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ON THE TECHNIQUES FOR PREPARING REFRACTORY METAL HYDROGEN ALLOY--ETC(U)
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ON THE TECHNIQUES FOR PREPARING REFRACTORY METAL -

HYDROGEN ALLOYS FOR T.E.M. STUDIES

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The preparation of refractory metal - hydrogen alloys for T.E.M. studies has presented many experimental difficulties. It is the purpose of this note to report some of the problems encountered and to describe a successful procedure for specimen preparation.

As discussed by Westlake (1) attempts to thin specimens after they have been charged with hydrogen, generally results in either increases or decreases in the hydrogen concentrations depending on the procedures used. Electrolytic thinning of the metals themselves often results in the introduction of significant quantities of hydrogen. Since the surface oxides which form provide excellent permeation barriers, removal of this hydrogen requires heating to above about 300°C with the concomitant introduction of oxygen in the thinned specimen even if the procedure is carried out under UHV conditions. Attempts to thermally charge specimens using hydrogen gas which was purified by diffusion through a Pd membrane in a UHV system, were also unsuccessful (2). Oxygen solutes were introduced due to the dissolving of the surface oxide into the metal as well as to an apparent transport of oxygen from the stainless steel vacuum chamber walls to the specimen via a reaction involving dissociated H_2 . Specimens charged in this way generally contained precipitated sub-oxides (2) (as shown in Fig. 1 for Nb). Electrolytic charging of thinned specimens using 85% H_3PO_4 at room temperature and at temperatures up to about 110°C was partially successful but the reproducibility of the hydrogen concentration obtained was very poor.

A very successful procedure was developed using a Pd surface layer on the refractory metal (3) as a means of overcoming the oxide permeation barrier. Relatively thick sheets of the metal are given a high temperature (2100°C) anneal in UHV ($p < 4 \times 10^{-8}$ Pa) to purify them by outgassing. On cooling the specimens below 800°C (on this anneal or after a subsequent heating to 800°C) a thin layer of Pd is evaporated on to the surface. Standard 3 mm discs are then cut or punched out of the sheet and these are thinned by jet and electropolishing using standard solutions. During these last steps a rim of the Pd coated specimen is masked off.

Any hydrogen picked up from the polishing can be removed at room temperature by placing the specimen in a low vacuum as the Pd coated surface provides a high permeability path. Furthermore, the thinned specimens can be charged to known concentrations of hydrogen at room temperature by placing them in a hydrogen atmosphere and controlling the pressure and/or the time of exposure. Typical calibration curves are shown in Figs. 2 and 3.

An alternative charging method is electrolytic charging at low currents. At the Pd cathodic surface all of the hydrogen ions which are reduced enter the metal and no gas bubbles are produced at concentrations less than about $NbH_{0.6}$. The hydrogen concentration can therefore be controlled by the total charge transferred as shown in Fig. 4. At higher concentrations some loss of hydrogen by bubbling is noted.

In both charging methods hydrogen loss occurs on removal of the specimen from the high hydrogen fugacity environment. To prevent this from occurring, the specimens are briefly immersed in mercury after charging, thus removing the Pd film and restoring the oxide permeation barrier. No further hydrogen loss has been noted even in vacuum environments.

The above techniques have been developed primarily for the Nb-H system but they have been shown to work for the Ta-H system. It is expected that they would have applicability for other systems as well.

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Acknowledgements

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References

1. P. G. Westlake and W. R. Gray, Appl. Phys. Let. 9, 3 (1966).
2. B. Makenas, to be published.
3. N. Boes and H. Züchner, Z. Naturforsch. 31a, 754 (1976).

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FIG. 1

Suboxides formed in high purity niobium sheet which was annealed in a U.H.V. system at 250 C in an atmosphere of purified H_2 at 2100 Pa. (See Ref. 2).

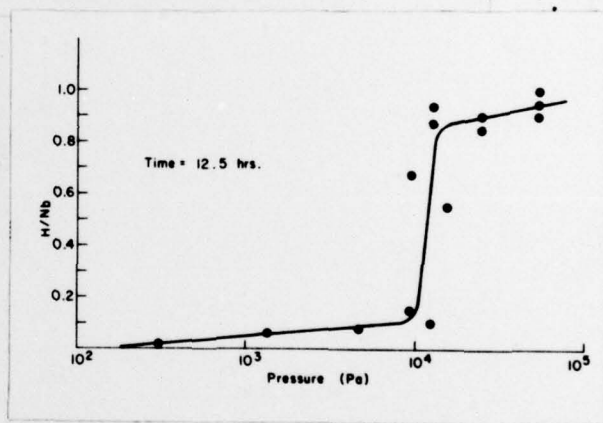


FIG. 2

Hydrogen concentration vs. pressure of H_2 gas for a constant charging time of 12.5 Hrs. Niobium sheet thickness is 0.01 cm.

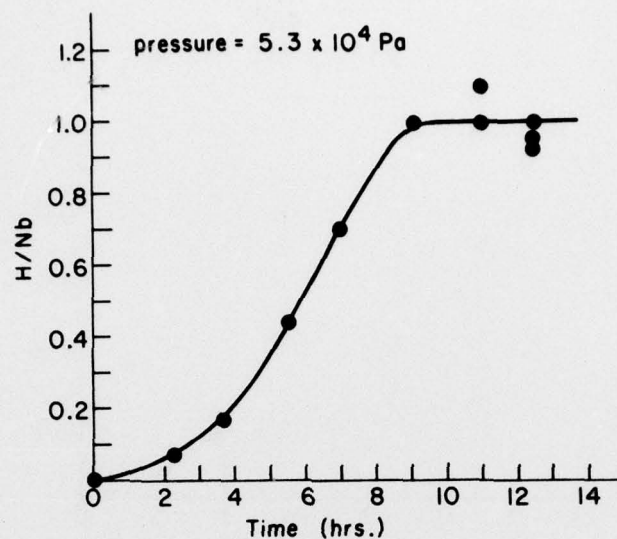


FIG. 3

Hydrogen concentration vs. charging time at a constant H_2 pressure of 5.3×10^4 Pa. Niobium sheet thickness is 0.01 cm.

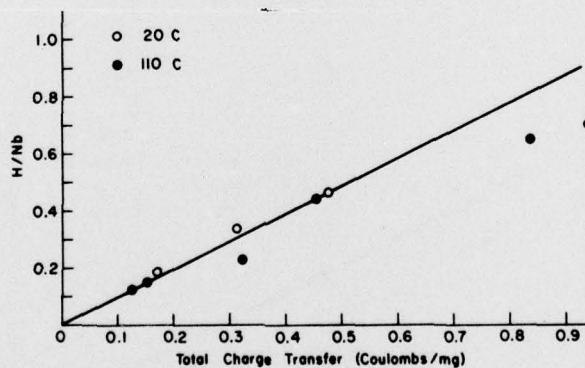


FIG. 4

Hydrogen concentration vs. electric charge transfer across the specimen interface for charging in H_3PO_4 at 20 C and at 110 C. Average charging current density was about 150 ma/cm^2 . Niobium sheet thickness was 0.01 cm. thick. The solid line is the predicted concentration if all of the hydrogen ions reduced entered the specimen.