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INTERNAL FRICTION IN MOLYBDENUM CONTAINING NITROGEN IN SOLID SOLUTION FORM

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Abstract.- Molybdenum samples nitrided at 2400 K for 10 min and quenched in the liquid Wood's alloy have been studied by the internal friction /IF/ method. Two relaxational peaks have been observed on the IF curves: A at 392 K and B at 498 K /f=1 cps/. Parameters of the Arrhenius law for both peaks have been determined from their temperature shift /f=1-10 cps/ and from numerical decompositions of the experimental curves into elementary processes. It has been proposed that peak A is one of the dislocation-α peaks in bcc metals while B is the nitrogen Snoek relaxation in Mo.

1. Introduction. Internal friction in molybdenum with nitrogen content was studied for the first time by Mairinger and Schwope [1] who considered the peak at 580 - 640 K obtained for f=1 cps to be the nitrogen Snoek relaxation. Ma and Son[2] found this relaxation at 433 K /f=1cps/. Verner et al [3] have shown that the presence of nitrogen atoms in samples saturated with oxygen gives rise to the appearance, beside the oxygen Snoek relaxation /T_p=343 K, f=1 cps/, of additional peaks at temperatures 323, 393 and 448 K /f=2 cps/. The authors of [3] have assumed that the peak at 448 K is the nitrogen Snoek relaxation and the peak at 393 K is related to the directional ordering of O-N pairs; however, they have not given any model of formation of the peak at 323K.

In investigations on the stress relaxation in very pure Mo [4], nitrided and quenched in mercury, one of three observed processes has been interpreted as the directional ordering of N atoms with following parameters of the Arrhenius law: Q=1.0 eV, \( T_0=2.5\times10^{-14}s \). An IF peak at 395 K for 1 cps corresponds with them.

2. Investigated samples, experimental method, results of measurements.

In the present paper a molybdenum wire, 1 mm in diameter, has been studied. It contained less than 0.03 pct substitutional impurities while concentrations of interstitials were following: N - 17 ppm, O - 150 ppm, C - 20 ppm. The material was initially cleaned by heating in vacuum /2x10^{-6} Tor/ at 2400 K for 1 hour. After such cleaning the chemical analysis of Mo revealed 8 ppm N, 8 ppm O, 10 ppm C. Nitriding of samples was carried out by heating them at 2400 K in the nitrogen atmos-
phere for 10 minutes under the atmospheric pressure. In order to get a supersaturated solid solution the samples were quenched from the nitriding temperature in the Wood’s alloy kept at approx. 400 K.

IF measurements were performed by means of an inverted KG pendulum, described in [5], in the temperature range 300 - 700 K in vacuum $10^{-4}$ Tr; linear heating with a rate of 1 K per minute was applied. The temperature was measured by a thermocouple situated in the close vicinity of the middle of the sample. The amplitude of vibrations was $2 \times 10^{-5}$ and the frequency varied from 1 to 10 cps. During measurements along the 12 cm long sample there was a linear temperature gradient varying linearly with temperature. Regarding the middle of the sample these variations were described by equations: in the range 300 - 400 K $-(0.0058xT - 1.7)$ K/cm and in the range 400 - 700 K $(0.015xT - 5.5)$ K/cm. A furnace heating the sample was situated so that the maximum temperature occurred successively at ends of the sample.

In fig. 1 is presented the IF curve obtained for a no sample cleaned by the heat treatment and quenched in the Wood’s alloy /curve 1/. The IF peak observed at 339 K $/f=6.3$ cps/ is related to a layer of the Wood’s alloy forming on the surface of the sample and disappears completely after chemical etching /fig. 1, curve 2/. The temperature of the observed peak does not depend on the vibration frequency and corresponds with the melting point of the alloy /~340 K/. Similar effects, related to a surface layer of oil occurring on investigated samples, was referred in [6]. In the course of further investigations before IF measurements samples were etched chemically in order to eliminate the described effects.

In fig. 2 /curve 1/ is presented the IF curve obtained for a sample cleaned by the heat treatment /2400 K/1h in vacuum/ and quenched from this temperature. On this curve only a small residual peak can be seen at 532 K $/f=5.9$ cps/. This peak may be related to residual interstitial impurities which cannot be removed from the sample by the applied method. In the same figure is presented the IF curve obtained for a sample cleaned by the heat treatment and subsequently nitrided at 2400 K for 10 min and quenched /curve 2/; the nitrogen concentration was 111 ppm. It can be seen that in consequence of the existence of nitrogen in solid solution two IF peaks appear: A at 425 K and B at 531 K $/f=5.5$ cps/. As a result of heating during IF measurements /approximately up to 700 K/ peak A disappears completely whereas peak B is reduced by 90 pct.

