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DISLOCATION PINNING EFFECT. A PROBE OF SELF-INTERSTITIAL AND HYDROGEN MIGRATION IN NIOBIUM AND TANTALUM

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Abstract. The internal friction and elastic modulus of high purity, dehydrogenated Nb and Ta single crystals were analysed after in situ cold-work and/or electron irradiation at temperatures down to 4 K.

In irradiated niobium, a marked dislocation pinning becomes evident at 6 K. Combined with previous resistivity data, this result is taken as evidence of long-range migration of self-interstitials.

In tantalum cold-worked at 4.2 K, a large pinning stage takes place during heating between 8 K and 13 K. It is interpreted in terms of point defect diffusion to dislocations. Possibly, minute amounts of hydrogen are involved. Typical activation enthalpies for the migrating defects are between 0.01 and 0.02 eV. Low temperature irradiation in the as-deformed state reveals additional pinning beginning at 6 K, which implies mobile intrinsic interstitials.

Résumé. Nous avons analysé le frottement interne et le module d'échantillons monocristallins de niobium et de tantale déshydrogénés, après écrouissage à 4.2 K et/ou irradiation électronique à cette température ou au-dessus.

Dans le niobium irradié, un stade d'ancrage des dislocations est nettement visible à partir de 6 K. Ce résultat, associé à des travaux antérieurs de résistivité, amène à conclure à la migration libre de l'interstitiel, dès cette température.

Dans le tantale écroui à 4.2 K, un grand stade d'épinglage se produit pendant le chauffage entre 8 K et 13 K. Nous l'interprétons en termes de diffusion de défauts ponctuels vers les dislocations. Il est vraisemblable que de très faibles quantités d'hydrogène soient impliquées. L'enthalpie de migration correspondante se situe entre 0.01 eV et 0.02 eV. L'irradiation à basse température d'échantillons déformés au préalable révèle un épinglage supplémentaire à partir de 6 K, ce qui implique la mobilité d'interstitiels intrinsèques.

1. INTRODUCTION

Interstitial atomic defects, created by irradiation, become mobile at very low temperatures in niobium [1-3] and tantalum [4,5]. This has been studied by resistivity techniques [3,4] and by dislocation pinning experiments using internal friction techniques [1,2]. We report here on dislocation pinning experiments on tantalum in comparison to niobium [1,2]. It is important for such experiments to have specimens almost free of hydrogen impurities [6], because interstitial hydrogen becomes mobile at very low temperatures and may also create dislocation pinning. Sometimes, hydrogen-free specimens may absorb hydrogen again in the course of the experiment and an overlap of several processes may occur. It is also more difficult to remove hydrogen completely from tantalum in comparison to niobium. Such effects appear to play a role in the experiments reported below. As a remarkable phenomenon, we noticed strong pinning effects in the unirradiated state, following cold-work at 4 K. If this results from residual hydrogen or intrinsic point defects or both has to be discussed. Similar experiments have been reported in [7,8]. However, at present no clear understanding could be obtained.

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2. SAMPLE PREPARATION AND EXPERIMENTAL APPROACHES

High-purity niobium and tantalum single crystals were prepared at the Max-Planck-Institut Stuttgart by UHV-electron beam zone melting. The 293 K to 4.2 K (under a magnetic field to suppress superconductivity) residual-resistance ratio of these single crystals was about 4000, and 8000, respectively, which indicates very small interstitial solute contents ($O, N, C \leq 3$ atppm). Plate-like specimens with orientation close to $\langle 110 \rangle$ and dimensions $0.5 \times 4.8 \times 25$ mm were cut by spark erosion, etched for surface cleaning and then additionally long-time degassed in UHV (for details see [6]). Residual traces of hydrogen were removed by evaporating palladium on the sample surface and conducting prolonged heating at 420–450 K in air. By virtue of the reaction $4 H (in Pd) + O_2 \rightarrow 2H_2O$ this treatment initially proposed by Rodrigues and Kirchheim [9] has been shown to result in H concentration well below 1 atppm [6, 10].

For the anelastic and irradiation study, the samples were mounted on a device specially designed to be operated in-line with a Van-de-Graaff accelerator, in the irradiation facility at the Centre Nucléaire, Grenoble [11]. Temperatures between about 2 K and 900 K are obtainable by combined use of a liquid helium stream and furnace heating. A Rh-Fe thermocouple is used to monitor the sample temperature.

