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Temperature and Orientation Dependence of Yield Stress and Plasticity in Molybdenum Single Crystals of High Purity

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Abstract. In order to study the influence of purification on the strength and plasticity of molybdenum single crystals in bending tests, the investigation was carried out on crystals of 6 orientations and two purity levels (r293K/r4.2K=95000 and 2000 respectively) in the temperature range from 77K to 373K. The dependence of yield stress and ductile-brittle transition temperature on crystal orientation and purity was established. The results are discussed in connection with the peculiarities of dislocation slip and multiplication in bending which are illustrated by X-ray epigrams.

1. INTRODUCTION

Metal purification is considered to be the best means for increasing low-temperature plasticity. Problems of low-temperature plasticity are currently a subject of discussion for refractory BCC metals, especially for metals of VIA group where the solubility of interstitial impurities is extremely low [1]. Production of single crystals with interstitials level less than 1 ppm [2, 3] opened the prospects for obtaining refractory metals plastic down to 4.2 K. An opinion appeared that sharp temperature dependence of the yield stress in refractory metals is entirely defined by impurities, and thorough purification can eliminate it and make any metal plastic at any temperature [4]. A group of scientists in IPMS headed by V. I. Trefilov [5, 6] follow another idea that the sharp yield stress temperature dependence in BCC metals is due to the partly covalent character of interatomic bond defined by their electron structure, and these metals can be brittle at temperatures lower than T* (characteristic deformation temperature, or knee temperature), for Mo it is about 0.2 Tm (Tm is the melting point). The temperature of ductile-brittle transition can be essentially lower depending on metal structure and purity as well as on testing conditions. In the case of single crystals the crystal orientation is of great importance.

The phenomenon of yield stress orientation sensitivity in BCC single crystals has been well known since the 60's [7]. It is noteworthy that no theory of impurity influence on the yield stress can give a satisfactory explanation to this phenomenon. The process of crack formation and propagation which defines crystal low-temperature plasticity may also depend on its orientation [8]. The overwhelming majority of experiments were done for uni-axial deformation. At the same time a very popular test for evaluating plasticity (e.g. in rolled sheets) is bending. For the case of a single crystal bend test, the orientations of both the large plane and the long edge of the specimen bent are important. A knowledge of single crystal properties, although of interest in itself, is necessary for analyzing the anisotropy of mechanical properties in sheets. The influence of impurities may be manifested in different ways for crystals of different orientations.

The present report is devoted to studying the anisotropy of zone-refined Mo single crystals in bending tests.
2. EXPERIMENTAL

2.1 Materials

Two types of Mo single crystals were used, both obtained by electron-beam zone melting in different equipment and from different charges. The charge for Mo I crystals was obtained by precipitation from the gaseous phase of molybdenum iodide vapour [9]; the Mo II crystals were grown from sintered rods of commercial molybdenum of MH trade mark [10]. Chemical content (Tab. 1) was analyzed by means of a spark mass-spectrometer with double focusing after vaporizing the surface layer of the specimen inside the spectrometer for 24 h [11].

Table 1. Impurity Content in the Mo Crystals under Investigation, ppm in mass

<table>
<thead>
<tr>
<th>Crystal</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo I</td>
<td>0.75</td>
<td>0.73</td>
<td>&lt;6.7</td>
<td>1, 9</td>
</tr>
<tr>
<td>Mo II</td>
<td>1.2</td>
<td>4.4</td>
<td>&lt;6.7</td>
<td>375</td>
</tr>
</tbody>
</table>

The content of other elements was less than or equal to the level of method sensitivity, which was an order or two less than 1 ppm. Hydrogen content in Mo I according to the certificate was about 0.07 ppm in mass.

The ratio of electrical resistivities $\rho_{300K}/\rho_{4.2K}$ for both types of crystals was about 95000 and 2000 respectively. Obviously, the difference is due mainly to the different levels of W: the content of interstitial impurities in Mo II differs from Mo I less than 10 times.

Dislocation density in as-grown crystals varied from $10^4$ to $10^6$ cm$^{-2}$; in Mo I dislocation distribution was more irregular.

2.2 Procedure

Specimens for bending 0.5x2x (6-12) mm in size were prepared by electrospark erosion cutting in distilled water, then ground, polished electrolytically and annealed in a vacuum furnace (about $5.10^{-4}$ Pa) at 2070 K for 2 h. The small size of the specimens is caused by the small diameter of the Mo I crystals. The accuracy of specimen crystallographic orientation was about 1°. Specimens of 6 orientations were studied, all of them cut from one crystal. Specimen orientation was characterized by $\{hkl\}$ - the orientation of the large plane and $[uvw]$ - the orientation of the long edge. Specimens were tested in an Instron-type machine with the speed of the bending knife $v = 2$ mm/min, the radius of knife curve $r = 0.5$ mm and the distance between supports $L = 4$ mm, corresponding to a deformation rate in the outer layer $\dot{\varepsilon} = 6.10^{-4}$s$^{-1}$. After bending the specimen through 90 deg. the test was stopped. The test was performed in the temperature range from 77 K to 373 K. Low temperatures were obtained by means of a liquid nitrogen and petroleum ether mixture, while elevated temperatures were obtained in an oil bath. For characterizing the stress of the beginning of macroplastic deformation, the proportionality limit $\sigma_{pr}$ was used, corresponding to the conditional yield stress at $\varepsilon = 0.02\%$.

