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Investigation of interaction of hydrogen with solute atoms by means of internal friction and diffusion data

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Abstract

A new method which can be used to obtain information about interaction of hydrogen with solute atoms is described. The method consists in computer simulation of internal friction spectra due to diffusion under stress of H atoms and/or tracer diffusion of hydrogen taking into account a long-range interaction of dissolved atoms. One can compare the calculated parameters with the experimental ones and obtain information about the interaction. The proposed method was used for investigation of H–H(D–D), H(D)\O(N) and H(D)-substitutional interactions in *bcc* metals.

Keywords: Hydrogen; Interatomic interaction; Computer simulation; Diffusion

1. Introduction

It is a common knowledge that the diffusion mobility of hydrogen in metal solid solutions is connected with the interaction of hydrogen atoms with other hydrogen and solute atoms. The diffusion mobility can be investigated by an internal friction method or by measurement of diffusivity. However it is normal practice to use these effects only to obtain rough estimates of effective interaction energies of solute atoms.

In the present paper the alternative procedure is described to connect the diffusion mobility with interatomic interaction. The procedure involves computer simulation of internal friction spectra due to diffusion under stress of hydrogen atoms and/or tracer diffusion of hydrogen taking into account long-range interaction of dissolved atoms. The verification and correction of models of interatomic interaction and determination of interaction energies were performed by comparing cases of coincidence of the calculated internal friction spectra (the peak temperatures) and the activation energy of diffusion with the experimental ones.

2. Calculation method

It was suggested that the long-range interatomic interaction of solute atoms effects diffusion and internal friction by changing the arrangement (a short-range order) and the energy of H(D) atoms in tetrahedral interstices of a *bcc* crystal lattice (by ΔE value) and therefore the activation energy of diffusion and internal friction. Thus the diffusion barrier H_p of the p-th H atom is equal to: $H_p = H_D - \Delta E_p$ where H_D is the activation energy of diffusion of single H atom in the solid solution with a low H concentration. The change of a saddle point of a diffusion barrier was neglected.

To calculate a short-range order and ΔE_p, Monte-Carlo computer simulation was carried out taking into account concrete values of H–H(D–D) and Ti–H(D) interaction in many coordination shells. At a given temperature T, the internal friction Q^{-1} can be calculated by summing up all interstitials' contributions according to the Debye law [1]

$$Q^{-1} = \frac{\Delta_p}{T} \sum_{p=1}^{N} \frac{\omega\tau_p}{1 + (\omega\tau_p)^2} \qquad (1)$$

where N is the number of H or D atoms in the model crystal, $\omega = 2\pi f$ is the angular frequency of vibration, τ_p is the relaxation time of the p-th atom, Δ_p is the relaxation strength, $\tau_p = \tau_0 \exp(H_p/kT)$. For diffusion through tetrahedral interstices of the *bcc* lattice [2] $\tau_0 = a_0^2/72D_0$ where D_0 is the pro-exponential factor of a diffusion coefficient and a_0 is a lattice parameter of a metal. H_D and D_0 were taken for H(D) in Nb, V and Ta from [3].

For the calculation of relaxation strength Δ_p of p-th H(D) atom it was suggested that the asymmetry of displacements of host and substitutional atoms around each H(D) atom can be treated as a 'tetragonal' elastic dipole to the first approximation and the relaxation strength is in direct proportion to the strength of the dipole. The

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Table 1
Results of investigation of H–H (D–D) interaction according to diffusion data

Alloy	Used exper. data	Temperature range, K	The last blocked shell	Full or partial blocking	Energy of max. elastic attraction after blocking, eV
V-2.0% (H/V)	[10]	410–573	3	Full	−0.045 (4th shell)
Nb-7.0% (H/Nb)	[11]	375–475	3	Full	−0.053 (4th shell)
Ta-5.6% (H/Ta)	[11]	320–425	4	Full	−0.036 (5th shell)
Nb-4.8% (D/Nb)	[11]	325–425	3	Full	−0.053 (4th shell)
Ta-3.8% (D/Ta)	[11]	320–420	3	Partial	−0.043 (3rd shell)
α-Fe-H	[12]	283–313	3	Partial	−0.059 (4th shell)

displacements of host atoms due to substitutional atoms were taken from [4].

The long-range tracer diffusion have been simulated by Monte Carlo method on the basis of random walk theory [5]. One traces the displacement of each p-th H(D) atom from their initial position $\boldsymbol{R}_{0_p}$ to the final position $\boldsymbol{R}_p$. A diffusion coefficient D_p was calculated for each p-th H(D) atom: $D_p \sim (\boldsymbol{R}_p - \boldsymbol{R}_{0_p})^2/t$, where t is the time. The diffusion coefficient D was obtained by averaging of all coefficients D_p. One can find the details of the calculations in [5,6]. From the temperature dependence of D the activation energy of tracer diffusion $H_{\mathrm{TD}}^{(\mathrm{cal})}$ was determined. The activation energy was used for comparison with experimental values of the activation energy of H or D tracer diffusion $H_{\mathrm{TD}}^{(\mathrm{exp})}$.

We shall show the results for the following three cases.

3. H–H(D–D) interaction

It is known that there are two contributions to H–H (D–D) interaction: the long-range strain-induced (elastic) interaction and short-range repulsion (‘hard core‘). The purpose of this part was to obtain the radii of the repulsion by means of computer simulation of diffusion. We used different radii of the repulsion and calculated energies of H–H(D–D) elastic interaction in Ta [1,7], Nb [8], V and α-Fe [9] for calculation of activation energies of H(D) diffusion. The radii of the repulsion were obtained by comparing cases of coincidence of the calculated activation energies with the experimental ones.

