oxygen, it appears that the oxides have grown well into the material. The slight increase in concentration in sample D in the depth range 200−400 nm could be an experimental artifact since similar samples measured during other runs showed no such effect.

V. CONCLUSIONS

The experimental results show that the interpretation of experiments on samples of niobium-hydrogen, or similar materials such as tantalum-, vanadium-, titanium-, zirconium-hydrogen, etc., hydrided in the manner described must take into account the possible existence of an appreciable hydrogen concentration gradient towards the surface. Experiments which are especially affected by this result are x-ray diffraction experiments and other techniques which probe the near-surface regions of a sample. In x-ray measurements the sampling depth is in the range of the hydrogen-depleted, oxygen-enriched zone; this may very well lead to misleading results. For example, this may be the reason for the finding of Zabel, Schöfeld, and Moss[4] that there was a ~1-μm-thick α-phase layer

on the surface of a crystal which was essentially in the α' phase. The α phase has a lower hydrogen concentration than the α' phase. In their description of the experiment they stated that their crystal had been repeatedly cycled in air to ~200 °C and had also been cycled numerous times in previous experiments. Moreover, in their original hydrogen charging of the sample they did not use the technique with the Pd layer. We therefore suggest that a possible alternative explanation of their findings is that they have observed the near-surface hydrogen-depleted layer induced by the presence of oxygen or oxides in the Nb, rather than the existence of a thin α-phase layer near the surface. A test of this hypothesis would be to repeat their experiment and see whether similar effects occur in samples which have been hydrided using the Pd-layer technique. Another test would be to use their hydriding technique but at a hydrogen concentration far from the critical point, e.g., 55 at. % H, where critical wetting should not occur. Also, the results of our depth-profiling measurements on samples with 33 at.% H showed qualitatively identical results to those containing 55 at.% H.

In our experiments on the samples charged at low temperatures, and therefore containing only small amounts of dissolved gases near the surface, we did not observe an increase in the hydrogen concentration towards the surface as predicted on the basis of elasticity considerations. This may be due to one or both of two reasons: (a) The thin but nevertheless still existing oxide- and oxygen-containing layer at and near the surface of these samples may distort and strain the surface sufficiently to eliminate the effect; (b) the depth of the region of enhanced concentration is less than the resolution of our ^{15}N profiling method (~30 nm at the surface). Crude calculations indicate that the latter could very well be the case.

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