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To cite this version:

HAL Id: jpa-00225405
https://hal.archives-ouvertes.fr/jpa-00225405
Submitted on 1 Jan 1985
THE EFFECT OF STATIC TENSILE BIAS STRESS UPON THE SOLUBILITY LIMIT
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O. FLORENCIO*, D.G. PINATTI** AND J.M. ROBERTS***

Departamento de Engenharia de Materiais, Universidade Federal
de Sao Carlos, 13560 Sao Carlos, S.P. Brasil

Abstract - Precision ultrasonic attenuation and velocity measurements have
been conducted on high purity Nb crystals containing 0, 200, and 300 ppm by
weight H. Variables in this study have been the number of thermal cycles
in the temperature range 77 to 340°K and various homogeneous tensile bias
stress values up to = 21 MPa. The hydrogen solvus temperature observed
upon the first thermal cycle is lower than that observed upon subsequent
thermal cycles. No measurable effect of bias stress upon the saturated
solvus temperature after several thermal cycles has been noted. All
results seem to be explainable from elementary thermodynamic and
dislocation principles.

I - INTRODUCTION

Precision ultrasonic velocity change measurements versus temperature in the Nb-H
system with and without static bias stress might clarify the effect of a
homogeneous tensile bias stress upon the solubility limit of H in Nb under
conditions of a closed system /1-5/. From the detailed discussion of the effect
of bias stress on hydride precipitation by Flanagan, Mason and Birnbaum /5/ with
respect to the Nb-H system, if the partial molar volume of hydrogen in the solid,
is equal or almost equal in the solid solution and hydride phases, and the system
is closed, then the solvus is unaffected or almost unaffected by a uniform bias
stress. This results because the stress cannot do work on the system. The
present investigation was undertaken in order to verify one way or the other the
validity of this concept.
II - EXPERIMENTAL METHODS

High purity single crystals of Nb were grown from Marz grade Nb (0.25 in. in dia. rod) from the Materials Research Corporation by the electron-beam floating zone method. Multiple passes in vacuum of $10^{-6}$ torr with Ti gettering to maintain O levels low in the atmosphere were growth conditions. Crystals Nb-1 and Nb-2 were oriented such that the specimen axis made angles of $38^\circ$, $19^\circ$ and $18^\circ$ with respect to the [001], [011] and [111] crystallographic directions respectively. Crystal Nb-3 had its specimen axis oriented along the [010] direction.

Precision ultrasonic velocity and attenuation measurements were made using a single quartz transducer according to the "Pulse Echo Overlap Method" as described by Papadakis /6/, wherein a tuning accuracy of one part per million is attained. The specific details of annealing the specimens, hydrogenizing and dehydrogenizing the specimens, the detailed ultrasonic technique (actual equipment used) and preparation of the flat surfaces for bonding on of the transducer etc. and specially designed cryostats to enable data to be taken in the temperature range 77 to 340°K are available in O. Florêncio's Master of Science thesis /7/.

III - EXPERIMENTAL RESULTS

Nb-1 contained either 0 or 200 pp H by weight whereas crystals Nb-2 and Nb-3 contained either 0 or 300 ppm H by weight. Many temperature cycles between 340 to 150°K were made on the samples with and without hydrogen and for specimen Nb-3 these cycles were made with and without various tensile bias stress values at various temperatures /7/. Typical data is shown in Figs. 1 to 4. All attenuation ($\Delta a$) and velocity ($\Delta V/V_0$) change data reported here and elsewhere /7/ are relative to zero values at 298°K. All specimens in the H undoped and annealed states did not exhibit any relaxation peaks in the temperature range studied (see Fig. 1 for example).
From a detailed analysis of all of our data it is found that the $\Delta a$ and $\Delta V/V$ changes detect upon first cooling a low observed solvus temperature of 250°K for 200 ppm H specimens and 270°K for 300 ppm H specimens respectively. These temperature correspond to the non-zero self stress temperatures ($T_s$) discussed by Grossbeck and Birnbaum /3/. After one or more thermal cycles, however, even though the attenuation and velocity appears to have fully recovered after hydride redissolution at elevated temperature, this technique detects a higher solvus temperature. The higher solvus temperature is almost up to phase diagram solvus temperatures presented by Wenzl and Welter /8/, i.e. about 284°K for 200 ppm H specimen's and 310°K for 300 ppm H specimens. All of these temperatures are predicted to shift upwards by only 0.2°K for a bias stress of 21 MPa /3/. A detailed analysis of all of the data shows that a homogeneous tensile bias stress up to $= 21$ MPa in Nb-3 with 300 ppm H causes no detectable rise in solvus temperature for this closed system in accordance with expectations of theory /5/. All of our bias stress data reveals our modulus defect ($\Delta M/M$) (when corrected for density and Poisson contraction effects under bias stress) to be negative and to become more negative with increasing bias stress.

IV DISCUSSION AND SUMMARY

Precision ultrasonic attenuation and velocity studies of Nb crystals containing 0, 200 and 300 ppm H by weight as a function of tensile bias stress up to $= 20$ MPa and varying number of thermal cycles in the temperature range of 77 to 340°K have shown:
(a) the non-zero self-stress solvus temperature \( T_s \) observed in the first thermal cycle \( /5/ \) rises upon subsequent thermal cycles and approaches the equilibrium solvus temperature predicted by phase diagram analysis \( /8/ \).
(b) the solvus temperature close to that predicted by phase diagram analysis is not observed to be affected by a homogeneous tensile bias up to \( \approx 20 \) MPa for this closed system as expected by theory \( /5/ \).
(c) bias stresses up to \( 2/3 \) of the yield point of Nb containing 300 ppm H by weight produce a modulus decrease as the bias stress increases in the temperature range 250 to 310°K.

Point (a) can be explained as follows. Upon formation of \( \beta \) hydride precipitate upon 1st cooling, the 12% volume expansion \( /3/ \) is accompanied by a lattice elastic strain and local dislocation generation and relaxation. Subsequent cyclic cooling nucleates the \( \beta \) hydride at these dislocated centers and hence at regions of inhomogeneous stress, which promotes a higher solvus temperature. The residual dislocations are so few in number, they hardly alter the high temperature attenuation or velocity values, thus suggesting redissolution of hydride is complete. Point (b) requires no explanation and point (c) suggests the bias stress is probably activating more double kinks on non-screw dislocations and hence contributing to the lower modulus.

Acknowledgments - One of the authors (O.F.) acknowledges a Master's Fellowship Grant from CNPq and another (J.M.R.) is grateful for support as a visiting professor at DEMS-UFSCar from CNPq, Brasil.

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