Internal Friction Peaks due to Hydrogen Reorientation and Hydride Precipitation in BCC Ti–V–H Alloys

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The internal friction and elastic modulus in hydrogenated β(bcc) Ti–25 at% V alloy have been measured in torsional and flexural modes of vibration for hydrogen contents, $0 < x = [\text{H}] / [\text{M}] < 1.0$. Two kinds of internal friction peaks are observed: A relaxation peak, which occurs around 84 K or 123 K for a frequency of 2 Hz or 1.5 kHz respectively, is identified as a Snoek-type peak of hydrogen dissolved in this alloy. It has an activation energy of $\sim 16 \text{kJ/mol}$ independently of the hydrogen content. Another peak, which is not of the relaxation type, occurs in alloys with $x \geq 0.6$ at temperatures strongly dependent upon the hydrogen content. This peak is attributed to the precipitation (or resolution) of γ(fcc) hydrides. From the shift of the temperature at the terminal point of this peak, the solid solubility for hydrogen has been determined. The characteristic strain of hydrogen and its diffusion coefficient deduced from the relaxation parameters of the Snoek-type peak are discussed.

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I. Introduction

In a previous X-ray diffraction study on the phase diagram of the ternary Ti–V–H system, we have shown that the β(bcc) phase of this system extends up to $x = [\text{H}] / [\text{M}] \sim 1.0$ in alloys with 19 to 38 at% V at room temperature; beyond this H content γ(fcc) hydride precipitates in the β-phase matrices. This anomalously wide β-phase field of the Ti–V–H system has been connected with the β phase of the Ti–H system which is stable at temperatures above 600 K; it might be pulled down to below room temperature via alloying with vanadium. Thus, Ti-rich Ti–V alloys appear to be suitable materials for investigating fundamental properties, such as local strain fields, diffusivity and precipitation, of hydrogen in bcc metals. However, these properties have been left unclarified in the previous study. In the present work, we therefore measure the internal friction to get information on some of the above properties of hydrogen in this ternary system.

Damping peaks associated with stress-induced reorientation (Snoek-type relaxation) of H atoms and with hydride precipitation are presented and discussed in relation to the phase diagram of the ternary system. The relationship between the Snoek relaxation and long-range H diffusion is also discussed. A preliminary report on the Snoek-type peak in this system has been presented elsewhere.

II. Experimental Procedure

Our previous X-ray study has revealed that, among several Ti-rich Ti–V alloys with the bcc structure, Ti–25 at% V alloy has a maximum terminal solubility for hydrogen in the β phase at room temperature. The present study is therefore concentrated on this alloy. Samples were prepared from raw materials of 99.7% purity via arc-melting under purified Ar-gas atmosphere. Buttons of this alloy, homogenized for 86.4 ks at 1273 K, were hot-rolled into plates of appropriate thickness at 873 K and machined into pieces suitable for internal friction measurements. They were polished mechanically and electrolytically, and annealed at 1073 K in high vacuum. Hydrogen
(or deuterium) charging was performed using a Sieverts-type apparatus in the same way as described previously\(^1\). The hydrogen contents were determined to an accuracy of \(\Delta x = \pm 0.01\) in the present experiment. The internal friction was measured in torsional and flexural modes of vibration using computer-controlled apparatus. Differential scanning calorimetry (DSC) was also employed to provide subsidiary information on the terminal solubility for hydrogen in this alloy.

III. Results

Figure 1(a) and (b) shows the internal friction, \(Q^{-1}\), and normalized oscillation frequencies, \(F/F_0\), of alloys with various H contents measured in torsion during heating from 10 to 373 K; here \(F_0 \sim 2\) Hz stands for the frequency at the lowest temperature. A well-defined internal friction peak appears at 84 K and grows with H content up to \(x = 0.40\), accompanied by appreciable peak broadening. A modulus defect (\(\Delta M\) effect) corresponding to this peak can clearly be seen in the frequency change. The peak reaches a maximum height around \(x = 0.50\) and then decreases for \(x \geq 0.60\). In this region a secondary asymmetric peak emerges on the high-temperature side of the original one, and it shifts toward higher temperatures with increasing \(x\), manifesting more asymmetric (\(\lambda\)-shape) forms; a characteristic dip is seen in \(F/F_0\) at a temperature near this \(\lambda\)-shape peak. As shown later, the original peak is attributable to hydrogen reorientation and the additional one to hydride precipitation (or resolution) in the \(\beta\) phase; they are hence referred to as reorientation and precipitation peaks hereafter.

