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The Hydrogen Influence upon Oxygen Snoek Relaxation in Nb-Ti Alloys

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Abstract. The oxygen Snoek peak was measured at frequency $f = 1..10$ Hz for Nb-0.05 wt.%O and 48wt.%Nb - 52wt.%Ti - 0.1wt.%O alloys. The alloys hydrogenizing leads to the decrease of height and to the shift of the temperature of oxygen Snoek peak for Nb-O and Nb-Ti-O alloys both. The new approach for computer simulation of temperature dependent internal friction spectrum has been carried out for the study of the hydrogen influence mechanism. The following pair interactions have been taken into account: H-O, H-Ti, O-Ti, H-H, O-O. The long-ranged strain-induced (elastic) interaction model, supplemented by short-range Coulomb repulsion for H-H, H-O, O-O and "chemical" interaction for H-substitutional and O-substitutional atom was used for simulation. The influence of the interaction on atoms arrangement (short-range order), the activation energy and the pre-exponential factor of oxygen relaxation time was taken into account. It is shown that the influence of hydrogen on oxygen Snoek peak can be explained by the influence of hydrogen on energy of oxygen atoms in solid solution and therefore on activation energy of diffusion.

1. INTRODUCTION

Internal friction (IF) spectra caused by interstitial atoms (IA) diffusion depend on interaction of solute IA with each other and with substitutional atoms [1,2]. The situation when substitutional atoms are considered as practically unmoveable at the measured temperature range in comparison with IA is studied rather well. For example, the influence of substitutional atoms on Snoek relaxation in b.c.c. metals or the influence of substitutional atoms and "heavy" IA (O, N) on Snoek-type hydrogen relaxation in Nb, V, Ta [1,3]. In these or similar cases the relaxation spectra could be explained from the viewpoint of interatomic pair interactions.

The situation with influence of mobile IA on diffusion under the stress of "heavy" IA is not enough studied. In particular, this case takes place with the hydrogen influence on oxygen Snoek relaxation in Nb and Nb-based b.c.c. alloys [9]. Further the goals of this paper are: 1) to study the hydrogen influence on oxygen Snoek relaxation in Nb and Nb-68at.%Ti (or 52 wt%Ti); 2) to study the influence of interatomic pair interactions on this effect with the help of computer simulation. Such an investigation seems to be interesting from the viewpoint of mechanism of relaxation as well as from the viewpoint of hydrogen behaviour in real Ti-Nb alloy used for hydrogen storage.

2. EXPERIMENTAL PROCEDURE

The Nb (0.05 wt.% or ~0.3 at.% O) and Nb-Ti (~0.1 wt.% or ~0.4 at.% O) samples with Ti content 68 at.% have been vacuum melted and drawn into wires of 1 mm in diameter. The samples were annealed at 1073 K during 2 hours. Hydrogenizing was carried out at 800 °C. After this heat treatment the concentrations of hydrogen in Nb were 0.005, 0.05; 0.09; 0.3 wt.% and in Nb-Ti that was 0.15; 0.22; 0.47; 1.0 wt.% H.

IF measurements were carried out with the use of different low frequency techniques*

- 1) free decay torsion inverted pendulum "RKM-TPI" ($f=1-2$ Hz),
- 2) forced, computer controlled, torsion inverted pendulum (1-10 Hz).

All the measurements were performed in vacuum of $6 \cdot 10^{-5}$ Torr or higher with heating-cooling rate 2 K/min.

* Experimental points marked as up triangles in Fig.1 and 2 are measured by E. V. Schinaeva (Mat.Sci.Dep. of MSAT University) using free-decay pendulum; marked as squares in Fig.1 are from [9]; all the other points are authors results, square points in Fig.2 are measured using forced pendulum.

3. EXPERIMENTAL RESULTS

The oxygen and nitrogen Snoek peaks are observed at ~ 425 K and ~ 560 K ($f = 1$ Hz) in Nb at temperature dependent IF (TDIF) curves. Peak parameters are in good agreement with the results of other researchers [1]. The hydrogen alloying leads to the increase in temperature (Fig. 1,a) and to the decrease in height (Fig. 1, b) of oxygen Snoek peak. Additionally to our experimental points (triangles) the temperatures of oxygen Snoek peak are calculated from activation energies and pre-exponential factors reported by Schmidt and Wipf [9].