IF measurements for nitrided samples were carried out for various vibration frequencies /1 - 10 cps/ and the Arrhenius law parameters $Q$ and $\tau_0$ have been determined for both observed peaks; for $(\omega\tau)_{\text{max}}=1$
the following values have been obtained: for A - $Q = (0.83 \pm 0.07)$ eV and $\tau_0 = (3.2 \pm 2) \times 10^{-12}$ s, for B - $Q = (1.30 \pm 0.06)$ eV and $\tau_0 = (1.4 \pm 0.7) \times 10^{-14}$ s. Suitable diagrams are presented in figs. 3 and 4. It is proper to add

Fig. 1: IF curve for a sample quenched from 2600 K in the Wood's alloy; 2 - IF curve for the same sample after chemical etching of the surface layer; $f = 6.3$ cps.

Fig. 2: IF curves for: 1 - a sample cleaned and quenched from 2400 K in the Wood's alloy; $f = 5.9$ cps; 2 - a sample cleaned, nitrided at 2400 K for 10 min and quenched in the Wood's alloy; $c_N = 111$ ppm $f = 5.5$ cps.

Fig. 3: Plot of the Arrhenius law for process A.

Fig. 4: Plot of the Arrhenius law for process B.
that for $(\omega \tau)_{\max} = 0.07$ [7] the pre-exponential factor for relaxation A is $4 \times 10^{-11}$.


The determined IF curves were decomposed into two elementary processes A and B/ using the method of fitting the physical parameters to experimental points by means of minimization of mean square deviations.

In the case of existence of a linear temperature gradient along the sample the $Q^{-1}(T)$ curve is described by the integral [8]:

$$Q^{-1}(T) = \frac{1}{L} \int_{-L/2}^{L/2} \text{sech} \left[ \frac{A}{k_B} \left( \frac{1}{T \cdot k_\gamma} - \frac{1}{T_p} \right) \right] dx \tag{1}$$

where $L$ is the length of the sample, $k$ - the temperature gradient, $x$ - the coordinate along the sample; $\Delta$, $Q$ and $T_p$ denote the intensity, the activation energy and the peak temperature of the relaxational process /fitted parameters/, respectively.

It can be shown that if the integration limits in (1) are symmetrical /a symmetrical temperature gradient/, the maximum of curve (1) occurs at $T_p$ with good accuracy. Taking into account variation of $k$ with temperature /as given above/ does not disturb this condition.

In fig.5 is presented as an instance a comparison of the theoretical curve calculated according (1) with experimental points /curve 2 of fig.2/. A certain misfit visible in the high-temperature side may be related to deformation of the curve due to the precipitation of nitrogen from solid solution. In this way nine curves have been decomposed and the obtained mean values for $Q$ and $\tau_c$ are as follows: for A $Q = (0.82 \pm 0.09)$ eV, $\tau_c = (1.5 \pm 0.4) \times 10^{-11}$ s and for B $Q = (1.25 \pm 0.04)$ eV, $\tau_c = (5 \pm 2) \times 10^{-14}$ s. Maximum deviations from mean values are taken as values of errors. It can be seen that parameters of the Arrhenius law for both processes agree in limits of errors with parameters obtained from temperature shift of peaks with frequency.

In fig.6 are presented intensities $\Delta_A$ and $\Delta_B$ of both relaxations versus concentration of nitrogen. The intensity of process B increases linearly with nitrogen concentration according to the equation:

$$\Delta_B = (0.19 \pm 0.01) \left[ \frac{1}{wt \%} \right] c_N + (1.6 \pm 0.9) \times 10^{-4}$$

This fact and the order of magnitude of the pre-exponential factor $\tau_c / 10^{-14}$ seem to point out that process B is the nitrogen Snoek relaxation in Mo /$T_p = 498$ K, f=1 cps/.

The pre-exponential factor $\tau_c$ for process A of the order $10^{-12} - 10^{-11}$ s indicates that this process should be related to dislocations.
which can originate in this sample during quenching in the liquid metal. The fact that for non-nitrided and quenched samples /fig.2,curve 1/ this peak does not occur points out that this process should be also related with nitrogen atoms in the solid solution; so, it is probably one of dislocational $\beta$ peaks observed in bcc metals [9-11].

As for peak B results of the present paper are inconsistent with findings of [3] /$T_p=438$ K, $f=1$ cps/ which confirmed the result obtained in [2] /$T_p=433$ K, $f=1$ cps/. However, it is worth to mention that the nitrogen Snoek relaxation has been obtained in [3] with the assumption that one of IF peaks revealed for samples containing nitrogen and oxygen atoms in the solid solution corresponds with this relaxation. Neither in [2] nor in [3] a linear correlation between the nitrogen concentration in the sample and the IF peak height has been obtained.

A linear correlation may also occur for the Snoek-Köster peak [12]. Yet it seems possible that peak B is not due to this relaxation because 1. for the S-K peak $T_p$ should increase with the concentration of nitrogen what has not been observed /e.g. for $f=1.05$ cps: $c_N=80$ ppm - $T_p=504$K $c_N=136$ ppm - $T_p=499$K/, 2.a characteristic for the S-K peak increase of $T_o$ and $Q$ with $c_N$ also has not been observed, 3.peak B may be well
described by a Debye curve with $\tau_0 \approx 10^{-4}$ s.

References.
11. P. Moser, as ref. [6], p. 25