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Stress-Induced Changes to the Triple-Point Phase Boundary of the Niobium-Deuterium System

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The effects of mechanical stress, due to cold rolling, on the triple-point phase equilibrium in the niobium-deuterium system have been investigated using differential scanning calorimetry. Both unstressed and stressed foil samples of niobium-deuterium were analyzed over the temperature range 323 to 398 K. Over this temperature range, niobium-deuterium undergoes several phase changes (depending on the composition of the niobium-deuterium specimen). Differential scanning calorimetry allowed determination of temperature, energy, and compositional characteristics of these phase changes. It has been found that mechanical deformation has a significant effect on all of these characteristics.

Keywords deuterium, niobium, phase diagram, thermal analysis, thermodynamic assessment

1. Introduction

The ability of certain metals and alloys to absorb appreciable amounts of hydrogen holds potential for meaningful applications in several areas of science and technology. Important among these applications are the use of hydrogen as a clean-burning and abundantly available alternative to fossil fuels (coal, petroleum, and natural gas) and the increasingly important area of hydrogen-powered fuel cells. Of course, a significant drawback to using hydrogen as a primary fuel is its extreme flammability—safe storage of the hydrogen is paramount in any application of hydrogen as a fuel. In virtually any application that involves the use of hydrogen, one of the significant benefits of storing hydrogen in a metal or alloy compared with storage as a pressurized gas or liquid is that the hydrogen is not flammable while absorbed in the metal matrix and thus is much safer to transport and store. However, many aspects (e.g., thermodynamic, kinetic, mechanical, structural, and phase stability) regarding hydrogen absorption by metals and alloys remain to be investigated and better understood before wide-scale applications of metal-hydrogen-based technology can occur. The present study involves an investigation of the phase stability of the niobium-deuterium system.

A large number of studies have been performed to characterize the temperature-composition phase diagrams for the niobium-hydrogen (Nb-H) and niobium-deuterium (Nb-D) systems. The techniques used have included x-ray diffraction,[1] electrical resistance measurements,[2] differential scanning calorimetry,[3] reaction calorimetry,[4] specific heat measurements,[5] and neutron-scattering studies.[6]

One of the current authors was involved in the aforementioned study that used differential scanning calorimetry (DSC) to investigate portions of the Nb-D system.[3] The earlier study focused on the relatively high-temperature region of the Nb-D system that involves the α, α', and β phases. The α phase is a dilute solid solution of deuterium randomly distributed among the tetrahedral interstitial sites of the body-centered cubic (bcc) niobium matrix. The α' phase is a more concentrated solid solution of deuterium randomly distributed among the tetrahedral interstices of the bcc niobium matrix. The β phase is a concentrated face-centered cubic (fcc) hydride phase with the deuterium restricted to an ordered occupation of tetrahedral sites of the niobium matrix. The α and α' phases are separated by a miscibility gap two-phase region, while the α and β phases are separated by a structural transformation two-phase region. This area of the Nb-D phase diagram also possesses a two-phase structural transformation region that separates the α' and β phases.

In the earlier study on Nb-D, DSC was used principally to characterize the triple-point phase boundary in the system. From its onset composition up to a D/Nb atomic ratio of ~0.50 (this composition corresponds to the eutectic point of the triple-point boundary), this phase boundary separates the $(\alpha + \beta)$ two-phase region from the $(\alpha + \alpha')$ two-phase region. From the eutectic point up to the terminal point of the phase boundary, the boundary separates the $(\alpha + \beta)$ two-phase region from the $(\alpha' + \beta)$ two-phase region. Represented simplistically (i.e., ignoring fractions of each phase present as dictated by the Lever Rule), the phase transition that occurs as the triple-point boundary is crossed on heating between the onset composition and the eutectic composition is $(\alpha + \beta) \rightarrow (\alpha + \alpha')$. Similarly, the heating transition that occurs between the eutectic composition and the terminal composition is $(\alpha + \beta) \rightarrow (\alpha' + \beta)$. On cooling, the reverse transitions occur as the triple-point boundary is crossed. For reference, the Nb-D phase diagram