Additionally to relaxation peaks the non-relaxation peak connected with hydride transformation is observed in the range of positive temperatures on TDIF curves for samples with 0.05 wt.% (4.4 at.%) H and more. This hydride phase transformation peak (HPTP) gives considerable difficulties to study oxygen Snoek peak. For example, the HPTP temperature for sample with $H/Nb = 0.28$ is ≈ 420 K, which is rather close to the oxygen Snoek peak location. The temperatures of HPTP depend on hydrogen content and coincide well with the solvus line of hydrogen in Nb, its height depends on heating-cooling rate and frequency on the very similar well known IF peak due to martensitic transformation, i.e. $Q^{-1} \sim A/f$ (where $A = dT/dt$ is heating or cooling rate: T - temperature, t - time, f - frequency of oscillations. The HPTP height (nearly $800 \cdot 10^{-4}$) for alloy with $H/Nb=0.28$ completely covers oxygen Snoek peak with height $Q^{-1} < 10^{-2}$. That circumstance leads to the increase in mistaken range of experimental data and to the scattering in our experimental data and data calculated from paper [9]. According to our results the oxygen Snoek peak shift in $H/Nb=0.1$ is ≈ 10 K, according to [9] that shift is smaller. Nevertheless, the effect is qualitatively similar: hydrogenizing leads to the increase in temperature and to the decrease in height of oxygen relaxation.

Fig. 1

Figure 1. The influence of hydrogen content on the temperature and relative height of oxygen Snoek peak in Nb; circles - results of computer simulation, other - experimental points.

Fig. 2

Figure 2. The influence of hydrogen content on the temperature and relative height of oxygen Snoek peak in Nb-68at.%Ti; circles - results of computer simulation, other - experimental points

The oxygen Snoek peak in Nb-68at.%Ti is observed at higher temperatures (468 K at 1 Hz, or 532 K at 10 Hz) in comparison with pure Nb. It is known that Nb alloying by Ti (1 at.%) leads to the additional oxygen peak appearance at the higher temperatures [10] as a result of oxygen jumps in the vicinity of Ti-atoms. The only one relaxation peak takes place in high alloyed Nb-68at.%Ti. The hydrogenizing increases its temperature (Fig. 2,a) and decreases height (Fig.2,b) in the very similar way as that in Nb-O-H case. The temperature shift is ≈ 10 K at $H/(Nb+Ti)=0.14$ in comparison with hydrogen-free alloy. Additionally to Snoek peak two more peaks are observed ($f=1$ Hz) in the alloy with 0.62 (H/Me): at ≈ 380 K and ≈ 600 K. The first peak is HPTP, the second one is supposed to be hydride transformation strain-induced peak. These peaks in Nb and Nb-Ti alloys will be reported in the another paper.

4. COMPUTER SIMULATION OF INTERNAL FRICTION SPECTRA

As it is above pointed the increase in relaxation peak temperatures is the result of the activation energies increase due to the additional interaction of moveable atoms with other atoms in solid solution [4-8]. The peculiarity of oxygen relaxation in hydrogenized alloys is the uncertainty of the mechanism of high-moveable hydrogen atoms influence on oxygen atoms diffusion under stress and its activation energy. Computer simulation helps to clarify the situation. Method of simulation is given in details in [5,6].

The following assumptions are made for IF calculations:

- 1). The long-range interaction O-O, H-H, H-O, O-Ti, H-Ti affects the arrangement of O and H atoms (creates short-range order), changes the energy of O-atoms in octahedral interstices by ΔE_p and consequently changes the individual diffusion barrier H_p of the p-th oxygen atom: $H_p = H_D - \Delta E_p$ where H_D is the activation energy of diffusion of a O-atom in a dilute solid solution of oxygen in Nb.
- 2). The pre-exponential factor τ_0 of the relaxation time τ is independent of the solute interaction and is equal to τ_0 of the oxygen Snoek peak in Nb ($2,56 \cdot 10^{-15}$ s).
- 3) Each O atom has the same relaxation strength δ .

Thus, calculation of the IF has been performed in two stages:

- a) Monte Carlo computer simulation of the arrangement of mobile H and O atoms in the model crystal with fixed Ti atoms (Nb-Ti alloy) or without Ti atoms (pure Nb).
- b) Determination of the contribution of each p-th O atom to IF according to its activation energy H_p :

$$Q^{-1} = (\delta / T) \cdot \sum_{p=1}^N [(\omega \tau_p) / (1 + (\omega \tau_p)^2)],$$

