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Interaction of dissolved atoms and "hydrogen Snoek-type relaxation" in Nb and Ta (computer simulation)

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Abstract

The internal friction due to "diffusion under stress" of H and D atoms in Ta(Nb)–O(N)–H(D) alloys was calculated to verify the applicability of the model of interaction of dissolved interstitial atoms and to investigate the relaxation mechanism. A long-range, strain-induced (elastic) interaction model, supplemented by repulsion interaction in the nearest coordination shells, was used. The short-range order in the interstitial solid solution was simulated by a Monte–Carlo method. It was assumed that the short-range order affects the internal friction by changing the energy of the H or D atoms in the solid solution and therefore the activation energy of the relaxation process.

Computer simulation was carried out using real values of the energy of elastic interaction with various radii of repulsion interaction. The calculated spectra are in good agreement with the experimental data when the repulsion interaction extends to the third coordination shell. It was shown that the strain-induced interaction model, supplemented by repulsion in three nearest shells, is useful for describing solid solutions. It was also shown that the relaxation mechanism consists of "diffusion under stress" of H(D) atoms through tetrahedral interstices of the third b coordination shell near the O(N) atoms.

1. Introduction

Relaxation effects in solid solutions are associated with the interatomic interaction of dissolved atoms and can be used for an investigation of these interactions [1]. However, it is normal practice to use these effects for qualitative analysis or for rough estimates of the interaction energy. In this paper, an alternative procedure has been developed which uses internal friction data for the investigation of the interatomic interaction. The procedure involves the calculation of the relaxation spectra using models of the interatomic interaction [2, 3]. A comparison of the calculated spectra with the experimental spectra enables the validity of the model used for the description of the solid solution to be tested, the model to be corrected and additional quantitative information on the interaction energies to be obtained. Furthermore, computer simulation gives additional information on the relaxation mechanism.

Earlier, this procedure has been used to investigate the interaction of O–O in Ta [2], O–V in Nb [3] and O, N and C with substitutional atoms in V, Nb, Ta and α-Fe [2]. In this paper, the method is used for the investigation of H–H, D–D and O(N)–H(D) interactions in Nb and Ta.

2. Model of interstitial interaction

To describe the interstitial–interstitial interaction, we used a model of long-range, strain-induced (elastic) pair interaction supplemented by repulsion in the nearest coordination shells.

A comparison of the calculated structure of a long-range-ordered interstitial solid solution in a b.c.c. metal with the experimental structure showed that the structure is determined, in general, by the strain-induced interaction but, in the nearest coordination shells, there is an additional repulsion interaction, probably due to screened Coulomb interaction of charged interstitials [4–6]. The energies of the strain-induced interaction have been calculated correctly using a model of a discrete crystal lattice [7–10]; however, reliable calculations of the Coulomb repulsion in transition metals are not available. This effect has been calculated roughly for H–H interaction in Nb [8]. However, there is no information on the H–O repulsion interaction. According to electrotransport data, oxygen has an effective positive charge in Nb and Ta [11], as does hydrogen. Therefore we suggest that the H(D)–O(N) screened Coulomb interaction is repulsive.

In this paper, we used the energies of the strain-induced pair interaction of interstitials [7–10] and took into account the additional repulsion interaction in the

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nearest coordination shells by suppression of the elastic attraction in these shells. We used different radii of repulsion (suppression) to determine the radius of the repulsion interaction and the residual energies of elastic attraction, which are effective energies of interstitial interaction.

For example, the energies $W(\vec{r}_i-\vec{r}_j)$ of strain-induced H–H and H–O interaction in Nb are shown in Fig. 1. The vectors $\vec{r}_i$ and $\vec{r}_j$ show the positions of two dissolved atoms. Positive interaction energy values $W(\vec{r}_i-\vec{r}_j)$ denote repulsion. We can see that this interaction is strong, long range and anisotropic. In Fig. 1, the numbers in parentheses are the coordination shell numbers. Two or three energy values in a coordination shell (3a and 3b; 5a, 5b and 5c) indicate that, in some coordination shells, the interaction energy is dependent on the orientation of the pair of interstitials in the crystal lattice. An example is shown in Fig. 1(c), where the O–H pair in the third a shell has a [100] axis and in the third b shell has a [122] axis; the interaction energy is equal to −0.12 and −0.064 eV respectively.

