J Mater Sci (2007) 42:7801–7805
DOI 10.1007/s10853-007-1631-9

Effect of natural ageing on the mechanical properties of molybdenum polycrystals

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Received: 12 August 2006 / Accepted: 20 February 2007 / Published online: 3 June 2007

Abstract Natural ageing of 99.95 at.% Mo polycrystals annealed at 700 °C influences its mechanical properties to a considerable extent. It is found that natural ageing for 6 months reduces the ductility by about 70% whereas yield stress and ultimate tensile strength are decreased by about 20 and 18% respectively. The stress-relaxation rate measured at a given initial stress level at which deformation is interrupted to observe stress relaxation at constant strain, is faster in aged specimens compared with that in unaged ones. Similarly, the strain-rate sensitivity of flow stress for a given stress level is also increased on natural ageing. The rate process of stress relaxation and of plastic flow at rather high strains corresponding to the parabolic stage of work hardening appears to be vacancy migration.

Introduction

There is ample evidence in the literature that thermal ageing of materials, whether natural or artificial, has a marked effect on their physical, functional, mechanical and electrical properties. By optimum selection of the ageing temperature and time, these properties can be tailored favourably for technological applications. Contrary to the extensive investigations carried out with reference to the ageing characteristics of alloys, e.g., [1–4], a little work has been done so far in the case of nominally pure metals. In particular no such attempt has been made as yet as far as body—centred cubic metals are concerned.

Nevertheless it is well established that mechanical strength of face—centred cubic aluminium crystals is increased on natural ageing. For instance, the yield stress of 99.996% Al polycrystals annealed at 500 °C and then aged at room temperature for 6 months was found to be nearly 30% higher than that of annealed but unaged aluminium [5–7]. This was attributed to the migration of above-equilibrium vacancies and/or residual impurity atoms to the cores of edge-dislocations during natural ageing, which pinned the dislocations and made their movement rather difficult. Similarly stress relaxation experiments [6] carried out on this material subjected to similar annealing and natural ageing treatments revealed that for a given initial stress level at which stress is allowed to relax at a constant strain, the stress-relaxation rate in aged aluminium increases by a factor of 1.3 as compared with that in unaged aluminium. This was ascribed to the local ordering of point defects near jogs resulting in a lowering of their misfit energy, and hence facilitates the migration of dislocations. Likewise, natural ageing of 99.996% Al polycrystals annealed at 500 °C was found [7] to cause a significant increase (≈ 30%) in the strain-rate sensitivity of flow stress at a given temperature. The observations of Butt and coworkers in the case of 99.996% Al polycrystals cited above were extended by Riaz [8] and Hafeez [9] to 99.9% Ni polycrystals annealed at 700 °C for 2 h and then aged at room temperature for 3 months. It was found that the yield stress of aged nickel increases by about 10% compared with that of unaged nickel, while no noticeable effect of natural ageing was observed in the case of stress relaxation at a constant strain as well as strain-rate sensitivity of flow stress.

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The main object of the present work was to extend the investigations carried out with face-centered cubic metals cited above to body-centered cubic ones. Thus effect of natural ageing on the mechanical response of 99.952 at.% Mo polycrystals annealed at 700 °C for 2 h was studied with special reference to yield stress, stress-relaxation at a constant strain, and strain-rate sensitivity of flow stress. The data obtained have been analyzed in terms of a single barrier model of plastic flow and a plausible explanation of the observations has been offered.

Materials and experimental techniques

The material used was polycrystalline molybdenum in the form of rolled sheet of 0.13 mm thickness. The main metallic impurities were Fe (0.034), Mn (0.005) Ni (0.005), and Cr (0.004), and the balance 99.952 at.% was Mo. Specimens 8 cm long and 1 cm wide were cut from the as-received sheet and were sealed in a Pyrex glass tube evacuated to 10^{-5} torr (1.3 mPa). These were then annealed at 700 °C for 2 h. The resulting mean grain—diameter was 37 μm. Half of the specimens were subjected to various deformation tests at room temperature just after the heat treatment while the remaining ones were allowed to age at room temperature for 6 months prior to deformation.

Both aged and unaged specimens were deformed in tension at a strain rate of $2.1 \times 10^{-3}\ s^{-1}$ (cross—head speed 5 mm/min.) till fracture in a Universal Materials Testing Machine (Model 1195 Instron Ltd., UK) at room temperature. Both ends of the specimen were held tightly in the wedge type flat jaws attached to the upper and lower pull rods of the machine such that the gauge length of the specimen was 4 cm. The chart of the load-time recorder was driven at a speed of 50 mm/min, and the full scale load range was 2 kN. Stress–strain curves were constructed from the load-extension data in the usual manner.