where $\tau_p = \tau_0 \exp (H_p / kT)$, N is the number of O atoms in the model crystal, $\omega = 2\pi f$ is the angular frequency of oscillations, f ($= 1$ Hz) is the frequency of oscillations, δ is the relaxation strength per one oxygen atom, T is the temperature, k is the Boltzman constant. For simulation of a short-order and determination ΔE_p value by Monte Carlo method the energies of pairwise interactions H-H, O-O, H-O, H-Ti and O-Ti were used. The model of solute interactions is a long-range strain-induced (elastic) interaction supplemented by screened Coulomb interaction in the nearest coordination shells in case of H-H, O-O and H-O interaction and "chemical" interaction in case of O-Ti and H-Ti interactions [4,5,12]. The elastic energies are calculated for crystalline lattice of Nb and corrected for Nb-Ti alloy according to its elastic constants. "Chemical" part of interaction energy for O-Ti (-0.15 eV) is determined with the help of computer simulation for oxygen Snoek peak in Nb-1at.%Ti alloy reported in [10]. Energy of "chemical" H-Ti interaction (-0.08 eV) is determined using method given in [12] by comparing calculated and experimental values of the activation energy of diffusion [13].

5. RESULTS OF SIMULATION AND DISCUSSION

Oxygen Snoek peaks simulated in Nb with hydrogen content up to 20 at.% H are plotted in Fig.3. The hydrogen content increase leads to the increase in temperature and to the decrease in height of peak, and coincides rather well with our experimental results (Fig. 1) and results reported in [9]. The same situation takes place for simulated and experimental results in Nb-Ti alloy. The scattering of experimental data does not give the opportunity to find out if the influence of hydrogen is stronger or not in the presence of Ti in solid solution. Computer simulation evidences that the oxygen peak shift due to hydrogen is slightly stronger in alloy containing Ti: 13 K instead of 7 K in Nb for H/Me = 0.1 or 18 K instead of 13 K for H/Me = 0.2.

Fig. 3

Figure 3. The hydrogen influence on simulated IF curves for Nb.

Fig. 4

Figure 4. The influence of H content and Ti on ΔE_p

That is connected with the preferable distribution of oxygen and hydrogen atoms in the vicinity of Ti atoms. The influence of hydrogen is connected with the change of $1/\Delta E_p^{av}$ energy of oxygen atoms due to their interaction with hydrogen and other solute atoms. The titanium increases that effect. Computer simulation predicts the effect saturation due to the increase in hydrogen, which was experimentally observed in [9]. The peak decrease is the result of broadening of ΔE_p distribution with the increase in hydrogen content. Oxygen atoms with the energies very different from the average values ΔE_p do not give contribution to oxygen Snoek peak. To sum up, the computer simulations show that the influence of hydrogen on the parameters of oxygen Snoek peak in Nb and b.c.c Nb-Ti alloy is qualitatively and quantitatively explained by its elastic interaction with oxygen atoms.

6. CONCLUSIONS

1. Hydrogenizing of Nb and Nb-Ti leads to the increase in temperature and energy, and to the decrease in height of the oxygen Snoek peak and to the appearance of new hydride transformation induced internal friction peaks.
2. The hydrogen influence is explained by the interaction of soluted atoms, which leads to the decrease of oxygen atoms energy and to the increase of the activation energy of diffusion in solid solution.

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References

- [1] Blanter M.S., Piguzov Yu. V., Golovin I.S. et al. The method of internal friction in metallurgical research (a reference book), Moscow: Metallurgia, 1991, 246 p. (in Russian).
- [2] Nowick A.S., B.S.Berry. Anelastic Relaxation in Crystalline Solids. Academic Press, New York and London, 1972.
- [3] Cannelli G., Cantelli R., Cordero F. et al. Materials Science Forum. Vol.119-121, (1993), p. 29-38,
- [4] Blanter M.S., Fradkov M.Y. Acta Met. et Mat., v.40, p. 2201 (1992).
- [5] Blanter M.S. Phys. Rev. B, v. 50, p. 3603, (1994).
- [6] Golovin, Blanter, Schaller., to be published
- [7] Koiwa M. Phil.Mag., v.24, p. 81, (1971).
- [8] Koiwa M. Phil.Mag., v.24, p. 107, (1971).
- [9] Schmidt R., Wipf H. Materials Science Forum. Vol.119-121, p.133-138
- [10] Szokopiak Z.C. and Smith J.T. J. Phys.D: Appl. Phys., v.8 (1975), p.1273
- [11] Blanter M.S., Khachatryan A.G. Met.Trans. v.9A, p. 753 (1978).
- [12] Blanter M.S. and Vasiljev A.V. in: Stability of Materials (Ed. by A.Gonis et. al.), Plenum Press, 1996, p.211.
- [13] Cannelli G. and Cantelli R. Proc. of 2-d Congress of Hydrogen in Metals. Paris, Pergamon Press (1977), p.1.