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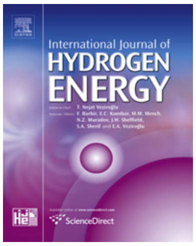

Long- and short-range motions of H and D in a NbMo alloy as studied by anelastic relaxations

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ABSTRACT

The diffusion of H and D has been investigated in the $Nb_{0.80}Mo_{0.20}$ alloy by Gorsky and dipole reorientation/reaction relaxations in the temperature ranges 130–370 K and 70–100 K, respectively. Between 130 and 370 K the chemical diffusion coefficient at infinite dilution of H and D obeys Arrhenius laws. Differently from the case of pure Nb no deviation from an exponential temperature dependence has been observed below 250 K. The activation energies in the alloy (0.113 ± 0.003 eV for H and 0.13 ± 0.02 eV for D) are slightly higher than in pure Nb (0.106 ± 0.006 eV for H and 0.127 ± 0.006 for D) for $T > 250$ K. The H diffusion data were fitted to a relationship provided by a trapping model and the binding energy of H to Mo was found to be as small as 0.009 eV. An internal friction (IF) peak occurring between about 70 and 100 K for frequencies in the range 0.50–6.62 kHz was proved to be due to stress-assisted changes in the directional short-range order of Mo–H(D) bonds. The Einstein diffusion coefficient of H(D) deduced from the IF peak does not match the higher temperature data due to differences in the tunneling regimes of free and trapped H atoms operating over the two temperature ranges. The mismatch is small for D for which the tunneling regime appears to be the same in the free and trapped states.

1. Introduction

The diffusion of hydrogen and deuterium in the transition metals V, Nb and Ta has attracted a lot of attention in the past mainly because these interstitials exhibit non-classical behavior at low temperature [1–3]. Relatively less work has been done in metal alloys where tunneling effects are hindered by atomic disorder. However, in the last few years progressively increasing attention has been paid to alloys in view of their possible application for hydrogen storage. In this respect some bcc alloys are of particular importance as they may exhibit storage capacities as high as 3.9% by weight (see Ref. [4] and references therein).

Another aspect of interest for investigating alloys concerns the interactions of H with solute atoms and the effect of these interactions on H(D) diffusion and terminal solubility. An increase in terminal solubility in the α phase has often offered the chance for studies on H(D) mobility at such low temperatures that would have been inaccessible due to hydride precipitation [5–8]. Hydrogen trapping at impurities has been and still is a subject of debate and has promoted the development of various diffusion theories [9–12]. Some of them are based on trapping concepts and are mainly applicable to dilute alloys [9–11], some others are based on site energy distributions and are valid also for concentrated alloys [12,13].

The available data on site occupancy by H in Nb_xMo_{1-x} alloys and on the interaction of this interstitial with Mo atoms

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are scarce and to some extent in conflict one with the other [7,8,14,15]. Therefore, a cooperative research program in these alloys was undertaken some time ago and part of the obtained results have been published elsewhere [16,17]. The purpose of the present work was to extend the investigation to long-range diffusion of H(D) and to correlate these data with those for short-range motions as deduced from an anelastic relaxation due to the Mo–H(D) interaction occurring at around 100 K.

2. Experimental

The alloy $Nb_{0.80}Mo_{0.20}$ used in the present experiments was prepared in Dubna by arc-melting high purity niobium and molybdenum. Two samples were cut from the ingot by a diamond saw, one to be used for the elastic after-effect (EA) measurements (Gorsky relaxation), the other for internal friction (IF) measurements (Mo–H(D) interaction relaxation). The bars of dimensions $38.7 \times 4.7 \times 0.54$ mm^3 and $18.0 \times 4.7 \times 0.54$ mm^3 were preliminarily annealed at 2100 °C in ultra-high vacuum for homogenization and reduction in their gaseous impurity content. Fusion analysis carried out at the end of the measurements gave a total atomic concentration of N, C and O of 0.1 at%. The EA data were recorded as a function of time after rapid removal of a constant stress prior applied to the sample, clamped at one end, for a sufficient length of time. The stress was imposed and removed by applying a rectangular electric signal to the sample/electrode capacitor. The IF measurements were carried out between 30 and 300 K by exciting free–free flexural modes of the bar supported along nodal lines by thermocouple wires. The excitation/detection of vibrations was accomplished by an electrostatic method. The sample was charged with H(D) electrolytically and the concentration $n_{H,D} = H(D)/(Nb + Mo)$ was determined at the end of the measurements by the vacuum extraction method.