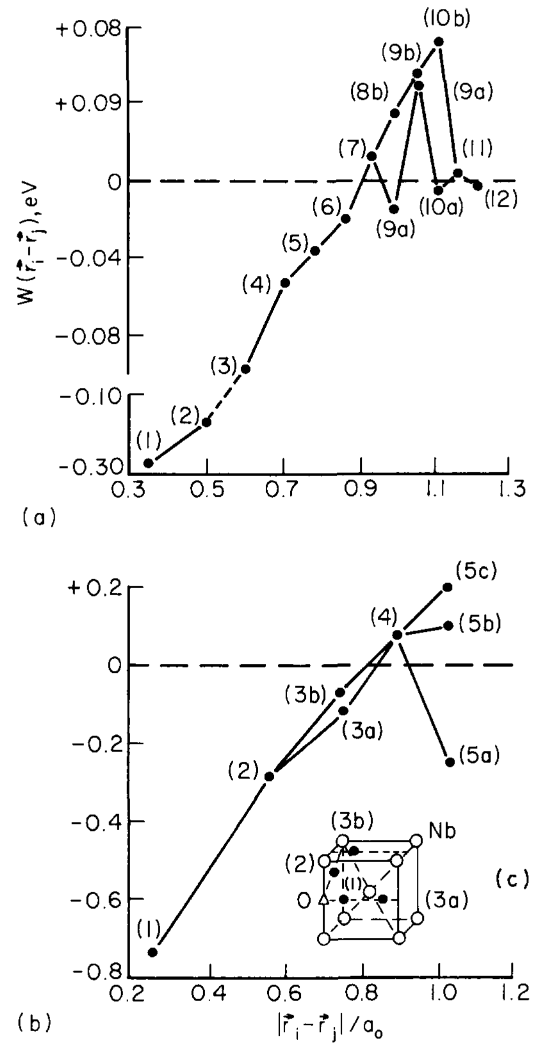

Fig. 1. The energy of the strain-induced pair interaction of hydrogen atoms (a) and oxygen–hydrogen atoms (b) *vs.* the interatomic distance in Nb and the position of tetrahedral interstices (filled circles) around O atoms (triangle) (c); numbers in parentheses are the numbers of the coordination shells.

The elastic interaction is strong and long range. We took it into account in many coordination shells. In all cases, the interaction is strongly attractive at the nearest distances up to the third shell ($W(\vec{r}_i-\vec{r}_j)<0$), but in other shells it may be repulsive ($W(\vec{r}_i-\vec{r}_j)>0$).

3. Calculation of internal friction

We used the model of "diffusion under stress" of H(D) atoms located in tetrahedral interstices near fixed O(N) atoms located in octahedral interstices [12, 13]. In a b.c.c. lattice, hydrogen or deuterium atoms create distortions of cubic symmetry. Therefore the single atoms do not "diffuse under stress". However, pairs of H(D)–O(N) atoms create distortions of lower symmetry and H and D atoms "diffuse under stress" near fixed oxygen or nitrogen atoms.

We assumed that the long-range interaction of interstitials creates O(N)–H(D) pairs and causes changes in the arrangement of interstitials (the short-range-order appearance) and the energy in tetrahedral interstices (ΔE value). Thus the diffusion barrier H_p of the pth hydrogen or deuterium atom is equal to

$$H_p = H_{\mathrm{D}} - \Delta E_p \qquad (1)$$

where H_{D} is the activation energy of diffusion of the H(D) atom and ΔE_p is the energy of interaction of the pth atom located in a tetrahedral interstice with other H or D atoms and fixed O or N atoms. We neglected the change in energy on the saddle point of the diffusion barrier according to calculations for Ta–O [2].

To calculate the short-range order and ΔE_p, a Monte–Carlo computer simulation was carried out using the approach of Metropolis *et al.* [14] (see details in refs. 2 and 3). The contribution of each pth H or D atom located in a model crystal to the internal friction is given by the Debye equation with the activation energy H_p. At a given temperature T, the internal friction Q^{-1} can be calculated by summing all the interstitial contributions.