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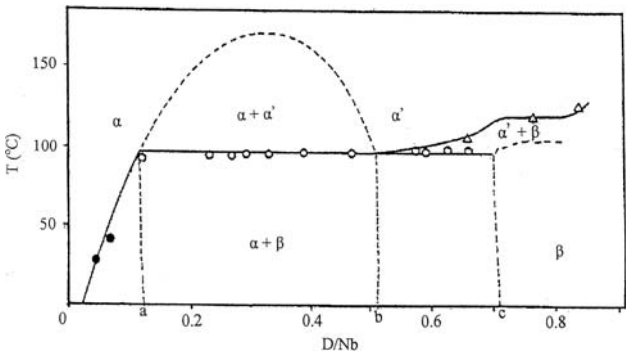

Fig. 1 Upper-temperature portion of the niobium-deuterium phase diagram. The dashed curves are based on Ref 3 and 7. The onset, eutectic, and terminal compositions are represented by the vertical dashed lines that intersect the composition axis at points a, b, and c

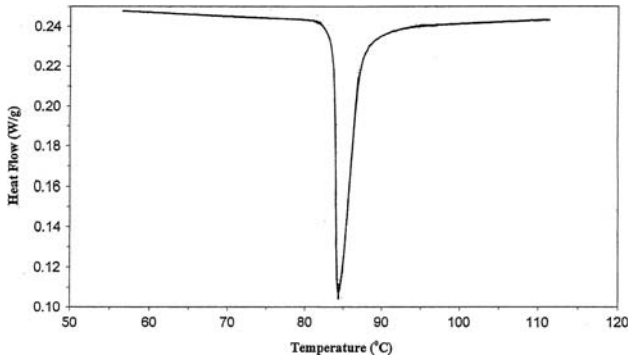

Fig. 2 Representative DSC heating scan for NbD sample with D/Nb = 0.22

determined in the earlier DSC study is given in Fig. 1. In this figure, the horizontal phase boundary at 370 K (97 °C) is the triple-point boundary. Points a, b, and c on the composition axis correspond to the onset composition of the boundary, eutectic point composition, and terminal composition of the boundary, respectively. The present study revisits this region of the Nb-D system and involves an investigation into the effects of cold work on the triple-point boundary of the Nb-D system.

2. Experimental Details

All samples were prepared from commercially available (Alfa Aesar Products, 25 Parkridge Road, Ward Hill, MA 01835, USA) Nb foil (99.99% pure with respect to metallic impurities and 99.98% total purity) of thickness 0.34 mm. Before exposure to deuterium, each niobium sample cut from the foil was lightly abraded with fine emery paper, then chemically polished in a 2:2:1 volume mixture of H_2SO_4:HNO_3:H_2O, followed by liberal rinsing, in an ultrasonic cleaner, with distilled water and acetone.

Each niobium sample was placed in a conventional Sievert's dosing apparatus of known volume and exposed to deuterium gas. The pressure of deuterium gas was monitored by a series of electronic diaphragm gages. A volumetric method was employed to determine the deuterium content of each sample from the measured drop in deuterium pressure during exposure. Following conventions for metal-hydrogen systems, sample composition was calculated and reported as D/Nb atomic ratios. In total, eight samples were prepared that ranged in D/Nb ratio from 0.103 to 0.681.

DSC analyses of the Nb-D specimens were carried out with a Mettler DSC822 (Mettler-Toledo Inc., 1900 Polaris Parkway, Columbus, OH 43240, USA) and a Thermal Analysis (TA) Instruments (TA Instruments, 109 Lukens Drive, New Castle, DE 19720, USA) 900 DSC. Nb-D specimens cut from dosed foil samples were weighed and then encapsulated in aluminum pans and placed in the sample chamber of the DSC. Pieces of undosed Nb (from the same starting foil as the specimen) of comparable weight to the specimens were encapsulated in aluminum pans and used as references. Each specimen/reference pair was heated from 323 to 398 K at a heating rate of 2 K/min under flowing nitrogen. Each sample was then cooled from 398 K back to 323 K at a cooling rate of 2 K/min under flowing nitrogen. For each sample of a particular D/Nb ratio, three specimens were cut and analyzed via DSC.

