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Stress-induced reorientation of oxygen–hydrogen complexes in a $Ta_{75}Nb_{25}$ alloy

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Abstract

The anelastic behaviour of a $Ta_{75}Nb_{25}$ alloy containing various amounts of H and O has been investigated between 67 and 700 K at kilohertz frequencies. A relaxation process has been observed at temperatures between 74 ($f = 1.27$ kHz) and 83 K ($f = 6.92$ kHz), which is about two times wider than a single Debye peak. Its relaxation parameters are: $W_R = 0.098$ eV; $\tau_0 = 3 \times 10^{-11}$ s. The process appears to be related to stress-induced reorientation of O–H complexes.

1. Introduction

The macroscopic diffusion coefficient D^* of H in a $Ta_{75}Nb_{25}$ alloy has recently been investigated at H contents of $n_H < 0.02$ ($n_H = H/(Ta + Nb)$ at.) by Gorsky relaxation between 130 and 415 K [1, 2]. Different from Ta and Nb pure metals, the alloy shows an Arrhenius-type of temperature-dependence for D^* down to 130 K. This behaviour has been attributed to a reduction in the H tunnelling rate between ground states at adjacent interstitial sites due to asymmetries in the double well potential. Actually, in a binary metal alloy a variety of interstitial sites occur depending on the composition and distribution of the two atomic species within the first and more distant shells of neighbours [3].

At low H contents, occupancy by H of such sites gives rise to elastic dipoles, which should, in principle, be susceptible to stress-induced reorientations and reactions [4]. In the TaNb alloy system, the spacing between adjacent site-energies are expected to be small and the populations of all the different sites (Ta_0Nb_4, Ta_1Nb_3, ...) comparable.

Relaxations associated with reorientation of O–H complexes and with long-range diffusion (Gorsky) in alloys appear to have been neglected in comparison to pure body-centred cubic (b.c.c.) metals [5–8], in spite of the possibility they offer for investigating the influence of compositional disorder on the state of H (localized or delocalized [8–10]) (see Fig. 1).

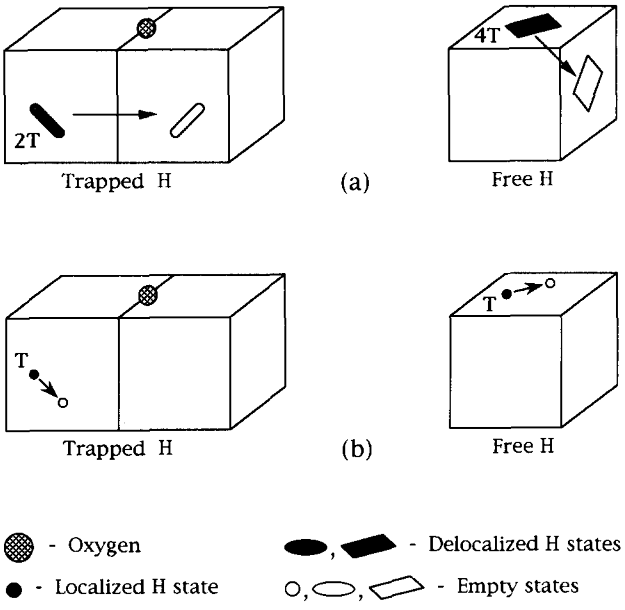

Fig. 1. Possible localized and delocalized configuration of trapped and free hydrogen in Nb (a) and in the $Ta_{75}Nb_{25}$ alloy (b).

The main aims of the present investigation were to study H mobility below 130 K, to detect relaxations associated with H redistributions over different interstitial sites and, lastly, to look for reorientational effects of O–H complexes.

