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a AND β PEAKS OF COLD WORKED AND HYDROGEN CHARGED MOLYBDENUM

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Abstract.— Internal friction of cold worked and hydrogen charged molybdenum was measured from 90 to 400K at about 800Hz. After cold work only the α peak was observed at 120K. When hydrogen was charged, the β peak was observed at about 380 ~ 400K in the first run, but in the second run this peak shifted to lower temperature around 300K. The α peak was suppressed and the β peak showed a maximum when hydrogen charging time increased. These behaviors were interpreted by Igata's model.

1. Introduction.— Molybdenum is considered to be a useful candidate base metal for nuclear fusion materials. Fundamental study on internal friction of molybdenum is not only important for clarifying the behavior of crystalline lattice defects in BCC metals, but also very useful for the characterization of nuclear fusion materials, for example, limiter or the first wall material. Hitherto the data on internal friction of molybdenum is few (1), and as for cold worked and hydrogen charged molybdenum there is only one paper (2). In this investigation, the objective is to investigate the relaxation spectra of cold worked and hydrogen charged molybdenum and to clarify the behaviors of dislocations and hydrogen atoms.

2. Experimental Procedure.— The material used is molybdenum which was made by Tokyo Shibaura Electric Co. The specimen sizes were 1mm x 7 ~ 9mm x 100 ~ 120mm. Those specimens were annealed at 1,700K for 1.5hr in vacuum of 5 x 10^{-6} torr. Then those were cold worked by Instron type tensile testing machine to 4.2 ~ 4.8%. Strain rate was 1 x 10^{-4} s^{-1}. Hydrogen was charged by a cathode electrolytic method. The charging conditions are as follows:

<table>
<thead>
<tr>
<th>Electrolytic solution</th>
<th>3.3N H_2SO_4 solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>platinum plate</td>
</tr>
<tr>
<td>Electric current density</td>
<td>50mA/cm^2</td>
</tr>
</tbody>
</table>

Hydrogen charge was controlled through charging time 5hr, 15hr, 18.5hr and 30hr. Internal friction was measured with the transverse vibration method, in both vacuum or air.
3. Experimental Results. - After annealing at 1,700 K for $5.4 \times 10^3$ s, there is no peak as shown in Fig. 1 and the background was as low as $\sim 10^{-4}$. Then after the same annealing process, hydrogen was charged for $5.4 \times 10^4$ s at the current of $5.0 \times 10^2$ Am$^{-2}$. The first run was done in air from 95K to 420K and the second run was the same, there were no peaks in both cases and the background was a little higher than the annealed state. After tensile cold work to 4.3%, the results for the first run and the second run in air are shown in Fig. 2. One peak was observed at about 130K. This peak seemed to be $\alpha$ peak which was found by Chambers et al.$^{(1)}$. In the second run the peak was a little lower than that in the first run. When the same specimen was measured in vacuum, only the background was lower.

Fig. 1 Internal friction of molybdenum annealed at 1,700 K for $5.4 \times 10^3$ s and measured in vacuum.

Fig. 2 Internal friction of molybdenum 4.2% deformed at 300K and measured in air.

In the next, when hydrogen was charged to the cold worked specimen one more peak except the $\alpha$ peak was observed. The result is shown in Fig. 3(a) and (b). As shown in these figures, two peaks were observed at 135K and 380K to 400K in air. The latter peak seems to be $\beta$ peak previously found by Chambers et al.$^{(1)}$. In the second run the peak shifted to lower temperature around 300K to 320K, which we designated as $\beta'$ peak. The $\beta'$ peak height increased in the second run compared with the $\beta$ peak observed in the first run. In the third run this peak remained and $\beta$ peak was not observed. The similar behavior were observed in vacuum. The result is shown in Fig. 4. The $\alpha$ peak was suppressed by hydrogen charging in both air and vacuum. The $\beta$ or $\beta'$ peak became smaller in vacuum compared with the results in air possibly because vacuum enhance the escape of hydrogen from the specimen.
Fig. 3(a) Internal friction of molybdenum, 4.3% deformed at 300K, hydrogenated for 2 $1.8 \times 10^4$ s at $5.0 \times 10^7$Am$^{-2}$ and measured in air.

Fig. 3(b) Internal friction of molybdenum, 4.2% deformed at 300K, hydrogenated for $6.7 \times 10^4$ s at $5.0 \times 10^7$Am$^{-2}$ and measured in air.

Fig. 4 Internal friction of molybdenum, 4.3% deformed at 300K, hydrogenated for 2 $1.8 \times 10^4$ s at $5.0 \times 10^7$Am$^{-2}$ and measured in vacuum.