To study stress-relaxation at constant strain between yield stress (YS) and ultimate tensile strength (UTS), tensile tests on both aged and unaged specimens were repeated at room temperature but deformation was done at a strain rate of $4.2 \times 10^{-4}\ s^{-1}$ (cross-head speed 1 mm/min.) and interrupted by arresting the cross head at a number of stress levels over the entire stress–strain curve in each case. The chart of the lood-time recorder was however driven now at a speed of 100 mm/min, which speed enabled one to attain adequate resolution of stress changes with the passage of time. For a given initial stress level σ_0 from which stress relaxation at constant strain is allowed to start, values of stress relaxed $\Delta\sigma(t) = \sigma_0 - \sigma(t)$ were measured as a function of relaxation time t.

Strain-rate cycling experiments were also carried out in tension with both aged and unaged specimens at room temperature. During the deformation leading to fracture, the strain rate $2.1 \times 10^{-3}s^{-1}$ (cross-head speed 5 mm/min) was frequently reduced to $2.1 \times 10^{-4}s^{-1}$ (cross—-head speed 0.5 mm/min), and after subjecting the specimen to a certain amount of strain at that deformation rate, the latter was returned to the original level. The chart of the load-time recorder was again driven at a speed of 100 mm/min to attain adequate resolution of stress changes accompanying the change in strain rate. Following Butt and Feltham [10], values of the changes in the flow stress $\Delta\sigma$ were always obtained from the cycles in which the strain rate was reduced from the higher level. Corresponding stress changes resulting from increases in the strain rate did not, however, differ markedly from the former.

Results and discussion

Work hardening

Reference to Fig. 1 shows stress–strain curves for unaged and aged 99.952 at.% Mo polycrystal specimens of mean grain-diameter 37 μm, deformed at a tensile strain-rate $\dot{\varepsilon} = 2.1 \times 10^{-3}s^{-1}$. The values of YS and UTS are 520 MPa and 790 MPa respectively for unaged Mo while those for aged Mo are 415 and 650 MPa respectively. Similarly the maximum tensile strain ε_m corresponding to UTS is 4.6 and 1.4% for unaged and aged specimens respectively. It can be readily noted that natural ageing

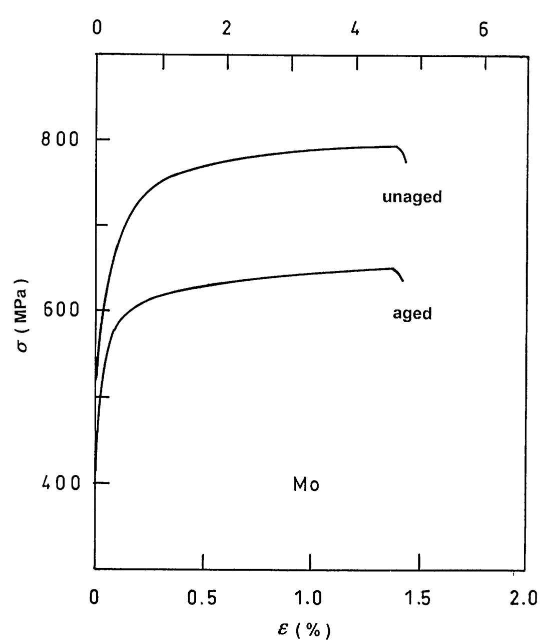

Fig. 1 Stress–strain curves of 700 °C annealed Mo polycrystals (mean grain-diameter 37 μm, $\dot{\varepsilon} = 2.1 \times 10^{-3}s^{-1}$). Strain scale at the top is for unaged specimens and that at the bottom is for aged ones

reduces the ductility of Mo polycrystal by about 70% whereas YS and UTS are also reduced by about 20 and 18% respectively. The observed 20% decrease in YS on natural ageing can be attributed to the redistribution of point defects, e.g., impurity atoms and above—equilibrium vacancies etc, during the course of ageing, which modify the Peierls field/dislocation core leading to lower Peierls energy per interatomic spacing along the length of screw dislocations trapped in Peierls valleys, and hence reduction in YS. The softening behaviour of Mo polycrystals is opposite to that of 99.996% Al polycrystals; the yield stress of the later is increased by about 30% due to pinning of edge dislocations with the point defects gathered close to the dislocation core during natural ageing, whereas UTS remains unaffected for the reasons discussed in [5–7].