Figure 2 shows a representative DSC curve. Downward peaks represent endothermic processes (transitions occurring during heating in the present study), while upward peaks represent exothermic processes (transitions occurring during cooling in the present study). Computer analysis of DSC scans determined onset temperatures, peak temperatures, and the total energy (in joules/gram) due to the process occurring.

After initial DSC analysis, specimens were carefully removed from their aluminum pans and mechanically thinned by cold rolling through a manual rolling mill. The rolling mill was calibrated to reduce the specimen thickness by 10%. Cold-rolled specimens were then chemically polished and rinsed thoroughly, reencapsulated, and reanalyzed using the DSC. Heating and cooling regimes were identical to those used on the specimens prior to cold rolling. Specimens that mechanically failed (i.e., fractured or broke) as a result of cold rolling were discarded.

3. Results and Discussion

3.1 Phase-Boundary Temperatures

Figures 3 and 4 show various representations of the triple-point boundary as determined in the present research. Other partial phase boundaries (represented by dashed lines) in these figures have been added for illustrative purposes and are based on previous investigations of the Nb-D system.[7] Figure 3 shows the triple-point boundary, before and after cold rolling, as determined during heating, while Fig. 4 shows similar results as determined during cooling. To be consistent with the earlier DSC investigation of the Nb-D system,[3] phase transition temperatures (T_{tr}) in the

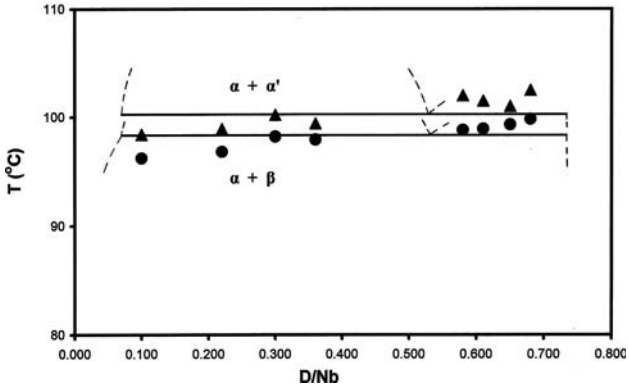

Fig. 3 The triple-point boundary on heating. ●, unstressed samples; ▲, stressed samples

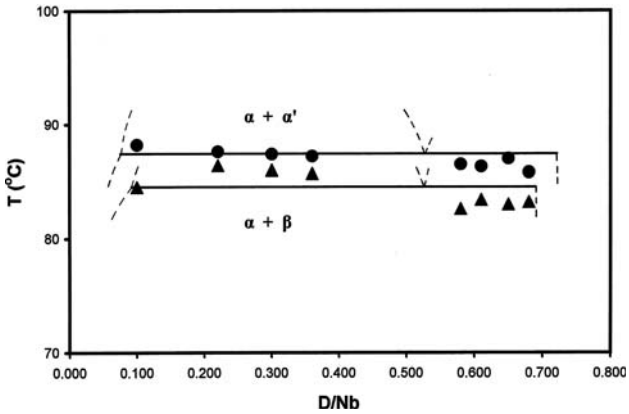

Fig. 4 The triple-point boundary on cooling. ●, unstressed samples; ▲, stressed samples

Table 1 Average triple-point transition temperatures for the Nb-D system

	Temperature, K	
	Unstressed Nb-D	Stressed (cold rolled) Nb-D
On heating	370.7	373.5
On cooling	360.0	356.4

present study correspond to the peak temperature of each DSC scan. There is some scatter of the plotted points, both before and after cold rolling, so the best-fit average values are shown by the horizontal lines in each plot. These average values are reported in Table 1.

