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S. Tanaka, M. Koiwa. AN INTERNAL FRICTION STUDY OF V-Ti-H(D) ALLOYS. Journal de Physique Colloques, 1981, 42 (C5), pp.C5-781-C5-786. 10.1051/jphyscol:19815121. jpa-00220991

 ${\rm HAL~Id:~jpa\text{-}00220991}$ 

https://hal.science/jpa-00220991

Submitted on 4 Feb 2008

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### AN INTERNAL FRICTION STUDY OF V-Ti-H(D) ALLOYS

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Abstract. The internal friction of V-1 at.% H alloys  $\overline{(M:Ti,Zr,Mo,Nb,Cr,Fe)}$  and Cu) has been measured over a temperature range from about 10 K to room temperature. Relaxation peaks are observed at lower temperatures for specimens containing  $\overline{Ti}$  or  $\overline{Zr}$ , but not for other specimens. A detailed investigation is performed for several V- $\overline{Ti}$  alloy specimens (0  $^{\circ}$  3.9 at.%  $\overline{Ti}$ ). For a small amount of hydrogen, a relaxation peak appears around 80 K for a frequency of about 0.8 Hz. With the increase in hydrogen contents, the peak increases its height and shifts towards lower temperatures until it reaches 62 K. With the addition of deuterium, a similar peak is also observed at a slightly higher temperature than the H peak. The peak is believed to be associated with the stress induced reorientation of  $\overline{Ti}$ -H(D) complexes.

1. Introduction. The solubility and the diffusivity of hydrogen in metals are generally affected by the presence of other interstitial or substitutional alloying elements. For vanadium, Tanaka and Kimura [1] have examined the effect of the addition of substitutional alloying elements by means of electrical resistivity measurements. Among seven alloying elements: Ti, Zr, Mo, Nb, Cr, Fe and Cu, titanium and zirconium decrease the diffusivity of hydrogen around room temperature, while the other elements have very small effects. The result may be interpreted in terms of different strengths of the interaction between hydrogen and substitutional foreign atoms; titanium and zirconium trap hydrogen atoms to form complexes.

The presence of substitutional-interstitial (s-i) atom complexes has been demonstrated by relaxation methods such as internal friction measurements or magnetic after-effect measurements. Cannelli and Cantelli [2], and Cannelli, Cantelli and Koiwa [3] observed internal friction peaks in Nb-Ti-H alloys, which they ascribed to the relaxation of Ti-H complexes. A similar interpretation has also been given to relaxation processes observed in the magnetic after-effect measurements on Fe-Ti alloys containing hydrogen [4,5].

As an extension of the previous resistometric study [1], this paper reports the result of internal friction measurements on vanadium

alloys containing hydrogen or deuterium.

2. Experimental. - Specimen wires of 0.45 mm in diameter used in this investigation were prepared from the same ingots as those used in the previous study; details of specimen preparation and compositions are given in the previous paper [1]. For V-Ti alloys, specimens with 0.4, 1.0, 1.8 and 3.9 at.% are used in this experiment, while for other alloys the solute concentration is 1.0 at.%M. The apparatus is the same as that used in previous investigations [6,7], although the temperature range is extended to about 10 K by using liquid helium. The frequency is typically about 0.8 Hz and the strain amplitude is about  $5 \times 10^{-6}$  in the maximum surface shear strain.

Hydrogen(deuterium) charging was made electrolytically, and the contents were estimated from the increase in electrical resistivity by using the values ,  $\rho_{\rm H} = 1.12~\mu\Omega cm/at.\% H~[1]$  and  $~\rho_{\rm D} = 0.8~\mu\Omega cm/at.\% D~[8].$ 

3. Results and Discussion. Figure 1 shows the internal friction versus temperature curves for V-1.0 at. $^{\circ}$ M-1.5 at. $^{\circ}$ H (M: Ti, Zr, Mo, Nb, Cr, Fe, Cu). Measurements were made on both cooling and heating at a rate of 0.5  $^{\circ}$ 1 K/min. Only the heating run curves are shown in this paper, because the two types of runs yielded virtually the same curves. Except for specimens with Ti or Zr, the internal friction is almost constant at lower temperatures and shows a monotonic increase at temperatures higher than about 80 K, which is associated with the hydride precipitation peak appearing at higher temperatures. The curve for the specimen with Ti exhibits a peak at about 62 K, while that with Zr shows a rather complex feature; two broad peaks seem to exist at about 90 and 115 K.

Detailed studies are made for V-Ti alloys. Figure 2 shows the result for specimens with various amounts of titanium:  $C_{\mathrm{Ti}}=0$ , 0.4, 1.0, 1.8 and 3.9 at.%. The hydrogen contents  $C_{\mathrm{H}}$  are about 1.5 at.% for all the specimens. The peak is absent in pure vanadium and the height of 62 K peak increases with  $C_{\mathrm{Ti}}$ .

The effect of the hydrogen concentration on the characteristics of the peak is examined for V-3.9 % Ti. A series of measurements were made on one specimen by successively increasing hydrogen contents. Figure 3 shows spectra up to 300 K for several hydrogen contents and Figure 4 shows in detail the lower temperature part. With the addition of hydrogen of 0.11 %, a peak appears at about 80 K. The peak increases its height and shifts towards lower temperatures with the increase in hydrogen contents. For hydrogen concentration of  $\rm C_{H} \geq 1.54$  %, the peak remains at the same temperature of about 62 K,

and the peak height decreases gradually. Peaks appearing at temperatures  $150 \sim 300$  K (Fig. 3) are the hydride precipitation peak. It is interesting to note that the precipitation peak is not observed at lower hydrogen contents, and is only observed for  $C_{\rm H} \geq 1.54$  %. Therefore, the saturation of the lowering of the peak temperature seems to be associated with the occurrence of the hydride precipitation.