Figure 2(a) and (b) shows internal friction spectra measured in flexure in the heating run. The reorientation peak now appears at 123 K for \(F_0 \sim 1.5\) kHz and varies with \(x\) similarly to that observed at lower frequencies. We have confirmed that this peak is completely suppressed when \(x\) exceeds 1.0. The precipitation peaks also occur, though less definitely, in the samples with \(x \geq 0.60\).

In Fig. 3, the peak heights, \(Q^{-1}_{m}\), of the reorientation peak measured in torsion and
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Fig. 2 The internal friction measured in flexure ($f_0 = 1.5$ kHz) for the samples with (a) $x = 0.05$ to 0.30, and (b) $x = 0.60$ to 0.97.

The peak height appears to change roughly parabolically with $x$. To evaluate the relaxation strength of this peak, the observed height must be corrected for the peak broadening as described below.

Table 1 summarizes the activation energies, $Q$, and the relaxation time constants, $\tau_0$, of the reorientation peak of different H contents. They were determined by the peak-shift analysis coupling the data obtained at the above two frequencies. We find that $Q \approx 16$ kJ/mol independently of the H content, whereas $\tau_0$ changes with the content.

For a single Debye peak with the relaxation time, $\tau = \tau_0 \exp (Q/RT)$, where $R$ is the gas constant and $T$ the temperature, the above value of $Q$ gives a peak width, $w_0 = 2.63R/Q \approx 1.3 \times 10^{-3}$ K$^{-1}$, against the reciprocal temperature. The peak width, $w$, of the reorientation peak measured in torsion has been obtained for each sample by reploting $TQ^{-1}$ vs $T^{-1}$, and the result is given as $w/w_0$ in Table 2. This table also includes the ratio, $Q_{m}^{-1}/(\Delta G/G)$, where $\Delta G/G$ denotes the $\Delta M$ effect associated with the torsional mode and can be evaluated from the corresponding change in $F/F_0$. We note that this ratio, which should be 0.50 for an ideal Debye peak, is as

Fig. 3 The heights of the reorientation peak measured in torsion and flexure, plotted against hydrogen content. The peak height is not corrected for the background damping.

| Table 1 | Activation energy, $Q$, and the relaxation time constant, $\tau_0$, for the reorientation peak in alloys with different H(D) contents. |
|---------|---------------------------------------------------------------------------------------------------------------------------------|
| [H]/[IM] | 0.05 | 0.10 | 0.20 | 0.30 | 0.60 |
| [D]/[IM] | 0.18 |
| $Q$/(kJ/mol) | 16.4 | 16.4 | 15.4 | 16.4 | 15.4 |
| $\tau_0/10^{-11}$s | 0.8 | 1.2 | 4.8 | 3.4 | 2.9 | 8.5 |

| Table 2 | Relations among the peak height, $Q_{m}^{-1}$, the modulus defect for torsion, $\Delta G/G$, and the normalized peak width, $w/w_0$, for the reorientation peak in alloys with different H contents. |
|---------|-----------------------------------------------------------------------------------|
| [H]/[IM] | 0.01 | 0.05 | 0.10 | 0.20 | 0.30 |
| $Q_{m}^{-1}/(\Delta G/G)$ | 0.19 | 0.17 | 0.16 | 0.14 | 0.12 |
| $w/w_0$ | 2.71 | 2.80 | 3.55 | 3.95 | 4.36 |
| $(w/w_0)Q_{m}^{-1}/(\Delta G/G)$ | 0.51 | 0.48 | 0.57 | 0.55 | 0.52 |
small as 0.1–0.2. However, if $Q_m^{-1}$ is corrected by multiplying $w/w_0^\dagger$, the above ratio gives values close to 0.50 expected for the ideal Debye peak, as shown in the table. We can thus conclude that the reorientation peak of concern is composed of an assemblage of Debye peaks with a distribution of the relaxation times.