2.3 Results

The representations of the early part of the test curves are given in Fig.1.
Absence of dotted lines mean that the specimen had failed. The differences in $\sigma_{pr}$ and strain hardening rates in specimens of different orientations are obvious. The orientation sensitivity of the yield stress is clearly revealed in the temperature dependence of $\sigma_{pr}$ (Fig.2). By the increase in the steepness of this dependence, the crystals form a sequence $\{001\}<100>$, $\{110\}<100>$, $\{001\}<110>$, $\{110\}<112>$, $\{110\}<111>$, $\{110\}<110>$, the curves for $\{110\}<112>$ and $\{110\}<111>$ orientation practically coincide. The influence of purification is most seen for $\{001\}<100>$ orientation: in this case purification decreases $\sigma_{pr}$ at 77 K by about 30%. The decrease of the athermal component $\sigma_{pr}$ is about 12-15%.

The effect of impurities is revealed much more prominently in crystal plasticity (Fig.3). In Fig.3 the plots are placed in order of increasing steepness of $\sigma_{pr}$ temperature dependence. Zero plasticity was obtained in no case, therefore the so-called physical, or lower, ductile-brittle transition temperature $T_{db\ell}$ [12] corresponding to the appearance of minimum detectable plasticity could not be measured. By convention the ductile-brittle transition temperature $T_{db}$ was determined as minimum temperature of specimen bending through 90 deg. without fracture. The sequence by the increase of $T_{db}$ is $\{001\}<100>$, $\{110\}<001>$, $\{110\}<112>$, $\{110\}<111>$, $\{001\}<100>$, $\{110\}<110>$, and it does not coincide with the preceding sequence. Depending on crystal orientation the interval between $T_{db\ell}$ and $T_{db}$ can be rather great: in the case of the crystal $\{110\}<110>$ Mo II it exceeds 250 deg.
3. DISCUSSION

3.1 Yield stress

The phenomenon of macro-yielding is a complicated process including motion, generation and interaction of dislocations, and at T<T* they are preferably screw. Trefilov and Milman have shown [13] that under the assumption of power laws for the dependence of dislocation density N and dislocation velocity v on the applied stress in slip plane N ~ \tau^{n} and v ~ (\tau/\tau_0)^m at temperatures close to T* the yield stress
where \( U \) is the activation energy of dislocation motion. The role of dislocation motion is characterized here by \( U \) and \( m \), the contribution of dislocation multiplication - by \( n \). It is important that in the strict sense in Eq. (1) under \( \tau_y \) the difference of yield stress and its athermal component \( \tau_a \) shall be implied, and \( N \) shall mean not the total dislocation density, but the density of mobile ones. We support the opinion [14] that orientation dependence of the yield stress \( \sigma \) in BCC single crystals could be explained by orientation sensitivity of dislocation generation, that is to say that a high level of \( \tau_y \) and \( \sigma_y \) in crystals tensed along \(<110>\) is caused by small rate of dislocation multiplication, i.e. low \( n \), and for tension along \(<001>\) the situation is the converse. The main mechanism of dislocation multiplication in Mo is shown to be double cross slip [15], and while uni-axial deformation along \(<100>\) axis it happens much more often than in the case of \( <110> \) axis [14].

It is usual to interpret the early stages of plastic deformation in bending as tension of the specimen’s outer layer, but the difference is in deformation geometry which can be understood from the analysis of standard pole figures. It can be seen that in \{001\}<100> and \{001\}<110> crystal bend is easily performed by slip in the same systems as in the case of tension along the directions of the respective long edges. Thus these crystals behave similarly to tensed ones, in that strong strain hardening (Fig.1) which could be a sign of intense dislocation multiplication, corresponds to low \( \sigma_y \) and vice versa. The contradiction is in the behaviour of \{110\}<110> crystals when intense strain hardening (Fig.1) is combined with the steepest temperature dependence of the yield stress (Fig.2). In these crystals no slip system with \((a/2)\langle111>\) Burgers vector could provide easy bending, so very many different systems must operate simultaneously, and dislocation intersections will be very frequent. A detailed analysis of dislocation reactions in this crystal has been carried out for the case of rolling [16], where similar problems take place. For bending it can be proved by the X-ray back reflection pattern (Fig.4).

\[
\tau_y = \text{const} \cdot \dot{\varepsilon}^{1/(m+n+1)} \cdot e^{U/(m+n+1)kT},
\]

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**Figure 4:** Epigrams in white X-rays (tube with Mo anode) from extended side of bent specimens: a){110}<110>, b){001}<110>, c){001}<100>. The direction of the long edge is horizontal.