The activation energy and the attempt frequency of the peak at 62 K are estimated, by combining the present data with those taken at a higher frequency (16.7 KHz) [9], as about 0.13 eV and 2.7 x  $10^{11}/\text{s}$ , respectively.

From the above observations, the peak is considered to be due to Ti-H complexes in the matrix and not due to those in hydride precipitates. The presence of the peak in the existence of hydride precipitates indicates that the binding energy of hydrogen atoms to titanium is strong enough to retain hydrogen in the matrix. The gradual decrease of the peak height at higher concentrations of hydrogen is tentatively attributed to excess trapping; Ti-H complexes having too many hydrogen atoms around a single titanium atom may not contribute to the relaxation process.

The shift of the peak towards lower temperatures with the increase in the hydrogen contents has also been observed for Nb-Ti-H-alloys, and a tentative interpretation is given in a previous paper[3]. It should be noted that, for higher hydrogen concentrations, a shoulder appears at about 30 K; a subsidiary peak is also observed on Nb-Ti-H alloys.

The effect of the addition of deuterium has also been examined and is shown in Fig.5 together with the result of the hydrogen addition. The peak does appear, which behaves similarly to the hydrogen peak. However, the peak temperature is higher and the height of the peak is lower than those of the hydrogen peak. If the frequency factor is assumed to be the same for H and D, the activation energy for the motion of D is estimated to be about 0.15 eV.

For a given metal, the diffusivity of deuterium is smaller than that of hydrogen. The peak temperature of a relaxation process due to deuterium is expected to be higher than that due to hydrogen. In fact, such trends have been reported for O-H and O-D complexes in niobium [10] and for Ti-H and Ti-D complexes in Fe-Ti alloys [4].

The isotope effect reported in this paper is consistent with the interpretation that the peak is due to the relaxation of Ti-H (D) complexes.

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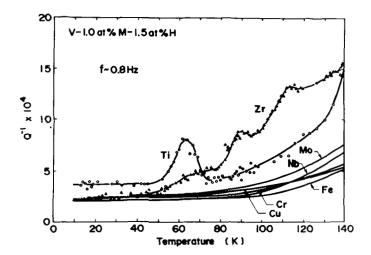


Fig. 1: The internal friction versus temperature curves for V-1.0 at. %M-1.5 at. %H alloys (M: Ti, Zr, Mo, Nb, Cr, Cu, Fe).

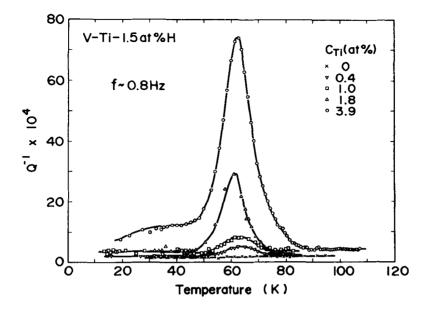
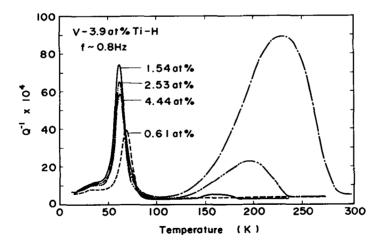


Fig. 2 : The internal friction versus temperature curves for V-Ti-1.5 at.%H alloys ( $C_{Ti}$ : 0, 0.4, 1.0, 1.8, 3.9 at.%).



 $\frac{Fig.~3}{curves}$ : The internal friction versus temperature  $\frac{3}{curves}$  for V-3.9 % Ti-H alloys (CH: 0.61  $\sim$  4.44 at.%). Higher temperature peaks are associated with the precipitation of hydrides. Details of the low temperature part are shown in Fig. 4.

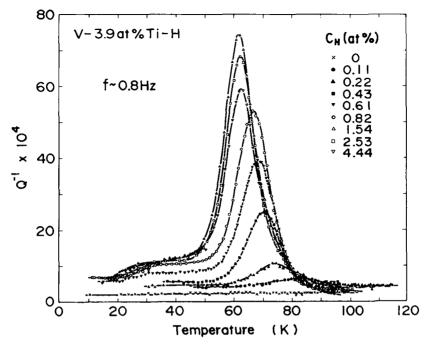
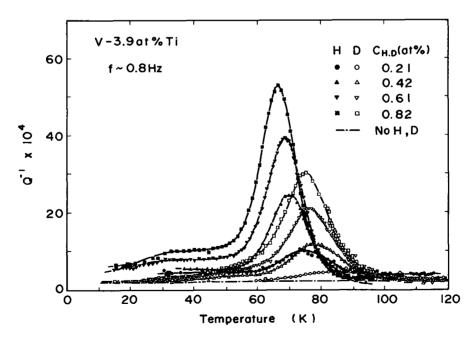


Fig. 4 : The internal friction versus temperature curves for V-3.9 at.% Ti-H alloys (CH: 0  $\sim$  4.44 at.%).



 $\frac{Fig.~5}{(C_{H,}~D)}$  : The isotope effect on the peak for V-3.9 % Ti alloys (CH, D: 0  $\sim$  0.82 at.%).