2. Experimental details

A sample of $Ta_{75}Nb_{25}$ in the shape of a thin sheet was used in the present investigation; its dimensions

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were $0.63\times40\times4$ mm^3. The specimen was charged with H contents n_H ranging from below 0.0015 to 0.029 by gas-phase surface reactions at appropriate pressures of H_2 gas and temperatures. The oxygen content n_O ($n_O = O/(Ta+Nb)$ at.) was similarly changed by exposing the specimen to an oxygen atmosphere at around 1300 K for a length of time sufficient to ensure homogeneous conditions within the sample. The hydrogen content was determined by vacuum extraction techniques, while that of oxygen was estimated from the strength S of the O–Snoek relaxation, by taking for the $Ta_{75}Nb_{25}$ alloy the same relaxation strength per unit atomic per cent of oxygen as for Ta ($S/n_O = 0.11$ [11]). This estimate was carried out under the assumption of a gaussian distribution for the relatively wide spectrum of relaxation times observed in this alloy [2]. Although this procedure may not be accurate, as the dependence of S on n_O is actually not known for the alloy, it is, nevertheless, adequate for the purposes of the following discussion of the data.

The elastic energy dissipation coefficient Q^{-1} was deduced from the decay of free oscillations of the specimen excited in flexure in its free–free fundamental and overtone resonant modes.

3. Results

The low temperature portions of $Q^{-1}(T)$ curves obtained for $n_H = 0.011$ and $n_O = 0.0086$ at three different frequencies are shown in Fig. 2. As can be seen, a well-developed peak occurs below 100 K, the height of which decreases with increasing peak temperature T_M by changing the resonant vibration frequency. Background dissipation, which is smaller at higher frequencies, is predominantly thermoelastic in nature.

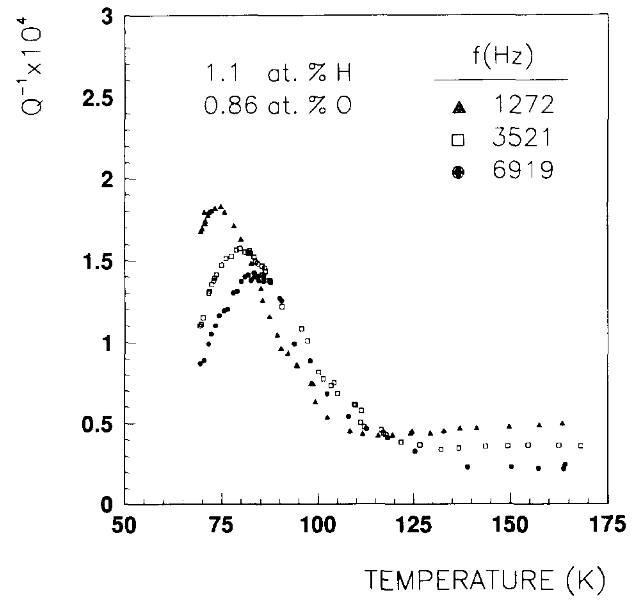

Fig. 2. Frequency dependence of $Q^{-1}(T)$ relationships in the hydrogen and oxygen-doped $Ta_{75}Nb_{25}$ alloy.

The relaxation features at various H and O contents are summarized in Table 1. The peak height Q_M^{-1} is large when O and H contents are simultaneously high, thus suggesting that the peak arises from reorientation of O–H complexes.

For H contents greater than the O content ($n_H = 0.004$, 0.009, 0.017, 0.024, and 0.029; $n_O = 0.0015$) together with O–H pair relaxation, a second peak was observed at around 140 K (for $f = 1262$ Hz). The $Q^{-1}(T)$ curve of the second peak displayed, for $n_H = 0.029$, a steep increase on its high temperature side indicating the onset of hydride precipitation [12]. In the presence of the second peak, the temperature T_M of the O–H relaxation appears to be higher, as can be deduced from a comparison of the first two entries of Table 1 with the fourth. This difference is likely to be due to interactions among free and bound hydrogen atoms. The features of the higher temperature peak, which