Stress relaxation

Now we shall analyse the data obtained in stress relaxation experiments carried out with unaged and aged Mo polycrystals. Figure 2 refers to the relationship between the amount of stress relaxed $\Delta\sigma(t) = \sigma_0 - \sigma(t)$ and relaxation time t in semi-logarithmic coordinates for various stress levels σ_o, denoted on the curves in the case of (a) unaged and (b) aged Mo specimens. The values of YS and UTS ($\dot{\varepsilon} = 4.2 \times 10^{-4}\mathrm{s}^{-1}$) were respectively 400 and 738 MPa for unaged Mo specimens, and 325 and 600 MPa for aged ones. It is apparent from Fig. 2 that for a given stress level σ_0 at which further deformation of the specimen was stopped, the amount of stress relaxed $\Delta\sigma$ increases linearly with logarithm of relaxation time t upto about 150 s, beyond which it becomes almost constant. One can evaluate the slope $s = \mathrm{d}(\Delta\sigma)/\mathrm{d}(\ln t)$ of the $\Delta\sigma - \ln t$ line drawn through data points for a given stress level σ_0 , and the $s - \sigma_0$ data thus obtained have been represented by filled and empty circles in Fig. 3 for aged and unaged Mo specimens respectively. The straight line drawn through the data points by least—squares fitting method in each case is encompassed by the relation

$$\text{unaged (o)} : s = 3.66 \times 10^{-2}\,\sigma_0 - 3.62 \tag{1}$$

$$\text{aged}(\bullet) : s = 2.63 \times 10^{-2}\,\sigma_0 - 2.62 \tag{2}$$

The values of correlation factors r are 0.94 and 0.98 respectively. It can be noted from Eqs. 1 and 2 that no relaxation occurs below $\sigma_0 \approx$ 99MPa, which is well below the macroscopic yield stress.

To explore the rate process of stress relaxation, a single barrier model of logarithmic stress relaxation [11] will be used. In this model, the intrinsic height of the rate-controlling energy barrier U_o is related to the relaxation rate s and initial stress level σ_0 through the expression:

$$s = kT\sigma_o/(U_o - mkT) \tag{3}$$

Here k is Boltzmann constant, T is temperature at which the experiment is carried out, $m = \ln(\dot{\varepsilon}_o/\dot{\varepsilon})$ is a constant, which on taking typical values of strain rate $\dot{\varepsilon}$ in the range 10^{-3} to $10^{-5}\mathrm{s}^{-1}$ and with $\dot{\varepsilon}_0 \approx 10^7\mathrm{s}^{-1}$, comes out to be equal to about 25. Equation 3, in its differential form, can be written as [12, 13]

$$U_o = kT[(d\sigma_0/ds) + m] \tag{4}$$

The values of $\mathrm{d}\sigma_0/\mathrm{d}s$ can be readily derived from the $s - \sigma_0$ curves in Fig. 3, and are found to be 37.0 and 27.4 for unaged and aged Mo specimens, respectively. Using these values together with T = 298 K, m = 25 and k = 0.8614×10^{-4} eV/K in Eq. 4, one gets U_o = 1.60 eV for unaged and U_o = 1.35 eV for aged Mo specimens. The values of U_o referred to are in good agreement with the activation energy for vacancy migration (1.25– 1.62 eV) in Mo crystals reported in the literature [14].

It should also be noted that the initial flow stress in high-purity Mo single crystals at temperatures between 125 and 460 K is controlled by the kink-pair formation on (a_o/2) < 111 > screw dislocations (a_0 being the edge length of the unit cell cube) in {112} planes; the kink-pair formation energy is found to be 1.27 eV, in excellent agreement with the activation energy of the so-called γ-relaxation in this