In a preliminary step, the samples were plastically deformed by in-situ bending, at a level of about 0.5 % at temperatures of 220 K for niobium, or 4.2 K for tantalum. This cold-work was to produce the dislocation density required for (i) proper determination of dislocations peaks in the non-irradiated condition, (ii) sensitive analysis of dislocation pinning during post-irradiation anneals.

For the damping and dynamic modulus measurements, the samples were operated in flexural vibrations, with used of electrostatic excitation. Typical measuring amplitude was 10^{-6} . Automatic data acquisition enabled direct recording of the resonant frequency, f , damping, Q^{-1} , irradiation flux, ϕ , and absolute temperature T .

3. DAMPING PROFILES IN THE COLD-WORKED CONDITION

In a preliminary analysis, the prepared materials were examined in the non-irradiated condition. Fig. 1 shows the typical variations of damping and modulus as a function of temperature, in niobium plastically deformed at 220 K. A pronounced relaxation peak centered on 60 K for a measuring frequency of about 1100 Hz is observed. Although it appears to be very broad, no structure is visible.

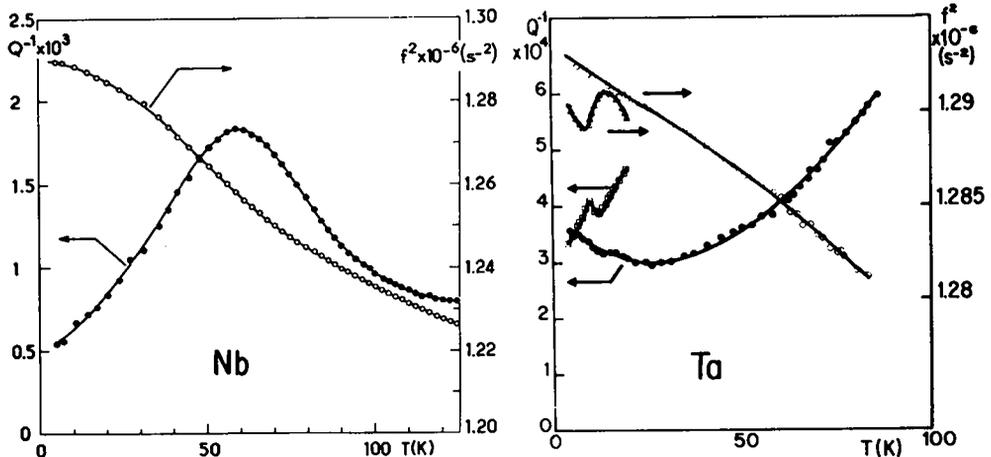


Fig. 1 (left). Temperature dependence of the internal friction, Q^{-1} , and the resonant frequency squared, f^2 , in monocrystalline niobium, following plastic deformation at 220 K. The peak centered at 60 K is the α peak.

Fig. 2 (right). Same for monocrystalline tantalum following plastic deformation at 4.2 K ; a) first heating to 20 K (dashed curve) and to 60 K (not shown) ; b) second heating to 85 K (full curve).

From prior work it is identified as the α -peak originating in the thermally activated kink-pair formation in non-screw (70°) dislocations [12,13]. It is recalled that it is of intrinsic character and exhibits extreme sensitivity to the eventual presence of dissolved hydrogen, since hydrogen concentrations as low as a few atomic ppm result in its suppression. See [14] for a resolution of this broad peak into two components, α_1 and α_2 . In that case, the existing dislocation population is different since the starting state is the one produced by cold-work at 4.2 K. The corresponding profiles for tantalum are presented in Fig. 2. This deformation was followed by two successive heating runs to 20 K and 85K, respectively. Consider the first anneal. The damping increases between 4.2 K and about 8 K, which denotes the onset of the α_1 (or α_2) peak. However, starting at 8 K, a marked drop occurs. Conversely the modulus is substantially increased. Now, on second heating, as is seen in the figure, both the damping and modulus vary smoothly, with no indication of the α_1 (α_2) peak any longer. This is well explained by considering that low temperature deformation results in the creation of dislocations of mainly screw character, while the preexisting non-screw dislocations, the ones responsible for the α peak get more curved and geometrically kinked. As a result less dislocation segments are available for the formation of kink pairs, which is hindered.

