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To cite this version:

HAL Id: jpa-00223341
https://hal.archives-ouvertes.fr/jpa-00223341
Submitted on 1 Jan 1983

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THE $\alpha$ PEAK IN DEFORMED NIOBIUM AND TANTALUM AND THE PROBLEM OF HYDROGEN IMPURITIES

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Abstract - Hydrogen degassing of Nb and Ta can be achieved effectively by Pd-surface layers and annealing in air or low pressure oxygen atmosphere at 420-450K. The H-Snoek-Koester peak can be removed completely and the intrinsic dislocation relaxation peaks $\alpha(\alpha')$ can be observed. Details of the experimental procedure are reported. The intrinsic $\alpha(\alpha')$ maximum appears in high purity Nb at 46 K (1 kHz), and in high purity Ta at 48 K (1 kHz).

Small traces of hydrogen in niobium or tantalum may suppress the intrinsic dislocation relaxation at low temperatures ($\alpha$ peak) and create a Snoek-Koester peak at somewhat higher temperature. A long standing controversy on this point was solved at the recent conference ICIFUAS-7 (1)-(4). In the studies of the authors on this problem it was shown that long time ultra-high vacuum (UHV) degassing treatments (~1 week) are required to remove hydrogen impurities from high purity niobium (2) (5) or tantalum (6) to levels below 1 at ppm. But even following such treatments some small traces of hydrogen are present, and usually one observes two dislocation internal friction peaks, a small residual H-Snoek-Koester (S-K(H)) peak and the intrinsic $\alpha(\alpha')$ peak ($\alpha$ and $\alpha'$ has not been separated up to now). In fig.1 we show the result of such a long time UHV degassing on the dislocation internal friction peaks in tantalum (6), which behaves very similar as earlier reported for niobium (2) (5).

Fig.1
Dislocation internal friction peaks of high purity Ta. (1) UHV degassed 7 days+1% plastic bending: $\alpha(\alpha')$ at 43 K and S-K(H) peak at 180 K. (2) Same specimen after (1) doped electrolytically with some at ppm H.

In the following we report on another technique of hydrogen degassing, which was recently suggested by Rodrigues and Kirchheim (7). A thin Pd layer, evaporated on the surface of an UHV annealed Nb or Ta specimen apparently reduces the surface barrier for the following reaction:

$$4 \text{H(in Nb)} + \text{O}_2 \rightarrow 2 \text{H}_2\text{O(in air)} + \Delta G^0.$$ 

As will be shown below, heating of Nb or Ta with a Pd surface layer in low pressure oxygen (200 mbar) removes hydrogen quantitatively from the metal.

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphyscol:19839107
Table 1: The preparation of high-purity hydrogen degassed Nb or Ta.

<table>
<thead>
<tr>
<th>1. UHV high-frequency heating device</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>decarburization of Nb or Ta</td>
<td>T(K)</td>
<td>p(mbar)</td>
<td>t(hour)</td>
</tr>
<tr>
<td></td>
<td>2150</td>
<td>4\times10^{-6}O_{2}</td>
<td>0.5</td>
</tr>
<tr>
<td>degassing of H for Nb or Ta</td>
<td>1500</td>
<td>1\times10^{-10}</td>
<td>3</td>
</tr>
<tr>
<td>degassing of O_{2}N</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>2600</td>
<td>3\times10^{-10}</td>
<td>2</td>
</tr>
<tr>
<td>Ta</td>
<td>2850</td>
<td>4\times10^{-10}</td>
<td>2</td>
</tr>
</tbody>
</table>

2. UHV-evaporation apparatus

Evaporation of Pd on all surfaces of the specimen (~0.2 μm)

3. UHV-measuring cryostate 10K-500K

H degassing in position for measuring of damping and frequency (bending oscillations) and plastic deformation in situ.