3. Results

3.1. *Gorsky relaxation*

Normalized isothermal curves of the time dependent anelastic strain $\varepsilon(t)$ of the $Nb_{0.80}Mo_{0.20}$ alloy containing hydrogen are reported in Fig. 1, where the quantity $1 - f$ in the ordinates represents the fraction of the recoverable strain $[\varepsilon(t) - \varepsilon(\infty)]/[\varepsilon(0) - \varepsilon(\infty)]$ at time t. These curves were obtained at various temperatures T and at the H content $n_H = 0.03$. The data could be fitted to double exponential curves of which only one exhibited a time constant τ_G monotonically increasing with decreasing temperature. This was the only component used in the following data analysis.

As demonstrated by neutron vibration spectra [16], for $n_H \le 0.05$ H is in solid solution in the $Nb_{0.80}Mo_{0.20}$ alloy from room temperature down to 10 K and it occupies tetrahedral sites. The same is assumed to be true for D. The H(D) chemical diffusion coefficient D_c was derived from the strain relaxation time τ_G according to the following relationship, which is valid for the case of a bar of thickness h deformed in flexure:

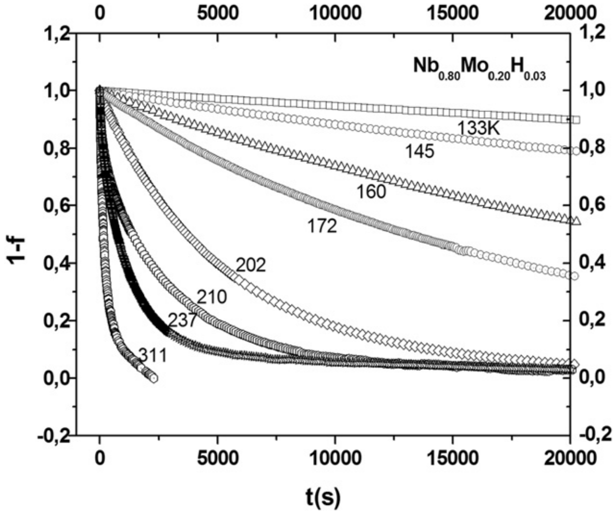

Fig. 1 – Normalized isothermal strain relaxation curves obtained at the indicated temperatures and the H content $n_H = H/(Nb + Mo) = 0.03$. The quantity $1 - f$ in the ordinates represents the fraction of the anelastic strain that is still to be recovered.

$$D_c = \frac{h^2}{\pi^2 \tau_G} \tag{1}$$

The obtained values of D_c were corrected for the H concentration dependence in order to get the diffusion coefficient at infinite H(D) dilution D_c^* to be compared with results reported in the literature for Nb. The data for D_c^* were obtained from the experimental ones by using the following relation [18]:

$$D_c^* = D_c \frac{T}{T - T_s} \tag{2}$$

where T_s is a quantity that takes into account H–H interactions:

$$T_s = \frac{u n_{H,D}}{k_B} \tag{3}$$

where u represents the interaction energy and k_B the Boltzmann constant. For u was assumed the same value as for Nb available in the literature that is 0.21 eV [18]. For $n_H = 0.03$ T_s turned out to be 73 K. The diffusion coefficients D_c and D_c^* are shown in the semi logarithmic plot of Fig. 2, where D_c^* for pure Nb [18] is also reported for comparison. The data points for the NbMo alloy are aligned along a single straight line, similar to the case of the NbV [13,18] and NbTa [19,20] alloys and differently from that of pure Nb, where two distinct temperature regimes are observed above and below 250 K, respectively. It is worth noting in Fig. 2 that on alloying Nb with Mo the diffusion coefficient of H decreases as it happens for the NbV and NbTa alloys.

The chemical diffusion coefficients D_c and D_c^* of deuterium are plotted against T^{-1} and compared with data for pure Nb [18] in Fig. 3. The values of D_c as taken at $n_D = 0.006$ were deduced from curves similar to those shown in Fig. 1. As seen, D_c andD_c^* for this low D content approximately coincide and are lower than for pure Nb.