The detailed features of the pinning process are presented in Fig. 3. Originally dislocations are pinned. This may be due to interstitial defects created by prior cold-work and/or to the presence of residual traces of hydrogen. Then plastic deformation was produced by bending at 4.2 K. It is noted that the damping gets slightly increased and the modulus substantially decreased, by about 7%. On subsequent heating as already mentioned, pinning takes place as manifested by drastic variations of both physical parameters. In the temperature interval from about 8 K to 13 K. Clearly this effect implies the diffusion of some mobile species at these temperatures.

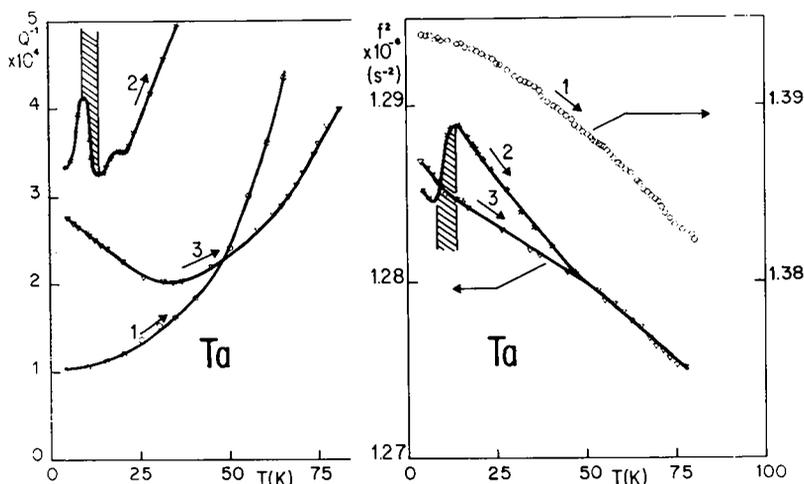


Fig. 3. Evolution of damping and modulus in tantalum as a function of various thermomechanical treatments (1) after 4.2 cold-working followed by annealing to 80 K, (2) during first heating to 45 K after additional cold-work at 4.2 K, (3) during a supplementary heating run. In run (2) dislocations which were freed from their pinning points by the plastic deformation get again pinned, at least partly, by diffusing hydrogen or intrinsic interstitial atoms, as appears in the hatched area.

Among candidates, hydrogen or possibly intrinsic interstitials created by the cold-work have to be considered. More detailed analysis is in progress to determine the corresponding kinetics. In a first approach the relevant activation enthalpy, H^M , could be obtained by use of different linear heating rates, V_1 and V_2 . As a result, the temperature location of the pinning stage is expected to be shifted from T_1 to T_2 , following the expression derived from consideration of Boltzmann statistics [15].

$$H^M = k \ln \left[\frac{V_2}{V_1} \times \frac{T_1^2}{T_2^2} \right] / (1/T_2 - 1/T_1)$$

In practice, heating rates were varied by a factor of about 8. The result is shown in Fig. 4. From the observed temperature shift of about 1 K., an activation enthalpy of 0.02 eV is inferred. As discussed in §5, this value is compatible with other information on hydrogen migration. However preliminary results obtained by the slope change method [15] at 7.7 K and 8.4 K indicate a somewhat lower activation enthalpy, close to 0.01 eV.

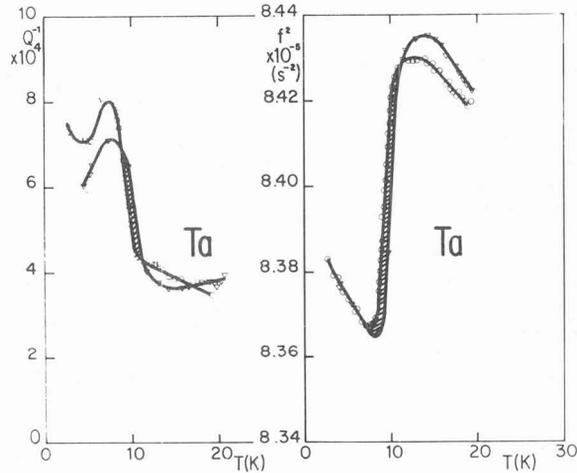


Fig. 4. Influence of the annealing rate, after 4.2 K plastic deformation, on the location of the pinning stage : heating rates for (a) and (b) were 4.4 and 0.56 K min⁻¹, respectively.

