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Mechanical loss studies of O–O interactions in Ta

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Abstract

Mechanical loss measurements are carried out on Ta with various O contents (0.01 to 0.6 at.%) by applying frequencies of about 1 Hz and about 1 kHz. The mean activation enthalpy of relaxation, as determined from the frequency shift of the peak temperatures, does not depend on the O content, *i.e.* $H_m = (1.10 \pm 0.01)$ eV. The Snœk maxima are broadened and shifted to higher temperature with increasing O content. The results are analysed in terms of the "random cooperative strain interaction" model for elastic dipoles. In this model, interactions between interstitial atoms, being long range in nature, are treated by a mean field approximation. The critical temperature characterizing the O–O interactions in Ta is proportional to the square root of the O concentration, and increases from 70 K for 0.036 at.% O to 260 K for 0.6 at.% O.

1. Introduction

The interaction of interstitial solute atoms in b.c.c. metals at higher contents give rise to a broadening of the Snœk maxima compared with a single Debye curve [1–8]. From the formal point of view, this broadening can be described by a continuous or discrete distribution of relaxation times. The discrete distribution was introduced in the so-called "clustering model" by assuming that interstitial–interstitial (i-i) interactions are short range in nature and lead to the formation of small clusters (pairs, triplets) of interstitial atoms. The clusters should give rise to additional mechanical loss maxima at temperatures higher than that of the Snœk maximum for isolated interstitials (see, for example, refs. 1 and 2).

The "clustering model" was later questioned [3–5] and was recently examined in detail for the case of Nb–O [6]. It was demonstrated [6] that the model cannot explain the experimentally observed behaviour: with increasing O contents, the Snœk maxima are continuously broadened and shifted towards higher temperatures. However, the mean activation enthalpies calculated from the frequency shift of the Snœk peaks (1 Hz, 1 kHz) do not depend on the interstitial content. Based on neutron scattering experiments, the existence of a short-range order was also questioned recently by Novion and coworkers for Nb–O and Ta–O [7, 8].

As demonstrated in refs. 9 and 10, from all of the i-i interaction models known at that time, the random cooperative strain interaction (RCSI) model gives the best description of the characteristics listed above. The assumptions that i-i interactions are long range in nature and that the interaction energies between the dipoles are distributed randomly in a Gaussian manner with the mean zero lead to the continuous distribution of relaxation times. In the mean field approximation (MFA), one can obtain the analytical formulae which describe the internal friction curve of the Snœk effect, thus allowing quantitative analysis of the experimental data [9, 10].

Later, researchers were able to show that the broadening of the Snœk maximum in Fe–C is accounted for equally well by the RCSI model as introduced in refs. 6 and 9. The aim of this paper is to perform a quantitative analysis of mechanical loss measurements on Ta–O and to check again the applicability of the RCSI model.

In the meantime, Blanter and Fradkov [11] have published a study on i-i interactions, in which a computer simulation method was applied. Basically, the broadening of the Snœk maxima is explained by the appearance of short-range order resulting from long-range i-i interactions. Qualitative agreement with the main observations can be achieved if a Coulomb repulsion, of importance up to the third coordination shell around an interstitial atom, is introduced. However, a quantitative application of this model to experiments – comparable with refs. 9 and 10 – has yet to be achieved.

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2. Experimental results and preliminary analysis

The samples were prepared from high purity Ta (supplied by Metallwerke Plansee, Reutte [12]). The main metallic impurity was Nb (less than 100 at.ppm). The content of interstitial impurities was reduced by resistance heating of the wires (about 100 mm long and 1.5 mm in diameter) to 2800 K until a pressure of less than 10^{-7} Pa was reached ($\rho_{273K}/\rho_{4.2K} \approx 3000$). Various O contents between 0.01 and 0.6 at.% (see Table 1) were introduced by annealing at temperatures between 2070 and 2670 K in flowing high purity O_2 at appropriate pressures [12]. Internal friction measurements (free decay method) were carried out with two different apparatus operating in two frequency ranges. For $f \approx 1$–15 Hz, we used an inverted torsion pendulum and, for $f \approx 1$ kHz, a resonant bar apparatus with flexure eigenvibrations was used.

The mechanical loss spectra $Q^{-1}(T)$ obtained by using both types of apparatus are presented in Fig. 1 for the same specimen containing 0.34 at.% O. The temperatures of the Snœk maxima measured at 2.5 Hz and 2.2 kHz differ by about 130 K.