T=420-450 K, P_{O_{2}}=200 mbar, 1-3 days

Our preparation steps are indicated in Table 1. Thin single crystals plates 30×3×0.4 mm, were obtained by spark erosion from single crystal rods, prepared by electron-beam zone melting in UHV. Preparation step 1 served for decarburization, degassing and doping with O or N (if required) by high-frequency heating inside a UHV system.

After step 1, the specimen was quickly transferred into another UHV-system, containing an evaporation source for Pd evaporation. During this transfer to the other apparatus, the specimen is exposed to the open air and the formation of a thin oxygen surface layer must be expected, which is known to act as barrier for hydrogen. Therefore a better procedure would be to evaporate the Pd layer in the same apparatus as used for step 1. However, by technical reasons our procedure was as described and was working satisfactorily. A Pd layer of ~0.2 μm thickness was evaporated as preparation step 2.

After step 2, the specimen was transferred into the measuring apparatus, an all-metal UHV-system, containing a cryostate, where the specimen could be operated in bending oscillations (0.3-1 kHz) by electrostatic driving and detecting between 10 K and 500 K (5). Inside this system the specimen was heated to 420-450 K in an atmosphere of 200 mbar oxygen gas for several hours or days (step 3). The specimen could be plastically deformed in situ by bending for introduction of dislocations. The complete removal of hydrogen is indicated by the disappearance of the S-K(H) peak. This required a degassing time of 2-3 days.

Fig. 2 shows for Ta the gradual decreasing of the S-K(H) peak near 180 K (1.2 kHz) and the appearance and growth of the intrinsic dislocation relaxation peak α(α') at 48 K. I should be noted that the degassing treatment near 450 K allows the migration of oxygen impurity atoms in Nb and Ta and creates dislocation pinning. This was also inspected and will be discussed later.
Fig. 2
Dislocation internal friction peaks of high purity Ta.
(1) UHV degassed 5h+Pd surface layer (step 1+2, table 1).
(2)-(4) degassed in 200 mbar O₂ at 450 K. (4) completely degassed, α(α') at 48 K.

Fig. 3a
Dislocation internal friction peaks of high purity Ta:
(1) Completely degassed as fig. 2 α(α') at 48 K.
(2) Applying of 20 mbar H₂ gas at 293 K for a few seconds, following (1). At 180 K the S-K(H) peak. The specimen has taken-up hydrogen.

Fig. 3b
The frequency vs. T of the specimen of fig. 3a. The relaxation strength has shifted from 50 K to 200 K by hydrogen pick-up.
In fig. 3a and 3b we show the effect of 20 mbar hydrogen gas, introduced to the apparatus for a few seconds at 293 K. The internal friction (fig. 3a) and modulus curve (3b) changed from (1) to (2). As can be seen, the relaxation effect has shifted from 50 K to 200 K by this procedure. Clearly, the specimen has taken-up hydrogen at 293 K from the hydrogen atmosphere. In the normal vacuum of the apparatus, 10^{-8} mbar during pumping, or 10^{-3} mbar at pumps off, no hydrogen pick-up was observed at 300 K from the residual vacuum pressure gas, as will be shown later.

The same treatment, as described for Ta, was applied to Nb. Fig. 4 shows the complete degassed state of a high purity Nb specimen, plastically deformed (1% bending). At 44 K (0.3 kHz) appears the $\alpha(\alpha')$ peak. In Nb we inspected the influence of oxygen migration during heating to 500 K on the pinning of dislocations. Fig. 5-8 shows a sequence of measurements related to isochronal annealing treatments in the range 300K-500K.

The specimen was a high-purity Nb single crystal, doped with 25 atppm nitrogen in order to achieve some kind of standard free loop length of free dislocations. The residual oxygen impurity content is expected as ~1 atppm.
Dislocation internal friction of high purity Nb (+25 atppm N). Isochronal annealing of $Q^{-1}$ (300 K) background damping. Same specimen as fig.5. The step at 420-460 K indicates dislocation pinning by mobile oxygen atoms (~1 atppm oxygen bulk concentration).