Finally, in the annealed condition at 85 K (curve 3 in Fig. 3), the same sample was irradiated at 6 K with 2 MeV electrons. No effect on damping or modulus was detected during the irradiation itself. In addition the successive pre- or post- irradiation damping and modulus profiles did not show any influence of the radiation-created defects. It is concluded that saturation pinning had been completed before irradiation for the structural condition considered such that dislocations could no longer act as sensitive sensors to detect the arrival of mobile defects at them. In the next section, only tantalum samples predeformed at 4.2 K right before irradiation are considered.

4. IN-FLUX AND POST-IRRADIATION EFFECTS IN TANTALUM

Fig. 5 illustrates the modulus variations which occurred in two tantalum samples I and II, which were initially given 0.5 % plastic deformation by bending at 4.2 K. Irradiation was then made at an approximate flux rate of 10^{11} e⁻.cm⁻².s⁻¹, at temperatures close to 4 K, 5 K or 6 K, respectively. A particular case is represented in the lower curve for which the sample had been annealed at 80 K after initial cold-work and prior to irradiation. All data points in the figure were recorded during the course of the irradiation except for the upper line which was obtained by momentarily stopping the irradiation and performing measurements at a reference temperature of 2.3 K. The vertical scales for the variations of the frequency squared were chosen to get the same sensitivity for the relative modulus variations in the two samples, indicated by the double arrow in the figure. It is seen that, for the 6 K irradiation, the relative modulus increase amounts to about 2×10^{-3} , for an irradiation dose of 2×10^{15} e⁻.cm⁻². It was verified that this increase did not originate in the diffusion of hydrogen or intrinsic defects created by the cold-work. In fact, the modulus of a sample only cold-worked but not exposed to irradiation varied by less than 2×10^{-4} during a several hour treatment at 6 K. Accordingly, the question is whether the increased pinning during the course of the irradiation arises from point defects created directly in the vicinity of the dislocation lines or arriving at them by random diffusion. Indicatively, the moduli of Cu and Mg irradiated at comparable doses and temperatures below those for the free migration of the self-interstitial, were increased by about 10^{-3} [11]. In the present work, irradiation at 4 K resulted in a smaller rate of increase, which seems to indicate that

some interstitial species become mobile between 4 K and 6 K. Fig. 6 shows typical profiles for the damping and the modulus behaviour during post-irradiation anneals following cold-work and cold-work + irradiation at 4.2 K. The pinning process starts at a slightly lower temperature than in the absence of irradiation which again suggests self-interstitial mobility in the vicinity of 6 K.

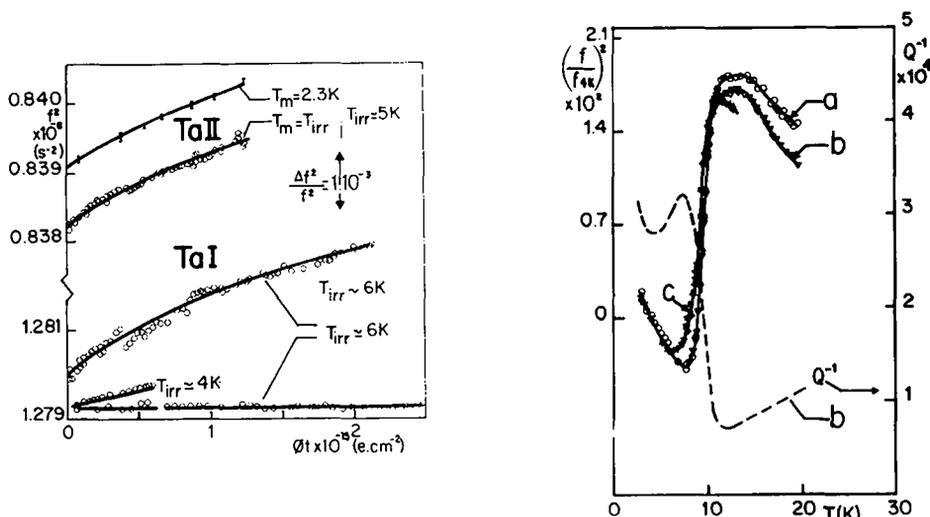


Fig. 5. Evolution of modulus during electron irradiation at various temperatures, T_{irr} . Indicated in the Fig. Only the data points for the upper curve were obtained in conditions of no flux, that is when flux was momentarily suppressed before irradiation was started again. Fig. 6. Relative modulus variations in tantalum during successive linear heating runs at a constant rate of $4 \text{ K} \cdot \text{min}^{-1}$: (a) cold-worked but unirradiated condition, (b) after cold-work at 4.2 K + irradiation at 6 K, (c) after cold-work + irradiation at 4 K. The dashed line shows the corresponding damping evolution in case b.