A preliminary analysis of the measurements was made by fitting the curves with a single Debye peak using the non-linear regression method described in ref. 13. In this way, we obtained for each curve the maximum temperature T_p of the loss peak and a value of the activation enthalpy H_d, which is strongly affected by the "peak width". From the T_p values for low and high frequencies (hertz and kilohertz), the "mean activation enthalpy" H_m may then be calculated as usual (see, for example, ref. 6).

The results of this analysis are presented in Fig. 2, where H_m and H_d are plotted *vs.* the O concentration c. Evidently, the mean activation enthalpy does not depend on c and $H_m = (1.10 \pm 0.02)$ eV (in good agreement with $H_m = 1.10$ eV [4]). H_d decreases systematically from 1.10 (0.01 at.%) to 0.9 eV (for 0.6 at.%). This means that the mechanical loss maxima are broadened up to 20% relative to a single Debye maximum corresponding to $H_d = 1.10$ eV. We can also confirm the earlier observations [4] that the peak temperature (normalized to the same frequency) increases slightly with the O content.

All these results indicate that the interaction of O interstitial atoms in Ta represents an interesting system for applying the RCSI model.

TABLE 1. Values of activation enthalpies H_{fit} and H_{fs}, parameter σ and critical temperature T_c for different O contents, obtained by applying the RCSI model

Oxygen content (at.%)	0.01	0.036	0.106	0.183	0.34	0.45	0.6
H_{fit} [eV]							
1 Hz	1.10_2	1.09_9	1.09_6	1.08_6	1.09_8	1.09_9	1.08_4
1 kHz	–	1.11_6	1.08_5	1.06_4	1.06_5	1.09_2	1.10_0
$\bar{H}_{fit}$ (eV)[a]	1.10_2	1.10_6	1.09_0	1.07_5	1.08_2	1.09_5	1.09_2
H_{fs} (eV)	–	1.08_8	1.09_2	1.09_0	1.09_5	1.10_7	1.08_8
σ (meV)							
1 Hz	0	5.6	10.0	11.2	14.6	19.4	23.1
1 kHz	–	6.7	10.9	11.1	16.7	17.5	21.0
$T_c = \bar{\sigma}/k$ (K)[a]	0	71	121	129	182	214	256

[a] $\bar{H}_{fit}$, $\bar{\sigma}$: mean values for 1 Hz and 1 kHz.

3. Analysis by applying the RCSI model

The basic ideas of the RCSI model are described in detail elsewhere [9, 14]. Here, we only want to point out that the mean field treatment given in ref. 14 should be supplemented by introducing the so-called "Onsager correction", as described in ref. 9.

In the framework of this model, by using a linearized MFA, one can obtain an analytical formula for the Snœk effect as the loss tangent Q^{-1} *vs.* $\omega\tau$ [9], *i.e.*

$$Q^{-1} = \frac{\Delta}{\beta^2\sigma^2}\left\{\left(\left[\{(1-\beta^2\sigma^2)^2 - \omega^2\tau^2\}^2 + 4(1+\beta^2\sigma^2)^2\omega^2\tau^2\right]^{1/2} - \{(1-\beta^2\sigma^2)^2 - \omega^2\tau^2\}\right]\Big/2\right)^{1/2} - \omega\tau\right\} \quad (1)$$

where σ is the standard deviation of the Gaussian distribution of interaction energies of elastic dipoles, τ is the relaxation time for a non-interacting system [9] and

$$2\Delta = 2\beta c v_0 (\delta\lambda)^2 / 9 J_u$$

is the relaxation strength, with $\beta = 1/kT$, where k is Boltzmann's constant, $\omega \equiv 2\pi f$ is the angular frequency, v_0 is the atomic volume, J_u is the unrelaxed compliance, and $\delta\lambda = \lambda_1 - \lambda_2$ ($\lambda_{1,2}$ are components of the λ tensor [1]). The model predicts the existence of a critical temperature, defined as $T_c = \sigma/k$, below which a local order can be expected. As $\sigma \propto c^{1/2}$, we expect $T_c \propto c^{1/2}$. Equation (1) is valid for $T > T_c$ and represents a non-Debye behaviour. With increasing σ, the half-width of the loss maximum increases, its position shifts slightly towards higher temperatures and its height decreases [9], as observed in the experiments.