TABLE 1. Features of O–H complex relaxation

n_O (p.p.m. at.)	n_H	f_M (Hz)	T_M (K)	$Q_M^{-1}\times10^4$
150	0.024	1262	82.5	~0.3
150	0.029	1262	82.5	~0.3
1700	⩽0.0015	1264	77.0	~0.3
8600	0.011	1272	74.0	~1.4
8600	0.011	3521	79.3	~1.3
8600	0.011	6919	83.3	~1.2

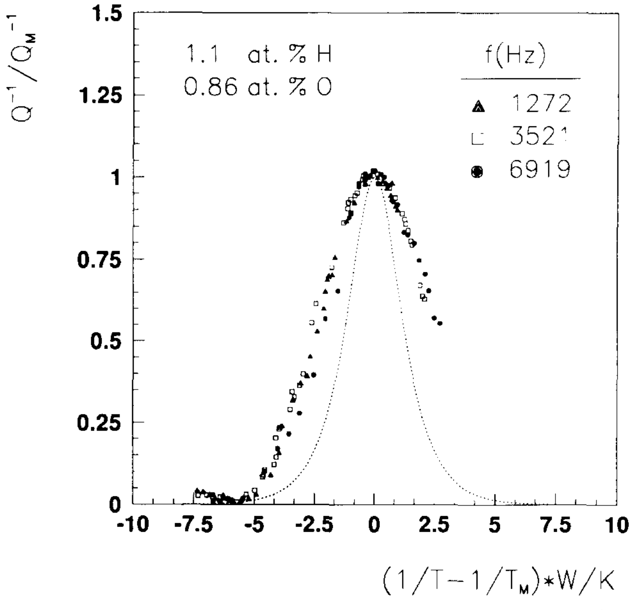

Fig. 3. Comparison of normalized experimental data $Q^{-1}(T)/Q_M^{-1}$ with the Debye curve for a single time relaxation. The value of $W_R = 0.098$ eV has been used.

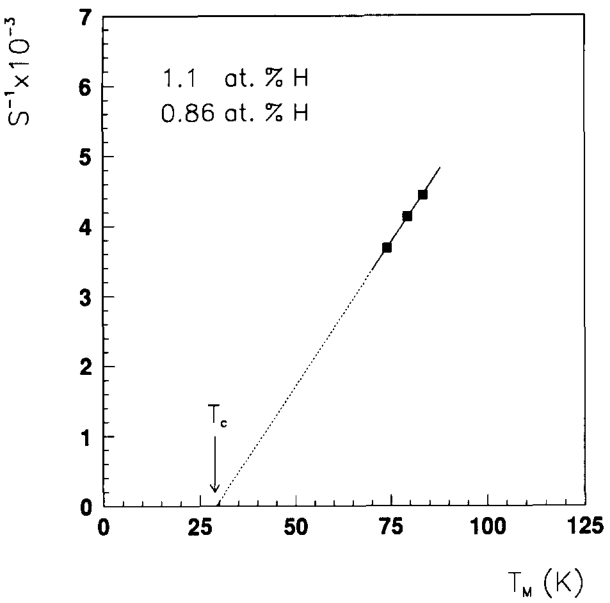

Fig. 4. Curie–Weiss temperature dependence ($S(T)=S_0/(T-T_c)$) of the relaxation strength S.

is probably associated with stress-induced redistribution of free H over non-equivalent tetrahedral interstitial sites, are still under investigation and will be reported soon.

The activation energy W_R and the limit τ_0 for the O–H pair relaxation were determined by considering only data at the same H and O contents, and turned out to be 0.098 eV and 3×10^{-11} s, respectively.

The O–H relaxation in $Ta_{75}Nb_{25}$ is about two times wider than the Debye peak, as can be seen from the normalized plot of Fig. 3. The extra width of the relaxation curve is presumably associated with compositional disorder or with interactions among O–H pairs. Actually, evidence of such interactions is provided by the Curie–Weiss type of temperature dependence ($S=S_0/(T-T_c)$) of the relaxation strength S, as demonstrated by the plot in Fig. 4, which gives for the self-ordering temperature T_c a value of 29 K.