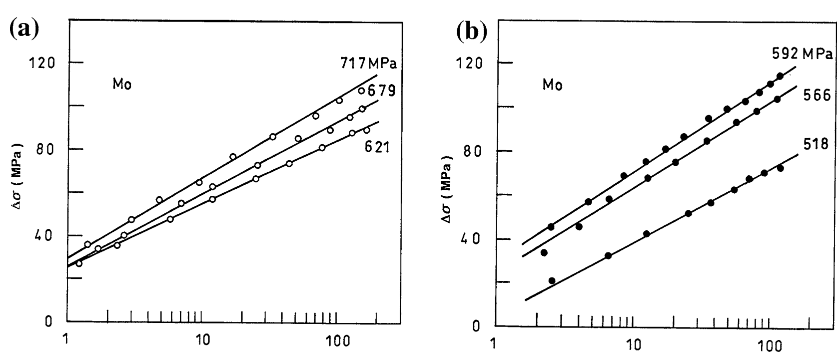

Fig. 2 Logarithmic stress-relaxation curves for 700 °C annealed Mo polycrystals deformed at $\dot{\varepsilon} = 4.2 \times 10^{-4}\mathrm{s}^{-1}$: (**a**) unaged and (**b**) aged at room temperature for 6 months

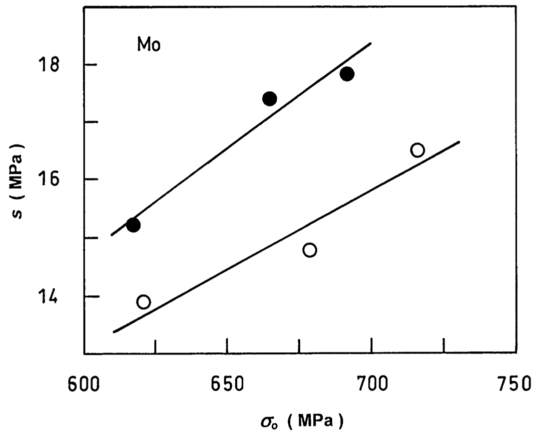

Fig. 3 Stress-relaxation rate s as a function of initial stress level σ_o for 700 °C annealed Mo polycrystals referred to in Fig. 2: (○) unaged (●) aged

metal [15]. However, due to rather large strains involved in the present work, one cannot ascribe U_o—values to the Peierls mechanism as the rate process of logarithmic stress-relaxation in 99.952 at.% Mo polycrystals.

Activation volume for plastic flow

Finally we shall examine the data obtained in strain-rate cycling experiments ($2.1 \times 10^{-3}s^{-1}$–$2.1 \times 10^{-4}s^{-1}$) carried out with Mo polyscrystals at room temperature. Figure 4 shows the dependence of reversible change in flow stress $\Delta\sigma$ on flow stress σ at which strain rate $\dot{\varepsilon}$ is lowered by a factor of 10; empty and filled circles denote the $\Delta\sigma$ values for unaged and aged specimens respectively. The line drawn through the data points by least-squares fitting method in each case correspond to the expression:

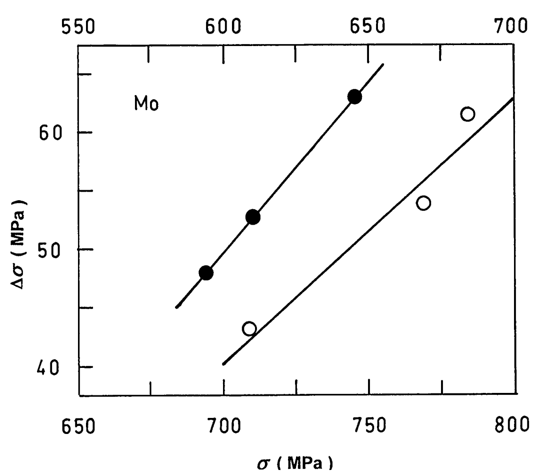

Fig. 4 Reversible change in flow stress $\Delta\sigma$ as a function of flow stress σ at which tensile strain-rate $2.1 \times 10^{-3}s^{-1}$ was lowered by a factor of 10 for 700 °C annealed Mo polycrystals: (○) unaged (●) aged. Upper σ—scale is for aged specimens while that at the bottom is for unaged ones

$$\text{Unaged (O)}: \Delta\sigma = 0.226\sigma - 118 \tag{5}$$

$$\text{Aged}(\bullet): \Delta\sigma = 0.288\sigma - 122 \tag{6}$$

The values of correlation factor r are 0.97 and 0.99 respectively. It is worthy of note that the straight line drawn through the data points for unaged specimen intersects the σ—axis for $\Delta\sigma = 0$ at 522 MPa, whereas that for aged specimen intersects the σ—axis for $\Delta\sigma = 0$ at 424 MPa. Both values of the intercepts are close to the yield stress values 520 and 415 MPa respectively for unaged and aged Mo specimens. Note that the σ—value for $\Delta\sigma = 0$, hereafter denoted as σ_i, is known as friction stress [16] or threshold stress [17] of the crystal.