In the epigrams of \{110\}<110> crystal (Fig.4a) Laue spots are strongly diffuse in all directions and for \{001\}<110> and \{001\}<100> crystals (Fig.4b, c) they are elongated along the long edge, indicating uniform bend. The intersections in \{110\}<110> crystal can stop dislocations very quickly, and the number of mobile dislocations here may be very small. This could explain the contradiction indicated above. Fig.4c could also be interpreted as a consequence of double complanar slip in the surface layer, which should be strongly expressed in BCC crystals of this orientation [17].

Impurities can retard the multiplication of dislocations through inhibiting double cross slip and double complanar slip and thus making \( \tau_y \) temperature dependence sharper in accordance with (1). Besides, they
Impurities can retard the multiplication of dislocations through inhibiting double cross slip and double complanar slip and thus making $\tau_y$ temperature dependence sharper in accordance with (1). Besides, they increase $\tau_b$. In general we cannot exclude some influence of impurities in the value of $U$ connected with double kink formation. But at the concentrations under investigation their influence on $\sigma_y$ is not so strong.

### 3.2 Plasticity

In the temperature region under investigation fracture of Mo single crystals occurs by the mechanism of quasi-brittle cleavage. Thoroughly polished crystals keep plasticity to rather low temperatures (down to 4.2K) because they contain no obstacles strong enough to form dislocation pile-ups leading to crack generation. Such obstacles are created by dislocation interaction after some plastic deformation. For BCC metals a Cottrell-type mechanism is considered to be most suitable [8], in which crack formation is a consequence of the intersection of two glide bands of different slip systems. Further crack growth depends on the capacity of the metal for stress relaxation by plastic deformation close to the crack tip. These considerations enable the observed anisotropy of plasticity in Mo crystals (Fig.3) to be explained.

Obviously, $\{001\}<110>$ crystals keep high plasticity to the lowest temperatures because of the lowest probability of dislocation intersections with the formation of a $<001>$ segments [14]. In all other crystals cleavage took place after remarkable plastic deformation which could mean a rather strong tendency of Mo towards stress relaxation by plastic deformation. This tendency is the weakest in chromium, and the interval between $T_{dbh}$ and $T_{db}$ in bent chromium single crystals is rather narrow and does not exceed 40 deg. [18]. Thus, in Mo the crack growth is much slower than in Cr. In $\{110\}<110>$ crystals $T_{db}$ is maximum for the highest probability of dislocation intersection. Strong influence of impurities in this case can be connected with hindering of stress relaxation process because impurities impede avoidance of obstacle dislocations by cross slip, and this influence is very pronounced. Maybe the same effect also takes place in $\{001\}<100>$ crystals, and is less pronounced in $\{110\}<100>$ crystals because of unequal participation in the gliding process of all slip systems with $(a/2)<111>$ Burgers vectors in this case. Increased $T_{dbh}$ in these crystals in spite of rather weak temperature dependence of $\sigma_y$, could be connected with known reduction of fracture stress $\sigma_y$ for cleavage in $\{001\}$ planes in BCC metals. Such reduction for chromium was estimated at 25% [18].

It should be noted that the difference in $T_{dbh}$ for Mo crystals $\{110\}<112>$ and $\{110\}<111>$ at both purity levels is rather small (not more than 20 deg.). Thus, the long edge direction $<111>$ in Mo is not a direction of low plasticity which was supposed earlier [19] to explain mechanical properties in rolled Mo sheets.

### 4. CONCLUSION

1. Purification of the content of interstitial impurities to a level less than 10 ppm cannot eliminate the tendency of molybdenum single crystals to fracture by quasi-brittle cleavage, and this tendency strongly depends on crystal orientation.

2. The effect of purification on the mechanical properties of molybdenum single crystals in bending tests is more pronounced for low-temperature plasticity than for yield stress.

3. Reducing the content of W from 375 to 1 ppm in mass, and content of each impurity from several ppm to about 1 ppm, reduced yield stress by about 30% and its athermal part by 12-15%. It was not possible to distinguish between the influence of W and that of the interstitials.

4. The influence of impurities on low-temperature plasticity strongly depends on the orientation of the large plane and long edge of the specimen and is greatest for $\{110\}<110>$ and $\{001\}<100>$ crystals.

5. The effect of impurities is thought to be connected mainly with their influence on cross slip of screw dislocations in BCC crystals.
Acknowledgements

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References