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

where N is the number of H or D atoms in the model crystal, Δ is the relaxation strength per H(D) atom, $\omega = 2\pi f$ is the angular frequency, f is the frequency and τ_p is the relaxation time dependent on the temperature T

$$\tau_p = \tau_0 \exp(H_p/kT) \tag{3}$$

where τ_0 is the pre-exponential factor and k is the Boltzmann constant. Dividing Δ by T takes into account the well-known temperature dependence of the relaxation strength. The internal friction was calculated at each temperature by averaging Q^{-1} over many atomic configurations.

We also assumed that the interaction does not have a substantial effect on the pre-exponential coefficient τ_0 (data in ref. 15 confirm this assumption) and that values of the relaxation strength per atom (Δ) of H or D atoms located in the five nearest coordination shells around O or N atoms (the area of significant H(D)–O(N) attraction) are the same (beyond the fifth shell Δ is equal to zero).

H_D and τ_0 were taken from diffusion data [16] obtained using the Gorsky effect. For diffusion through tetrahedral interstices of a b.c.c. lattice [1]

$$\tau_0 = \frac{a_0^2}{72D_0} \tag{4}$$

where D_0 is the pre-exponential factor of the diffusion coefficient and a_0 is the lattice parameter.

4. Results and discussion

Experimental data are available on the temperature of the "hydrogen Snoek-type maximum" in seven Nb(Ta)–O(N)–H(D) systems. For three systems (Nb–O–H, Nb–O–D and Ta–O–H), experimental data are available over a broad range of frequencies and temperatures. For the other systems, except Nb–N–D, data are available only at one frequency. As we possess detailed experimental data on Nb–O–H alloys, we describe the results of computer simulation of this alloy in detail.

4.1. Nb–O–H alloys

Preliminary analysis was carried out at $f = 1$ Hz. At $f = 0.76$ Hz, the experimental temperature of the hydrogen maximum in Nb is 50 K [17]. Experimental data were recorded for specimens containing different concentrations of "light" and "heavy" interstitials. However, the temperature of the "hydrogen Snoek-type maximum" is almost independent of concentration, but its height is affected by concentration. Preliminary simulation of Nb–O–H alloys over a wide range of H (0.09–0.38 at.%) and O (0.23–1.85 at.%) concentrations showed that the calculated peak temperature is also independent of concentration. Therefore all results in this paper are given for one concentration (0.26 at.% of H or D and 0.8 at.% of O or N).

The results of computer simulation of the internal friction spectra in the range 30–80 K are shown for different radii of H–H and H–O repulsion in Table 1. When the repulsion is not taken into consideration, there are no internal friction maxima in the temperature range investigated. The absence of peaks is caused by values of ΔE_p and therefore H_p which are too high. In this case, if the maximum appears, its temperature is much higher than the experimental temperature. Internal friction maxima are also absent when the H–O repulsion extends to the third b coordination shell (the numbering of the shells is shown in Fig. 1). In this case, the H–O elastic attraction is too weak to hold hydrogen near oxygen and therefore $Q^{-1} = 0$.

For H–O repulsion in the two or three nearest shells and H–H repulsion in the three nearest shells, a maximum appears as in experiment. However, there is also a weak additional peak at higher temperatures in the calculated spectrum. The peak has been described in some experiments [17]. Generally, we can conclude that the calculated spectrum is in qualitative agreement with the experimental spectrum. There is quantitative agreement only for H–O repulsion up to the third shell and H–H repulsion up to the third shell. In this case, the calculated temperature (56 K) is in good agreement with the experimental temperature (50 K).

The shortest radius of the H–H repulsion interaction (three shells), which is necessary for agreement between the calculated and experimental spectra, is similar to the data obtained from the structure of hydrides [18].

For analysis over a broad range of temperature and frequency, we used two versions of potentials: H–O repulsion interaction in the first and second shells (version A) and in the first, second and third a shells (version B). The H–H repulsion was taken in the three nearest shells. The results of the energy calculations for version B are in good agreement with the experimental results over a wide frequency range (see Table

TABLE 1. Calculated internal friction spectra of Nb–H–O alloys (30–80 K, $f = 1$ Hz)

			H–O interaction				
			Radius of repulsion (shell number N)				
			0	1	2	3a	3b
H–H interaction	N	0	–	–	–	–	–
		1	–	–	–	–	–
		2	–	–	–	–	–
		3	–	–	B	A	–
		4	–	–	C	A	–
		5	–	–	C	A	–

Types of internal friction spectra: A, one peak at 56 K; B, one peak at 76 K; C, two or three peaks; –, peaks are absent.