One can now evaluate activation volume v_σ by substituting the experimental values of $\Delta\sigma$ in the expression

$$v_\sigma = kT(\Delta \ln \dot{\varepsilon}/\Delta\sigma) \tag{7}$$

The values of the v_σ obtained in this manner have been depicted as a function of flow stress σ in log–log coordinates in Fig. 5 for both unaged (o) and aged (•) Mo specimens. It is found that the data points in each case fall close to a straight line with slope $d(\ln v_\sigma)/d(\ln\sigma)$ equal to –3.6. The same activation volume data have also been plotted as a function of σ–σ_i in Fig. 5, where σ_i = 522 MPa for unaged specimens and σ_i = 422 MPa for aged specimens. The line drawn though the data points in each case has a slope $d\ln v_\sigma/d \ln(\sigma-\sigma_i)$ equal to –1 such that the product $v_\sigma(\sigma-\sigma_i)$ is equal to 1.56 eV for unaged and 1.49 eV for aged Mo polycrystals.

To explore the rate-determining process of plastic flow we shall use the following expression [6]:

$$U_o - v_\sigma(\sigma - \sigma_i) = mkT \tag{8}$$

which is a modified version of the rather simple single barrier model [18] of plastic flow. Here U_o is the intrinsic height of the effective energy barrier to plastic flow and its value comes out to be 0.92 eV for unaged specimens and

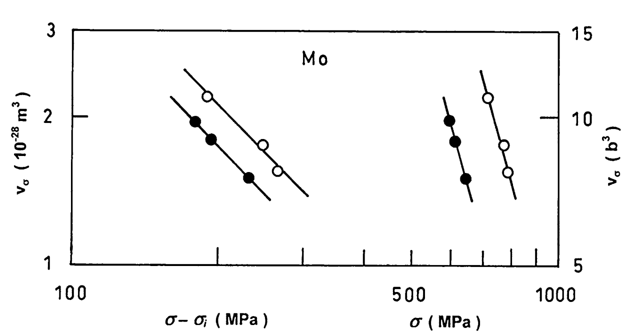

Fig. 5 Activation volume v_σ as a function of flow stress σ and of parameter $\sigma - \sigma_i$ for 700 °C annealed Mo polycrystals: referred to in Fig. 4: (○) unaged (●) aged

0.85 eV for aged specimens on using the relevant values of $v_{\sigma}(\sigma - \sigma_i)$ referred to above. It is readily evident from this analysis that the values of U_o are of the order of magnitude for recovery processes, e.g., vacancy migration (≈1.39 eV), which is therefore the rate-process of plastic flow in Mo polycrystals in the stress range corresponding to the parabolic stage of work hardening.

One can readily note from the 8 to 9% reduction in the U_o—values found in both stress relaxation and strain-rate cycling experiments that natural ageing facilitates the dislocation glide in both cases. This is probably due to redistribution of point defects, e.g., above equilibrium vacancies, gaseous and metallic impurities etc., present in Mo polycrystals during natural ageing.

Conclusions

From the foregoing evidence, we arrive at the following conclusions:

(1) Natural ageing for 6 months has no effect on the shape of σ–ε curves of annealed Mo polycrystals but ductility decreases by about 70%. Likewise, the yield stress and ultimate tensile strength for a given strain rate are also decreased on natural ageing by 20 and 18% respectively.

(2) The stress relaxation behavior of both aged and unaged Mo polycrystals is logarithmic. However for a given initial stress level at which deformation is interrupted to observe stress relaxation at constant strain, the relaxation rate is faster in aged specimens compared with that in unaged ones. The rate process of stress relaxation is vacancy migration as the intrinsic height of the energy barrier to relaxing dislocations U_o is 1.35 eV for aged and 1.60 eV for unaged specimens.

(3) For a given stress level at which imposed tensile strain-rate is lowered by a factor of 10, the reversible change in flow stress $\Delta\sigma$ is higher in aged specimens than in unaged ones. The values of $U_o = 0.92$ eV for unaged and $U_o = 0.85$ eV for aged specimens determined from strain-rate cycling experiments show that the rate process of plastic flow in Mo polycrystals at relatively high strains is vacancy migration.

Acknowledgements Special thanks are due to Pakistan Council for Science and Technology, Government of Pakistan, Islamabad, for financial assistance under the Research Productivity Allowance Scheme.

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