The average temperatures of the triple-point boundary for the unstressed system are in good agreement with the earlier DSC study on Nb-D. The earlier study determined the average triple point temperature on heating to be 370.0 K and on cooling to be 359.0 K.[3]

Two features are clearly evident from Fig. 3 and 4 and the values in Table 1. First, the phenomenon of temperature hysteresis is observed in the triple-point phase transitions, both in stressed and unstressed Nb-D. In particular, hysteresis manifests itself in the form of the triple-point transition temperature differing on heating compared with cooling. Second, cold rolling has a marked effect on the triple-point transition temperature. Compared with the unstressed system, cold rolling results in an increase in the transition temperature on heating and a decrease in the transition temperature on cooling. This latter feature obviously translates into a noticeable increase in the magnitude of the observed hysteresis due to cold rolling.

A consequence of cold working a metal is an increase in the number of dislocations within the metal matrix.[8] It has been shown that interstitial hydrogen (and its isotopes) in a metal is strongly attracted to dislocations within a metal matrix.[9] The result of this hydrogen-dislocation attraction is that the hydrogen is drawn to and strongly held in the proximity of a dislocation (i.e., dislocation trapping of the hydrogen). Thus in the stressed samples of Nb in the present study, enhanced trapping of deuterium atoms may occur at locations within the Nb matrix that have increased dislocation densities (compared with the unstressed samples) and the deuterium atoms are trapped by the dislocations.

This enhanced trapping of deuterium as a result of dislocations generated by cold rolling may be a major factor in the observed shifts in the triple-point boundary. The stability of any phase (or two-phase coexistence region) is intimately related to the atomic and molecular level interactions that occur in the system.

Using a pairwise interaction model, in the unstressed Nb-D system there are obviously three dominant interactions energies to consider—those caused by Nb-Nb interactions, Nb-D interactions, and D-D interactions. The introduction of dislocations into the Nb matrix undoubtedly will affect all of these interactions (and their corresponding energies) as well as create significant deuterium-dislocation interactions. It seems reasonable to conclude that the changes in energies of various pairwise interactions brought about by the introduction of dislocations into the Nb-D system and the accompanying creation of significant deuterium-dislocation interactions alter the stability of the α, α′, and β phases. These changes in stability of the phases may manifest themselves in the observed shifts in the triple-point phase boundary.

This interpretation is consistent with earlier results that showed that perturbation of pairwise interactions in the Nb-D system as a result of impurities in the Nb matrix have a pronounced effect on the triple-point boundary.[3]

3.2 Width of the Triple-Point Boundary

Transition enthalpies ($\Delta_{tr}H$) were determined from computer integration of the peak in each DSC scan. Figure 5 shows $\Delta_{tr}H$ values on heating as a function of the D/Nb atomic ratio for unstressed and stressed Nb-D. Figure 6 shows similar results on cooling.

For the heating process (Fig. 5), $\Delta_{tr}H$ values beyond the eutectic composition were not plotted because of an overlap of two DSC peaks—the triple-point transition peak and the peak due to the $(\alpha' + \beta) \rightarrow \alpha'$ transition (see Fig. 1). Upon cooling (Fig. 6), the triple-point transition peak is resolvable

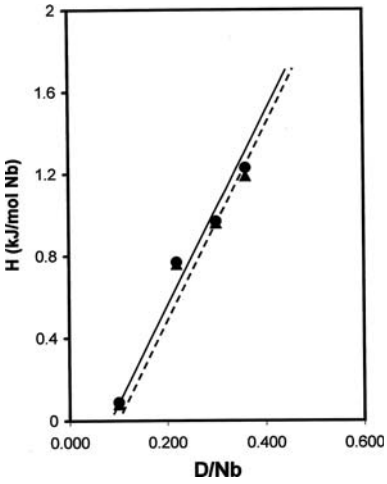

Fig. 5 DSC transition enthalpies on heating as a function of deuterium content. ● and solid lines, unstressed samples; ▲ and dashed lines, stressed samples