For the relaxation time τ (as usually), and Arrhenius equation is assumed, *i.e.*

$$\tau = \tau_\infty \exp(H/kT) \quad (2)$$

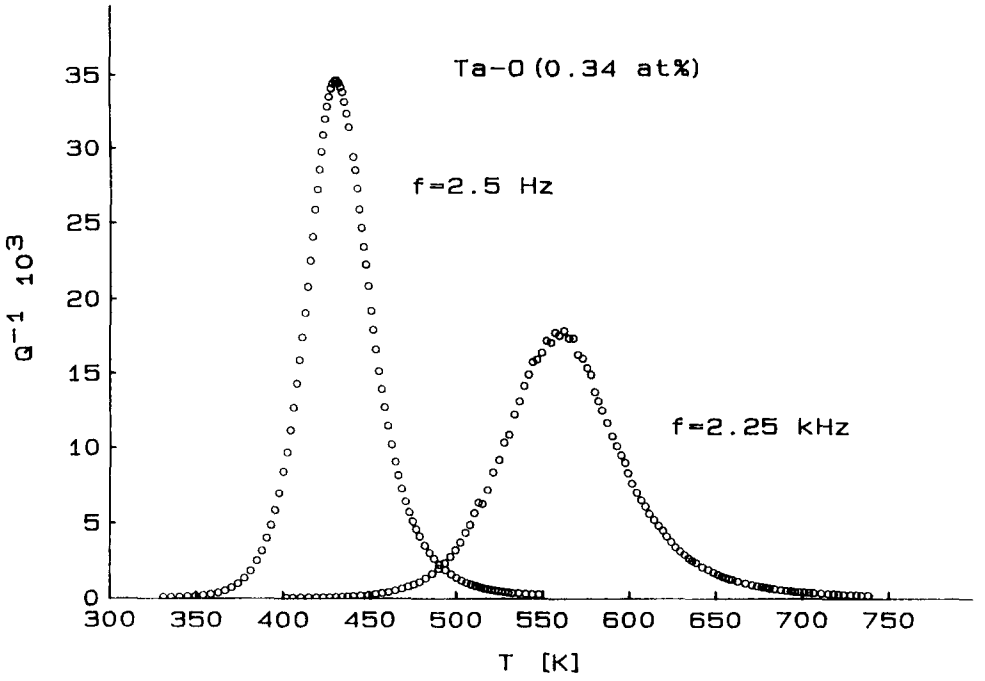

Fig. 1. Internal friction *vs.* temperature for Ta with 0.34 at.% O measured at two frequencies (f=2.5 Hz and 2.25 kHz).

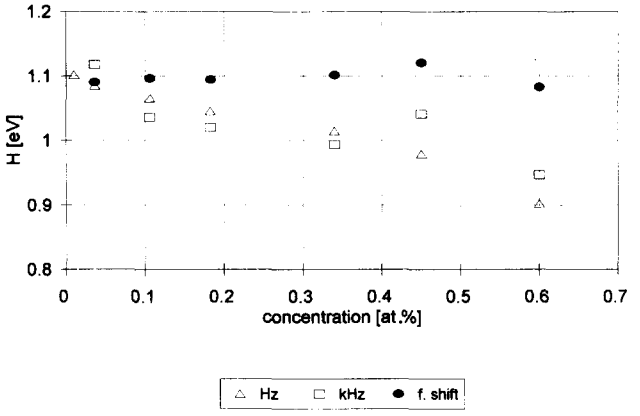

Fig. 2. Variation of the activation enthalpies H with O content. H_d is obtained by fitting single Debye maxima to the experimental data (△, 1 Hz; □, 1 kHz); H_m (●) is determined from the frequency shift of the maxima.

where τ_∞ is the pre-exponential factor and H is the activation enthalpy. Taking into account that internal friction measurements are not usually carried out at precisely constant frequency (because of the slight temperature variation of the modulus), the term $\omega\tau$ in eqn. (1) can be expressed [5, 13] as

$$\omega\tau = \exp\left\{\frac{H}{k}\left(\frac{1}{T} - \frac{1}{T_p}\right) + \ln\frac{f(T)}{f(T_p)}\right\} \quad (3)$$

where T_p corresponds to $\omega\tau = 1$. The form of the model function $Q^{-1}(T)$ describing the internal friction as a function of temperature is obtained by substituting eqn. (3) into eqn. (1). This function depends on four parameters, *i.e.* T_p, H, Δ and σ, representing the fit parameter vector. In evaluating experiments, the background damping may be approximated by a linear function of $A+BT$. The parameters A and B were calculated by fitting a straight line to the experimental points at both sides of the $Q^{-1}(T)$ maximum.