When the cold worked and hydrogen charged specimens were measured in vacuum, the $\alpha$ peak became higher and the $\beta$ peak or the $\beta'$ peak became smaller possibly because hydrogen diffused out from the specimen. When the hydrogen was charged for longer time, the $\alpha$ peak was suppressed and the $\beta$ peak or the $\beta'$ peak became higher. Fig. 5 and Fig. 6 show the change of $\alpha$ peak and $\beta$ peak measured in air as the function of hydrogen charging time after cold work. The peak heights in those figures were taken assuming that the minimum value was background damping. The $\alpha$ peak height decreased with the hydrogen charging time, and when measured in vacuum the change was less compared with data taken in air. The $\beta$ peak height increased with hydrogen charge and there was maximum at a certain hydrogen charging time. The peak temperature of the $\alpha$ peak decreased with the hydrogen charge.
charging time in both air and vacuum. The change was less in vacuum than in air. The peak temperature of the $\beta$ and $\beta'$ peak did not change so much with the hydrogen charging time in either air and vacuum.

![Graph](image1)

**Fig. 5** Relation between $\alpha$ peak height and H charging time, measured in air.

![Graph](image2)

**Fig. 6** Relation between $\beta$ peak height and H charging time, measured in air.

4. Discussions

4.1 The activation energy and the frequency factor.—The $\alpha$ peak and the $\beta$ peak reciprocal peak temperatures are plotted with measuring frequency in Fig. 7. The $\alpha$ peak temperature in our experiment was a little higher than the previously reported data. But if those data are combined with Fouquet's data(6) the activation energy was 0.18eV and the frequency factor was $10^{11.9}$. The activation energy of the $\beta$ peak was 0.46eV and the frequency factor was $10^{10.5}$.

![Graph](image3)

**Fig. 7** Arrhenius plot of $\alpha$ peak and $\beta$ peak

- Present work
  - 4.2% deformed (1981)
  - Chamber et al.'s result(3)
  - 5.0% deformed (1962)
  - Fouquet et al.'s result(4)
  - 5.0% deformed (1970)
  - Gibala et al.'s result(5)
  - 30% deformed (1973)
4.2 Effect of cold work and hydrogen.- The α peak appears only in cold worked specimens, and even in zone-refined molybdenum (6), the α peak appears at the same temperature with the less pure specimen used in this work. So, the α peak is considered to be due to intrinsic dislocation relaxation. As for the intrinsic dislocation relaxation, kink migration and double kink formation processes are expected. However, in the case of kink migration, it is considered that the frequency factor is sensitive to the impurity concentration (7). In this result, since the frequency factor seems not to be depending on impurity concentration, the relaxation would be attributed to the double kink formation mechanism (8).

The α peak is suppressed in the cold worked and hydrogenated molybdenum. This behavior is similar with the results of iron (9)(10), but different from the results of niobium (11)(12) and vanadium (13). This suppression of the α peak can be understood by the model of the pinning effects on double kink formation (14)(15)(16).

With increasing hydrogen charging time, the α peak height continues to decrease as shown in Fig. 5, but the β peak height increases and then decreases beyond the maximum as shown in Fig. 6. This phenomena can be interpreted by the model of the catastrophic unpinning initiated from thermal unpinning of double loops proposed by Igata et al (14)(15). The reason why the β peak shifts to the lower temperature after heating to 400K would be that the migration of hydrogen atoms to dislocations and the increase of the hydrogen atom concentration along dislocations lead to the increase of the frequency factor at the thermal unpinning of dislocations or to the decrease of pinning energy through the decrease of elastic modulus by hydrogen atmosphere (17). The hydrogen atom would be mobile during the 1st run, if the diffusion constant is given by $D = 2 \times 10^{-2} \exp \left(- \frac{14700}{RT} \right)$. Electron microphotography of cold worked and hydrogen charged molybdenum showed the dislocation tangling structure, and no evidence for hydride precipitates was observed. This shows the importance of solute hydrogen atoms.

5. Summary.
(1) By cold working of molybdenum only the α peak was observed at 130K in the measurement at 800Hz, but no β peak was observed.
(2) By hydrogen charging the β peak appeared at about 400K, and the α peak was suppressed.
(3) In the second measurement run after heating to 400K, the β peak shifted to lower temperature, which was designated as the β' peak, but the α peak little shifted.
(4) The above behaviors in molybdenum are very similar with the results of hydrogenated iron, and different from the results of hydrogenated niobium or vanadium.

(5) The $\alpha$ peak only decreased with hydrogen charging but the $\beta$ peak showed the maximum versus hydrogen charging time.

(6) The behavior of the $\beta$ peak was interpreted by Igata's model.

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