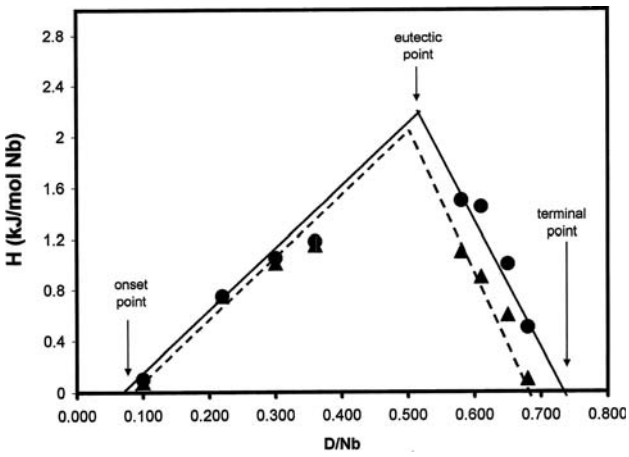

Fig. 6 DSC transition enthalpies on cooling as a function of deuterium content. ● and solid lines, unstressed samples; ▲ and dashed lines, stressed samples

from the peak for the $(\alpha' + \beta) \rightarrow \alpha'$ transition, and thus the $\Delta_{tr}H$ values for the triple-point transition are obtainable. The occurrence of peak overlap on heating and its absence on cooling are the result of hysteresis effects in both the triple-point boundary and the $(\alpha' + \beta) \rightarrow \alpha'$ phase boundary (albeit unequal hysteresis effects in the two phase boundaries).

Transition entropies $\Delta_{tr}S$ were calculated from measured $\Delta_{tr}H$ and T_{tr} values via the relationship $\Delta_{tr}S = (\Delta_{tr}H/T_{tr})$. Figure 7 shows $\Delta_{tr}S$ values on heating as a function of the D/Nb atomic ratio for unstressed and stressed Nb-D. Figure 8 shows similar results on cooling. As with $\Delta_{tr}H$ values for the heating process, $\Delta_{tr}S$ values are not included beyond the eutectic composition due to overlapping transition peaks in the DSC scans.

Craft et al. have shown, through thermodynamic arguments, that the point of intersection of the initial positive

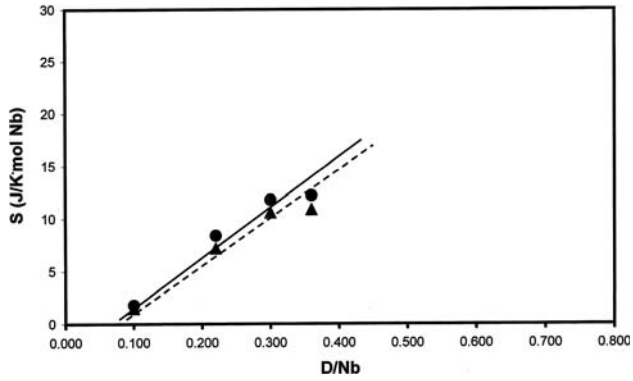

Fig. 7 Calculated transition entropies on heating as a function of deuterium content. ● and solid lines, unstressed samples; ▲ and dashed lines, stressed samples

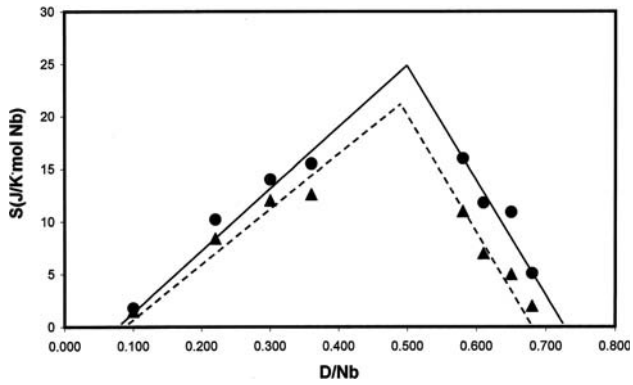

Fig. 8 Calculated transition entropies on cooling as a function of deuterium content. ● and solid lines, unstressed samples; ▲ and dashed lines, stressed samples

(upward) sloping portion of such plots with the x-axis (composition axis) corresponds to the onset composition of the triple-point boundary, while the point of intersection of the negative (downward) sloping portion of such plots with the *x*-axis corresponds to the terminal composition of the triple-point boundary.[3] These thermodynamic arguments also show that the point of intersection of the positive sloping line with the downward sloping line corresponds to the eutectic point of the triple-point boundary. These points are labeled on Fig. 6.