In the framework of this analysis we can introduce the following notations: H_{fit} is the activation enthalpy obtained from fitting individual curves with $Q^{-1}(T)$ according to eqns. (1) and (3); H_{fs} is the activation enthalpy calculated from the frequency shift of the loss maximum by making use of the fitting parameters T_p obtained for low and high frequencies.

According to the predictions of the RSCI model, we expect the following: H_{fs} and H_{fit} should be equal for all O concentrations; the parameter σ describing the broadening of the maxima should be proportional to $c^{1/2}$ and independent of the temperature range of measurements (1 Hz or 1 kHz).

4. Results and discussion

The results of the analysis made by applying the RCSI model are presented in Table 1. The values for H_{fit}, H_{fs} and σ obtained for both frequencies are listed for various O contents.

Figure 3 shows H_{fit} and H_{fs} *vs.* the O concentration. From this figure and Table 1, it can be recognized that, within the error limit ($\pm 0.01_3$ eV), the values of H_{fs} and H_{fit} agree for all O concentrations examined.

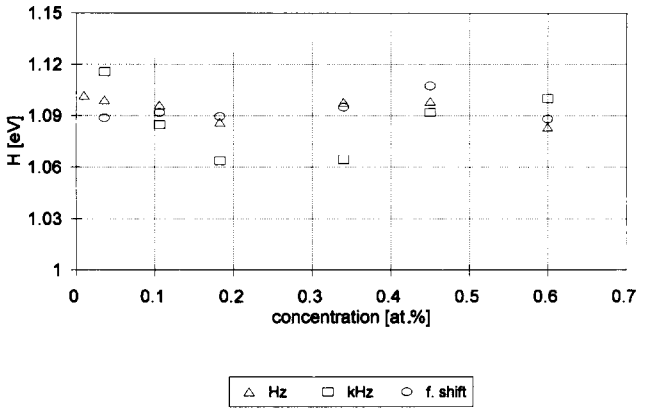

Fig. 3. Variation of the activation enthalpies H_{fit} (△, 1 Hz; □, 1 kHz) and H_{fs} (○) with O content. Results obtained by applying the RCSI model.

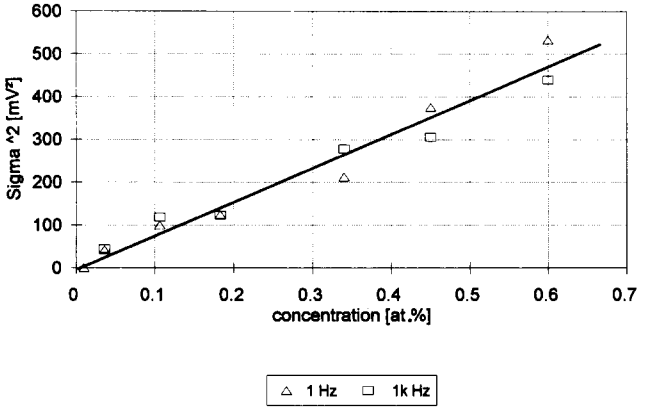

Fig. 4. Dependence of σ^2 on the O content (△, 1 Hz; □, 1 kHz).

The mean H_{fit} value of all concentrations is $H=1.09_1$ eV. This is in good agreement with the result of the preliminary analysis, *i.e.* $H_m=1.10$ eV, and with earlier experiments [4] (1.10 eV).

Figure 4 shows the variation of σ^2 with the O concentration. Both low and high frequency measurements may be well approximated by the same straight line, which is in good agreement with the prediction of the RCSI model. The critical temperature T_c, below which a local order can be expected, increases from 71 K for 0.036 at.% O to 256 K for 0.6 at.% O. Taking into account the results presented in Table 1 and Figs. 3 and 4, we may conclude that the RCSI model gives a good quantitative description of the interactions of interstitially dissolved O atoms in Ta.

5. Conclusions

The quantitative analysis of the Snœk maxima in Ta–O shows the following:

(1) The interaction between O atoms dissolved in Ta can be described well in terms of the RSCI model.

(2) The critical temperature characterizing this interaction varies between 70 K for 0.036 at.% O and 256 K for 0.6 at.% O.

(3) The activation enthalpy for thermally activated reorientation (diffusion) of O in Ta, determined by applying the RCSI model, is $H=(1.09\pm0.01)$ eV.

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