On the basis of the above argument, the relaxation strength, $\Delta_G$, of the reorientation peak is given by $2(w/w_0)Q_m^{-1}$, or equivalently by $\Delta G/G$. Figure 4 shows $\Delta_G$ evaluated from $\Delta G/G$ as a function of $x$ for the samples with $0<x<0.4$. It manifests a convex increase with $x$ in this range. The initial part of this curve (dashed line) gives

$$\Delta_G = (2.6 \pm 0.4)x. \quad (1)$$

Beyond this range of $H$ content, precipitation of hydrides takes place, and it prevents precise evaluations of $\Delta_G$ and the solute $H$ contents.

Figure 5 shows hysteresis behavior of the precipitation peak for $x=0.90$ measured in torsion during cooling and heating. The difference in the characteristic temperatures, $T_p$, between the two runs, defined by the onset or the terminal points of the precipitation peak (marked by vertical bars), is clearly seen. Similar hysteresis behavior has been observed in other transition metal-hydrogen systems\(^3\). Since most of the measurements have been carried out in the heating run in the present work, we tentatively choose $T_p$ of the heating run as the precipitation temperature for each sample. It falls around 300 K for $x=0.90$, which is in reasonable agreement with the hydrogen solubility in the $\beta$ phase of this alloy as determined by X-ray diffraction\(^1\).

Figure 6 shows a DSC result on samples with different $H$ contents between $x=0.78$ and 1.60. It clearly shows endothermic (heating run) or exothermic peaks (cooling run) associated with the resolution or precipitation of hydrides between $x=0.90$ and 1.20. From these DSC data, the $T_p$ points corresponding to the heating run have been determined (marked by arrows), and are plotted against $x$ in Fig. 7, together with those determined by the internal friction measurements. Both kinds of data points appear to fall on a common curve, i.e. the solvus line for hydrogen in this alloy.

In Fig. 8(a) and (b), internal friction spectra of samples containing deuterium are shown and compared with those for hydrogen. The relaxation parameters for the reorientation peak for $D$, which is located a few degrees above that for $H$, are given in Table 1. On the

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\(^\dagger\) The area of a single relaxation peak, which is proportional to the width $w_0$ times its height $Q_m^{-1}$, is kept approximately constant when a distribution of the relaxation time is allowed to cause the peak broadening. One therefore obtains $wQ_m^{-1} = w_0Q_m^{-1}$, where $w$ and $Q_m^{-1}$ are the corresponding width and height of the broadened peak, respectively. Thus, the height of the unbroadened peak is given by $Q_m^{-1} = (w/w_0)Q_m^{-1}$.
other hand, the precipitation peak for D with \(x=0.75\) appears around 250 K, about 50 K higher than that for H with a similar composition. This may suggest that the terminal solubility for D in this alloy is constricted to some extent in comparison with that for H.

IV. Discussion

The present results indicate that the behavior of the reorientation peak has a strong relevance to the state of hydrogen atoms in the \(\beta\) phase of Ti–25 at\% V alloy\(^\text{(1)}\). We interpret it as a Snoek-type peak of hydrogen in this alloy. The relaxation strength of this peak deviates from a linear increase with the H content for

\(^\text{(1)}\) Our subsidiary study has shown that this peak can prominently be observed only in alloys with 19 to 38 at\% V, where an anomalously wide \(\beta\)-phase field has been observed at room temperature\(^\text{(9)}\).
$x > 0.05$, which would be a manifestation of the onset of H–H interaction in the alloy. On the other hand, the disappearance of this peak in the region of extremely high H contents ($x \geq 1.0$), where the $\beta$ phase should still be present in major fraction, may be attributable to a blocking effect; i.e. virtually full occupancy of the interstitial sites prevents individual H atoms from making atomic jumps necessary for the relaxation.

