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THE CONCENTRATION PROFILE OF HYDROGEN NEAR THE SURFACE OF NIOBIUM

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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 used different x-ray wavelengths to measure the lattice parameters near the surface of a Nb-single crystal containing hydrogen at the critical concentration, 31 at.%. They found that a layer approximately 1 μm thick at the surface contained appreciably less hydrogen than the bulk. They interpreted their findings as evidence for critical wetting. On

the other hand, it can be assumed that the energy it costs to expand the metal lattice by the insertion of a hydrogen interstitial is minimized at or near the surface. 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,⁵ 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 $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ reaction.

EXPERIMENTAL

Samples hydrided in two different ways were investigated. The materials used were thin foils (50 μm , MARZ grade) of niobium, 10 x 25 mm in size. The two methods of hydriding 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 in UHV to remove virtually all the interstitial impurities from the bulk and surface.⁶ A small spot of Pd was then deposited onto the clean surface of the niobium in situ in the UHV-system by evaporation from a hot Pd filament. Such a layer allows hydrogen to subsequently be absorbed at low temperatures, 100-250 C, in a diffusion-pumped and cold-trapped hydriding unit.^{2,7} Finally, the palladium is removed by immersion in mercury.

The second method of hydriding was similar to that used by most investigators of metal-hydrogen systems. A sample is placed in the hydriding unit and allowed to absorb a premeasured amount of hydrogen while cooling from ~ 800 C where the surface oxide is dissolved into the bulk. 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 1×10^{-5} Torr oxygen.

The hydrogen concentration depth profiles were measured utilizing the 6.385-MeV (lab) resonance of the $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ nuclear reaction ($Q = 4.966$ MeV). The hydrogen-containing target is bombarded with a ^{15}N beam, and the number of 4.43-MeV gamma rays from the deexcitation of the residual carbon-12 nuclei is counted.⁸ As an ion beam passes through a target, it loses energy continuously within 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:

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

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 tables⁹) can indeed be assumed to be constant, 2.9 keV/rm, between the beam energies 6.385 and 10.0 MeV. The depth resolution varies from approximately 3 rm at the resonance energy to 40 rm at 10 MeV.

RESULTS

Two typical results of measurements made simultaneously on several samples prepared by the two methods described above are shown in Fig. 1. The spectra were 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. Curve B is shifted in energy by 0.2 MeV so as to facilitate comparisons. The lower abscissa shows depth scales for both curves. The gamma count can be taken to be proportional to the local hydrogen concentration.

Both samples 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. Sample A was cleaned in UHV, Pd-plated in situ, and hydrided at approximately 230 C. Sample B was cleaned in UHV and then charged in the diffusion-pumped hydriding unit after heating to 800 C in 1×10^{-6} Torr.

DISCUSSION

The experimental curves show several distinguishable features. The first feature to appear 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 set-up. Under the vacuum condition in the sample chamber of the Van de Graaff accelerator, an overlayer of the residual gas will develop in seconds.

Below the surface peak the samples generally show an intensity minimum. 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 Halbritter¹⁰ 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 minimum in the hydrogen concentration, caused by the oxide layer, is followed by an increase in hydrogen concentration, which is more or less rapid and depends on the sample, to a value which reflects the bulk concentration.

The results shown as curve A represent material which was outgassed in UHV and then Pd-plated, therefore containing virtually no interstitial impurities such as oxygen, carbon or nitrogen. It was heated to 230 C for one hour prior to hydriding. We can explain the hydrogen profile 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, can diffuse into the sample at this temperature. Taking into account the diffusion lengths, $l = \sqrt{2Dt}$ using literature values for the diffusion coefficients,¹¹ we conclude that a penetration of the Nb surface by an appreciable amount of oxygen is consistent with the experimental 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 by Halbritter mentioned above.¹⁰ 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.^{12,13}

Sample B was heated to approximately 800 C for one hour prior to hydriding. The diffusion length l 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 a different effect must predominate, namely the precipitation of oxides in the near-surface region. Electron microscopic investigations by Hurlen¹⁴ 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 increases therefore as the volume fraction of the Nb oxides decreases. This region is then followed by a region from 400 to well over 1200 nm in which the hydrogen concentration is depressed below the bulk value due to the presence of oxygen in the Nb. The effect was more pronounced in the case where oxygen was deliberately added to the residual gas in the vacuum system at 800 C. In this case, due to the availability of sufficient oxygen, the oxides grew much further into the material.

CONCLUSIONS

The results show that experiments on samples of niobium-hydrogen, or similar materials 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 and oxygen-enriched zone, and this may very well lead to misleading results. For example, this may be the reason for the finding of Zabel, Schönfeld, and Moss⁴ that there was a $\sim 1 \mu\text{m}$ thick hydrogen-depleted layer on the surface of a crystal which was essentially in the α' -phase.

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REFERENCES

1. For a recent review see: Hydrogen in Metals, Vols. I and II, ed. G. Alefeld and J. Völkl (Springer Verlag, Berlin, 1978).
2. M. A. Pick, F. W. Davenport, Myron Strongin, and G. J. Dienes, Phys. Rev. Lett. **43**, 286 (1979).
3. M. A. Pick, Phys. Rev. B **24**, 4287 (1981).
4. H. Zabel, B. Schönfeld, and S. C. Moss, J. Phys. Chem. Solids **42**, 897 (1981).
5. D. O. Welch and M. A. Pick, to be published.
6. H. Wenzl and J.-M. Welter in: Current Topics in Material Science, Vol. 1, Ed. E. Kaldis (North-Holland, Amsterdam, 1978).
7. M. A. Pick, M. G. Grzeme, and Myron Strongin, J. of the Less-Common Met. **73**, 89 (1980).
8. W. A. Lanford, Nucl. Instrum. Methods **149**, 1 (1978).
9. L. C. Northcliffe and R. F. Schilling, Nucl. Data Tables **7**, 233 (1970).
10. J. Halbritter, to be published in Surf. Sci.
11. E. Fromm and G. Gebhardt, Gase und Kohlenstoff in Metallen, (Springer Verlag, Berlin, 1976).
12. G. Pfeiffer and H. Wipf, J. Phys. F: Metal Phys. **6**, 167 (1976).
13. P. E. Zapp and H. K. Birnbaum, Acta Met. **28**, 1523 (1980).
14. T. Hurlen, J. Inst. of Met. **89**, 273 (1960-61).

Fig. 1. Depth concentration profile of hydrogen in two representative samples of niobium containing 55 at.% (H/M). See text for the differences in sample preparation.