5. DISCUSSION AND CONCLUSIONS

In short, the experiments described show pronounced dislocation pinning at 8 - 13 K in tantalum following cold-work or irradiation, indicating the presence of a mobile defect. Similar pinning effects were observed in niobium in the temperature range 6 - 11 K following irradiation, as described in more detail in [1,2]. In-flux results on tantalum are compatible with defect mobility beginning at 4 - 6 K.

Close to the temperature range where pinning was observed, large resistivity recovery stages exist, in niobium at 6.3 K, in tantalum at 7.5 K, in which about 40 % of the radiation induced resistivity is recovered [16]. These recovery stages can be partly suppressed by impurities, indicating long-range migration of a radiation induced defect. As discussed in [16], the resistivity recovery is so large that it cannot be explained by hydrogen impurities, which were present in the resistivity specimens. However, the resistivity results give no clear information on the exact temperature for the onset of defect migration but could also support a temperature below 5 K. A naive straightforward interpretation can explain the pinning stages and the resistivity stages as due to the initiation of free interstitial migration in both metals. But some care appears necessary. The resistivity investigations extend only to temperatures of 4.7 K and more information should be obtained, and the pinning experiments, typically carried out in a range of very low defect concentrations, could be influenced by the action of additional impurity traps.

Other questions have been risen during this work: in the course of the experiments on niobium [1,2], the specimens remained apparently free of hydrogen. In tantalum of the present work this is not completely clear. In the beginning of the investigations the tantalum specimens showed the intrinsic α peak, which indicates a hydrogen-free

specimen. During the experiments, by pre-irradiation heatings between 4 K and 80 K following cold-work at 4 K the structure of the α peak changed. The high-temperature part of the intrinsic α peak was suppressed and only the 20 K component of the α relaxation remained, also indications of a H-Snoek-Koster peak appeared. Therefore, we assume for the following that the suppression of the high-temperature part of the α -peak is due to some minute traces of hydrogen, absorbed during the experiment.

The diffusion coefficient of H in Ta is known from perturbed angular correlation (PAC) experiments in the temperature range 15–30 K [17]. The data may be fitted to a power law of temperature or to an Arrhenius function with $Q=0.01$ eV and $D_0=10^{-9}$ cm² x s⁻¹. Extrapolation to 10 K yields values of 10^{-13} to 10^{-14} cm² x s⁻¹ for the diffusion coefficient of H in tantalum. From the usual relation between D and the mean residence time τ , that is $D=a^2/48\tau$, using 3.3 Å for the lattice parameter a, values of 5×10^3 to 5×10^2 s⁻¹ are inferred for the jump rate of hydrogen atoms at 10 K. This indicates enough mobility to enable pinning in the 8–13 K stage at the time scale of the experiments. Now it is interesting to note that dislocation break-away experiments on tantalum containing hydrogen [7] have evidenced two pinning stages, one at 7 K, the other near 30 K. Both were explained by the authors by the arrival of hydrogen at dislocation sites. The 7 K effect in [7] corresponds to our pinning stage.

The present discussion suggests the following interpretation: the pinning stage at 8–13 K in tantalum is due to residual hydrogen. Intrinsic interstitials become mobile at 4–6 K. If this interpretation is correct, the pinning experiments are a remarkable probe of hydrogen migration near 10 K. Interstitial migration at 4–6 K is compatible with the resistivity recovery results. However the observed pinning at 8–13 K may result from other causes. At low temperatures, hydrogen is usually present as hydride, and it is not certain that near 10 K enough free mobile hydrogen becomes available to create the observed effects. Cold-work at 4 K may also produce intrinsic interstitials and these defects may be responsible for the observed pinning. The effective activation enthalpy of 0.01 to 0.02 eV observed here would then refer to self-interstitial mobility. Further experiments are in progress to unambiguously identify the defect species involved in the drastic pinning effects evidenced.

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