Dislocation internal friction of high purity Nb (+25 atppm N). After annealing to 500 K (fig.6) the S-K(H) peak appears again at 160 K, the $\alpha(\alpha')$ peak (45 K fig.5) has disappeared.

Same specimen as fig.7 followed by a H-degassing by Pd-surface layer technique; $\alpha(\alpha')$ at 40 K appears again. Background damping $Q^{-1}$ (300K) same as in fig.7.
Fig. 5 shows the $\alpha(a')$ peak near 45 K as observed after H-degassing (450 K) followed by plastic bending (-1%) at 293 K. The specimen was isochronal annealed from 300 K to 500 K in the vacuum of the apparatus (10^{-5} mbar) and the background damping at 300 K was measured following each annealing step. (Fig. 6). The steplike decrease of $Q^{-1}(300 K)$ between 420 and 460 K indicates pinning by mobile oxygen atoms. The measurement of the damping at lower temperatures (Fig. 7) indicates that following 500 K annealing (10^{-5} mbar) the specimen shows the S-K(H) peak at 160 K, that means the specimen has picked-up hydrogen from the residual vacuum gas at 500 K. Another degassing treatment (420 K, 200 mbar oxygen, 65 hours) removed the S-K(H) peak again and we observed the $\alpha(a')$ peak near 40 K (0.6 kHz), somewhat reduced in size compared to Fig. 5, however, the background damping at 300 K in Fig. 8 is the same as in Fig. 7. Therefore, we conclude that the additional degassing between Fig. 7 and Fig. 8 has not introduced further pinning.

The pinning after annealing to 500 K is not complete. We observe a reduction of $Q^{-1}(300 K)$ by 75%. This indicated that either not enough oxygen atoms for complete pinning are present, or the binding energy dislocation-oxygen is relatively low, so that at 500 K only a dilute atmosphere of oxygen around the dislocation is formed. One can estimate that for a binding energy of 0.5 eV and bulk concentration of 1 atppm oxygen we obtain at 500 K a dilute atmosphere of oxygen atoms, where 3.5% of the dislocation sites are occupied (10^9 dislocation/cm^2 assumed), see (8). This situation appears realized in our specimen Nb 70/6, Fig. 5-8.

Finally, we compare the position of the intrinsic $\alpha(a')$ peak in niobium and tantalum, as observed here, with earlier observations. In our publication Maul et al. (2) we reported the intrinsic $\alpha(a')$ peak in niobium at 30 K (1.5 kHz) for a crystal doped with 800-1000 atppm oxygen. This appeared to agree approximately with the earlier reported $\delta$ peak of Mazzolai et al. (3) at 27 K (40 kHz) in "impure" material. In contrast with this result we reported in (2) for high purity Nb a peak temperature of 70 K (1.5 kHz) and considered this difference 30 K to 70 K as due to the influence of the free loop length of dislocations. This was questioned by Fantozzi and Ritchie (1). Here, in our present paper, we observed for high purity Nb 46 K (1 kHz) as peak temperature. This is compatible with the result of Mazzolai et al. (3) regarding the frequency difference. Inspecting again our earlier results on the 70 K (1.5 kHz) peak, we notice that this peak position resulted from a specific specimen history: Plastic deformation at 20 K followed by annealing steps at 40 K, 80 K, 100 K ... (see (5), Fig. 17,18). The peak showed a development and shifted from 45 K to 70 K during this treatment. We assume that the 70 K peak is an anologue to the Hasiguti peaks in f.c.c. metals, and reflects a specific dislocation point defect interaction. In Ta we observe the intrinsic $\alpha(a')$ peak at 48 K (1 kHz). This agrees reasonable with Mazzolai's (3) $\delta$ peak at 27 K (20 kHz). It follows that the early observations of Mazzolai and Nuovo (3), concerning the intrinsic dislocation internal friction peaks in Nb and Ta, obtain full support by the new degassing technique, and that the formerly named $\alpha$ relaxation (9)-(14) is indeed a S-K(H) relaxation, as suggested also by Ferron, Quintard and de Fouquet (4), and Shibata et al. (15).

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