TABLE 2. Calculated parameters of "hydrogen Snoek-type maxima"

Parameter	Calculated or experimental	Nb–H–O	Nb–D–O	Ta–H–O
T_p (K) at	Calculated	74	98	87
$f = 1000$ Hz	Experimental	79	106	77
H'_{eff} (eV)	Calculated	0.145	0.17	0.13
	Experimental	0.135	0.17	0.12
References[a] for experimental data		[19, 20]	[20, 21]	[19]

[a] The experimental data were used for the calculation of T_p and H'_{eff}.

TABLE 3. Comparison of calculated and experimental temperatures of internal friction maxima

Alloy	f (Hz)	T_p (K)	
		Calculated	Experimental
Nb–H–N	0.76	65	60 [23]
Ta–H–N	0.61	63	50 [24]
Ta–D–O	20000	143	126 [25]
Ta–D–N	0.76	98	65 [24]

2, where the experimental data were used for the calculation of the experimental values of H'_{eff}). There is no agreement for version A.

It is interesting that the calculated spectrum is not determined by the highest energy of H–O attraction after compensation for elastic attraction in the nearest shells, which is equal to -0.064 eV in the third b shell. We calculated the internal friction using, in succession, the value of -0.064 eV in the first, second and third a or third b shells without attraction in the rest of the shells. The temperature of the peak was in agreement with the experimental temperature only for the third b shell. This means that the axis of the H–O pair in Nb is close to the [111] direction but not to [100]. Therefore we can observe the peak in monocrystals when an alternating load is applied in the [111] direction but not in the [100] direction. This result is confirmed by experiment [22]. Figure 1 shows that the hydrogen atom can move during relaxation from one tetrahedral interstice in the third b coordination shell near an oxygen atom to another tetrahedral interstice in the same shell.

4.2. Other alloys

Computer simulation of the internal friction of Nb–O–D and Ta–O–H alloys, for which experimental data are available over a wide frequency range, confirmed the results for Nb–O–H alloys. Using version A of the potentials gives results which do not agree with experiment. When version B was used (Table 2), we obtained good agreement for the calculated temperatures of the peaks and the effective activation energies of the relaxation process with experiment. An increase in the repulsion radius of O–H(D) pairs up to the third b shell results in the absence of a peak.

Thus in all three investigated systems (Nb–O–H, Nb–O–D and Ta–O–H), the repulsion interaction is essential up to the third a shell and the model of the strain-induced interaction of H–H(D–D) and O–H(D) atoms, supplemented by repulsive interaction, is useful for the description of the internal friction due to "diffusion under stress" of H and D atoms.

It is interesting that the calculated effective activation energy H'_{eff} is close but not equal to the sum of the activation energy of diffusion of H or D atoms and the maximum energy of attraction of O and H(D) atoms (in the third b shell). For the Nb–O–D alloys, the difference is equal to 0.02 eV; for Nb–O–H, -0.012 eV. The result shows that the internal friction is not determined only by the maximum interaction energy, but also by the interaction in several coordination shells.

In the case of the four other alloy systems, the computer simulation was performed using only version B of the potentials (Table 3). In three cases (Nb–N–H, Ta–N–H, Ta–O–D), the calculated temperatures of the internal friction peaks are in good agreement with experiment. In one case (Ta–N–D), the difference is significant, but the results do not mean that the model of interatomic interaction is not useful for the description of these solid solutions.

5. Conclusions

(1) The model of long-range, strain-induced (elastic) H–H(D–D) and O(N)–H(D) interaction, supplemented by repulsion interaction in the nearest coordination shells, is useful for the description of solid solutions.

(2) The repulsion interaction of interstitial atoms in b.c.c. metals extends to the third coordination shell.

(3) The mechanism of the "hydrogen Snoek-type relaxation" consists of "diffusion under stress" of H(D)

atoms through tetrahedral interstices of the third b coordination shell near the O(N) atoms.

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