Now, we attempt to estimate the magnitude of tetragonal strain ($\lambda$-tensor) associated with hydrogen in this bcc alloy. The calculation has been done as described earlier(2), assuming a random distribution of grain orientations in the samples. The shape factor of the tetragonal strain is calculated from eq. (1) as

\[ |\lambda_1 - \lambda_2| = 0.126 \pm 0.009. \tag{2} \]

This value is appreciably larger than one evaluated earlier (=0.088)(2), since in that calculation the $\Delta G$ value for $x=0.20$ was used; for this high H content $\Delta G$ obviously levels off from the linear increase of eq. (1) (see Fig. 4). On the other hand, the lattice expansion due to hydrogen absorption is given by(1)

\[ \frac{1}{a} \frac{\partial a}{\partial x} = \lambda_1 + \frac{\lambda_2}{3} = 0.039 \tag{3} \]

where $a$ is the lattice parameter of the alloy. Coupling eqs. (2) and (3), and assuming $\lambda_1 > \lambda_2$, one obtains $\lambda_1 = 0.123 \pm 0.007$ and $\lambda_2 = -0.003 \pm 0.003$. This result shows that a hydrogen atom accompanies a rather anisotropic strain about it, though it is much smaller in magnitude than those of C, N and O atoms in bcc transition metals(4). For a more accurate evaluation of the $\lambda$-tensor, measurements on single crystals are required. Studies along this line are now in progress.

From the relaxation parameters of the reorientation peak given in Table 1, the diffusion coefficient of hydrogen may be calculated. Assuming that H atoms occupy octahedral interstices, the following equation can be derived, omitting a correlation term, for the (tracer) diffusion coefficient of hydrogen:

\[ D = \frac{a^2}{36 \tau_0} \exp \left( -\frac{Q}{RT} \right) \]

Putting $a = 0.322$ nm(6) in this equation, one obtains for $x = 0.05$

\[ D = 3.6 \times 10^{-10} \exp \left( -\frac{16.4}{RT} \right) \]

in the unit of m$^2$/s. Now, we have separately performed a Gorsky-effect experiment on Ti-25 at% V alloy to measure the (chemical) diffusion coefficient of hydrogen in this alloy(5), and obtained for $x = 0.12$, $D_c = 4.4 \times 10^{-8}$ exp ($-15.5/RT$), in the temperature range between 243 and 443 K. In the above two kinds of diffusion coefficients, the activation energies agree well with each other as has been expected, but the pre-exponential factors differ by $\sim 10^2$; the pre-exponential factor of $D_c$ is of a comparable order of magnitude with those reported for other bcc transition metals(6). In relating $D$ to $D_c$, certain factors must be taken into account. One is a thermodynamic factor, $(\partial \mu / \partial x)(x/RT)$, where $\mu$ is the chemical potential of hydrogen(6). This factor is unity in an ideal solid solution but becomes larger as the concentration increases; its actual value for the present hydrogenated alloy is yet unknown. The others could be correlation and quantum effects, both of which may play important roles for hydrogen diffusion in concentrated alloys at low temperatures. To reveal these effects, further studies are necessary over wider ranges of frequency and temperature than presented in this work.

V. Summary and Conclusion

A Snoek-type relaxation peak has been observed in $\beta$-phase Ti-25 at% V alloy charged with hydrogen or deuterium. It has an activation energy of $\sim 16$ kJ/mol with a width a few times broader than one calculated from the activation energy. The relaxation strength changes roughly parabolically with $x$ and becomes null for $x \geq 1.0$. This may suggest that the relaxation strength is given by the product of dissolved H atoms and the number of unoccupied interstitial sites available for the Snoek relaxation. A small but definite isotope effect has been observed for this peak. The characteristic strain ($\lambda$-tensor) and the diffusion coefficient of hydrogen in this alloy have
been evaluated from the measured relaxation parameters of this peak.

An additional peak with an asymmetric shape has been observed at temperatures well above the Snoek-type peak for $x \geq 0.60$. This peak is caused by the precipitation (or resolution) of $\gamma$ hydrides in the $\beta$-phase matrices. From the shift of the temperature at the terminal point of this peak against H content, the solvus line for hydrogen has been determined. It gives a result consistent with a DSC experiment.

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