4. Discussion and conclusions

In Nb the temperature dependence of the relaxation time τ_R associated with reorientation of O–H complexes is not exponential [13]. In view of the narrow range of peak temperatures of the present work, conclusive remarks concerning τ_T *vs.* T relationships in the $Ta_{75}Nb_{25}$ alloy can not be made. However, as W_R turns out to be sensibly smaller than the diffusion energy W_D measured between 130 and 415 K by Gorsky relaxation ($W_D=0.14$ eV [1]), and τ_0 some orders of magnitude longer than usually found for point defect relaxations, it can be inferred that below 83 K tunnelling transitions between ground states at adjacent sites start to dominate over the phonon-assisted transitions between excited states. This conclusion is also supported by the plot in Fig. 5, where the macroscopic diffusion coefficient D^* (which for low H levels involved in the experiment ($n_H<0.02$) should coincide with the Einstein diffusion coefficient D [1]) is compared with values of D deduced from the relaxation time τ_R assuming tetrahedral–tetrahedral transitions ($D=a^2/72\tau_R$; $a=$ lattice parameter). In this figure the two sets of data match one another and taken all together they seem to clearly indicate a slight deviation from exponential behaviour. This match does not occur for Nb where much higher jump rates are found for untrapped than for trapped H atoms.

The different behaviour of H in Nb and in the $Ta_{75}Nb_{25}$ alloy can be accounted for under the assumption that, in the alloy, trapped and free H atoms are both localized at a single tetrahedral site, due to the removal of site degeneracies by compositional disorder and, furthermore, that stress-induced reorientation of the O–H elastic dipole takes place through intra-pair transitions of H, as shown in the left-hand side of Fig. 1(b). Actually, these transitions are expected to be hardly affected by the presence of O, thus, occurring at rates comparable to those of untrapped H, in agreement with the experiment. In Nb, on the other hand, reorientation of the O–H complexes probably takes place through transitions of H between the two delocalized 2T states indicated in the left-hand side of Fig. 1(a) [10–14]. These transitions and, consequently, their rates

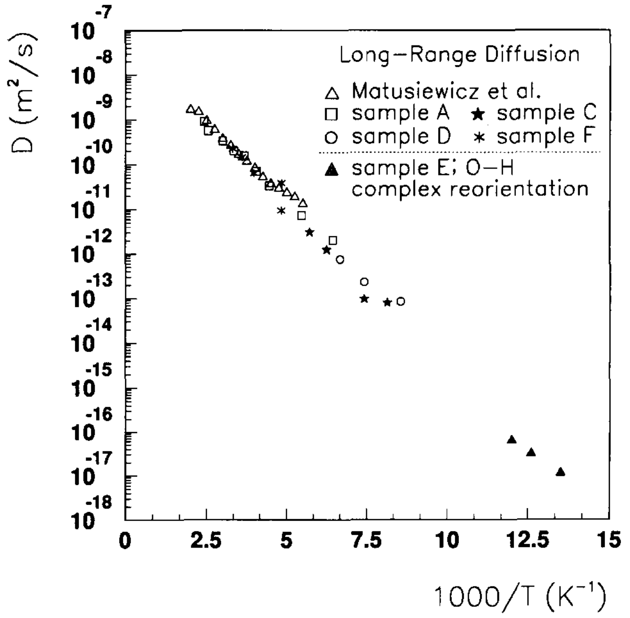

Fig. 5. Comparison of long-range diffusion data for various sample thicknesses and data deduced from the relaxation time τ_R assuming tetrahedral–tetrahedral jumps ($D^*=a^2/72\tau_R$; $a=$ lattice parameter).

are substantially different from those of untrapped H probably occurring between 4T delocalized states, as indicated in the right-hand side of Fig. 1(a) [9]. The experimental results indicate much lower transition rates for 2T–2T than for 4T–4T transitions.

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