For the most investigated alloys the radii of the repulsion are equal to three coordination shells (Table 1). The computer simulation of the hydrogen Snoek-type internal friction peak in Nb–O–H [1] gives the same distance. This result is in a good agreement with information about hydride structures [13].

4. H(D)–N interaction in Nb and Ta

For this case there are also the same contributions to the interaction energy as for the H–H interaction. The elastic contribution was calculated in [14] and corrected in [1]. The radii of short-range repulsion were obtained by means of computer simulation of diffusion as in the case H–H(D–D) interaction and are displayed in Table 2.

One can see that the repulsion expands up to the third shell. This result is in a good agreement with those results obtained by simulation of internal friction [1].

5. H(D)-Ti interaction in Nb

For this case there are experimental data on internal friction [15] and diffusion [16]. The used model for the H(D)-Ti interatomic interaction was of the long-range strain-induced (elastic) these [17] supplemented by a short-range ‘chemical‘ interaction. The unknown energy of the chemical interaction in the first coordination shell $H_{\mathrm{chem}}^{(1)}$ was obtained by comparing cases of coincidence of the calculated temperature of the internal friction peak due to diffusion under stress of H(D) atoms near Ti atoms with the experimental ones.

Since we use the values H_{D} and D_0 obtained for very

Table 2
Results of investigation of H(D)–N interaction

Alloy (at.%)	Used exper. data	Temperature range, K	The last blocked shell	Full or partial blocking	Energy of max. elastic attraction after blocking, eV
Nb-0.6H-0.44N	[3]	250–330	3b	Partial	−0.060 (3bth shell)[1]
Nb-0.44D-0.26N	[3]	300–400	3b	Partial	−0.100 (3bth shell)
Ta-0.3D-0.9N	[3]	210–300	3b	Partial	−0.020 (3bth shell)

[1] A tetrahedral interstice in the third-a coordination shell is separated from the nitrogen atom in a octahedral interstice by the vector $(300)a/4$, in the third-b shell by the vector $(221)a/4$.

low concentrations of H(D) the model used for internal friction is more applicable for alloys with low H(D) and Ti concentrations. In the calculated spectrum there was one main peak whose width was greater than that of a single Debye peak as in the experiment. The results of the calculation of peak temperatures T_{max} as a function of the unknown energy of chemical H(D)–Ti interaction in the first coordination shell $H^{(1)}_{\mathrm{chem}}$ for the alloys with 0.11 at.% H(D) are shown in Fig. 1. For the sake of comparison the experimental temperatures of the hydrogen Snoek-type peak [15] were taken for the same alloys for which the calculated temperatures are presented in Fig. 1. According to data of Fig. 1 the energy is equal to $-0.09-0.10$ eV. Taking into account the H–Ti elastic interaction [17] the energy of maximum Ti–H(D) attraction equals to -0.075–0.085 eV.

For verification of the model used for internal friction we calculated internal friction spectra of alloys with 1 at.% H taking into account the obtained energies of chemical interaction. According to [15] such an increase of a H concentration does not change T_{max} for 0.5 at.% Ti and decreases T_{max} to ~100 K for 2 at.% Ti. The calculated values (100 K for 0.5 at.% Ti and 90 K for 2 at.% Ti) are in a good agreement with the experimental ones. This means that the obtained energies of chemical H(D)–Ti interaction are useful for the description of a solid solution with a higher hydrogen concentration (1 at.%).

Simulation of diffusion gives the $H^{(1)}_{\mathrm{chem}}$ value equal to -0.06 eV. The difference of $H^{(1)}_{\mathrm{chem}}$ can be explained by the difference of temperatures: 220–350 K for diffusion and 100–160 K for internal friction.

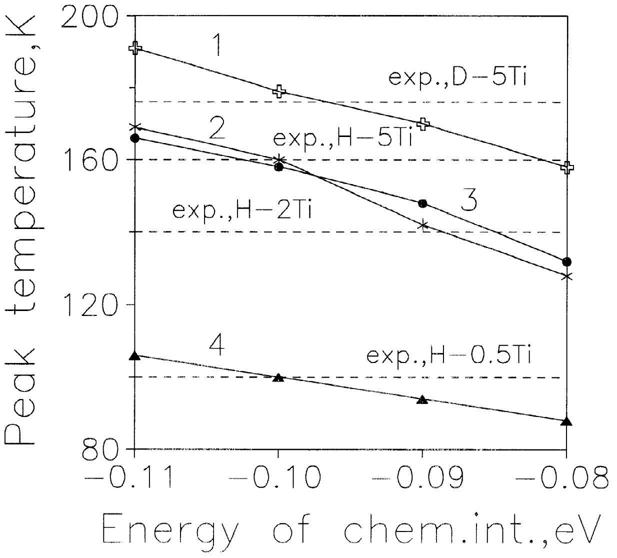

Fig. 1. Dependence of the calculated hydrogen internal friction peak temperature on the value of the energy of chemical interaction in the first coordination shell (0.11 at.% H(D), 20 kHz): 1. D-5 at.% Ti; 2. H-2 at.% Ti; 3. H-5 at.% Ti; 4. H-0.5 at.% Ti. The energies of chemical interaction can be determined by comparing cases of coincidence of the calculated temperatures (solid lines) with the experimental ones (dashed lines).

6. Conclusion

The three examples described above showed that the proposed method can give the values of short-range and long-range interaction of hydrogen with solute atoms. These values can be used for calculation of atomic structure and properties of alloys containing hydrogen.

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