An analysis of Fig. 6 and 8 shows that the onset point, eutectic point, and terminal point of the triple-point boundary are affected by cold rolling. Values of these composition values are given in Table 2.

As with the temperature values, the composition values for unstressed Nb-D from the present investigation are in good agreement with the results of the earlier DSC study. The earlier study reported values of the onset, eutectic, and terminal compositions of the triple-point boundary to be 0.08, 0.52, and 0.73, respectively. The shifts in the onset, eutectic, and terminal compositions are indicated in the triple-point boundaries in Fig. 4. They are not represented in the triple-point boundary determined on heating (Fig. 3) due

Table 2 Onset, eutectic, and terminal compositions on cooling of the triple-point boundary for the Nb-D system

	Unstressed Nb-D	Stressed (cold rolled) Nb-D
Onset composition (D/Nb atom ratio)	0.07	0.08
Eutectic composition (D/Nb atom ratio)	0.53	0.51
Terminal composition (D/Nb atom ratio)	0.74	0.68

to the aforementioned difficulties in analyzing energy values due to overlapping peaks in the DSC heating scans.

It is clear from the results in Table 2 that the width of the triple-point boundary decreases as a result of cold rolling. It is reasonable to assume that a similar reduction in width of the boundary occurs during heating.

There is evidence, based on pressure hysteresis in hydrogen solubility studies, that support the observed shifts in the onset, eutectic, and terminal compositions. It has been found that dislocations introduced into the metal matrix do shift the onset composition of the dilute hydrogen-metal phases (e.g., the α phase in Nb-D) to higher values while lowering the terminal composition of the concentrated hydrogen-metal phase (e.g., the α′ and β phases in Nb-D).[10]

4. Conclusion

The current investigation has found that cold working significantly alters the triple-point phase boundary in the Nb-D system. Cold working results in an increase in the phase boundary temperature on heating of 2.8 K and a decrease in the transition temperature on cooling of 3.6 K. This combination of temperature shifts causes a pronounced increased in the temperature hysteresis that the Nb-D system displays. Unstressed Nb-D has a temperature hysteresis of 10.7 K, while the hysteresis in cold-rolled Nb-D is 17.1 K. Cold rolling has also been found to affect the width of the triple-point boundary. Cold rolling decreases the width of the boundary with the most prominent shift occurring in the terminal point of the boundary. One factor that may play an important role in the observed changes to the triple-point phase boundary is the creation of copious amounts of dislocations in the niobium matrix as a result of cold rolling. The dislocations may alter the energetics of the various phases that coexist along the triple-point boundary, and these energy changes may contribute to the observed changes. Preliminary results on the niobium-hydrogen (Nb-H) system indicate similar effects due to cold rolling.[11] A thorough investigation of the Nb-H system is currently under way.

It is clear from the present work that mechanical stress can have a significant influence on important characteristics of some metal-hydrogen systems. The transition temperatures between phases of differing hydrogen content can be affected, as can the compositional characteristics of the phases of the metal-hydrogen systems. Certainly in the case of the Nb-D system, the temperature and compositional characteristics of the primary phases (α, α′ and β phases) were altered as a result of being in a state of significant mechanical stress. The observed decrease in the width of the triple-point boundary indicates a decrease in the ability of the niobium matrix to store deuterium without significant increases in the deuterium pressure during absorption. The observed temperature shifts due to mechanical stress will clearly influence the temperature changes that niobium can accommodate while retaining specific deuterium storage characteristics.

Changes in vital properties of metal-hydrogen systems caused by mechanical stress need to be fully understood so they may be accommodated in any application of metal-hydrogen systems. Such information will be crucial in the application of metal-hydrogen systems. The present work provides a foundation for a better understanding of this phenomenon.

Acknowledgment

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