INTERFACE CONTROLLED DIFFUSIONAL CREEP OF NANOCRYSTALLINE PURE COPPER

B. Cai1, Q.P. Kong1, L. Lu2 and K. Lu2

1Laboratory of Internal Friction and Defects in Solids, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People’s Republic of China
2State Key Laboratory for RSA, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110015, People’s Republic of China

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1. Introduction

There have been many investigations on the mechanical behaviour of nanocrystalline materials [e.g.1-6]. Nevertheless, the creep mechanism of nanocrystalline materials is not clear.

Sanders and coworkers [7] studied the creep of nanocrystalline Cu, Pd, and Al-Zr over a wide temperature range. Wang and coworkers [8] investigated the room temperature creep behaviour of nanocrystalline Ni. In both the works, high flow stresses and low strain rates were observed.

We have studied the high temperature creep of Ni-P and Fe-B-Si nanocrystalline alloys [9–12]. Based on the measurements of stress exponent and activation energy, we suggested that the creep of both the nanocrystalline alloys is dominantly controlled by grain (and/or phase) boundary diffusion. Owing to the lack of diffusion data of these alloys, quantitative comparison between the measured and theoretical creep rates has not been made.

The purpose of the present work is to study the tensile creep behaviour of a nanocrystalline single element material (pure copper). To avoid grain growth during creep, the tests were carried out at low temperatures (0.22 to 0.24 Tm, Tm is the melting point). The results suggest the creep can be contributed to the “interface controlled diffusional creep.”

2. Experimental

The nanocrystalline Cu with purity of 99.995% was prepared by means of the electrodeposition technique with a electrolyte of CuSO4 and a substrate of Ti. The thickness of the n-Cu sheets was about 1.7 mm. The average grain size of n-Cu was measured to be 30 (±4) nm by X-ray diffraction spectrum and transmission electron microscopy.

The sample density was measured to be 8.91±0.03 g/cm3, which is equivalent to 99.4% of the theoretical density for pure Cu. The total oxygen content in the as deposited n-Cu was determined to be 24 (±1) ppm.
Tensile creep specimens were carved from the n-Cu sheet by spark erosion, mechanically polished with fine emery papers, chemically polished with dilute nitric acid, and cleaned. The final dimensions of the creep specimens were 20 mm in gauge length and $1.0 \times 0.7$ mm$^2$ in cross section.

A series of annealing experiments of the n-Cu samples indicated that grain growth occurred when the annealing temperature was higher than 100 °C. Hence we restricted the creep temperature in the range of 20 –50 °C (0.22 to 0.24 $T_m$) to avoid grain growth during creep. Before creep tests, all the specimens were annealed at 70 °C for 1 h to keep the initial microstructure identical at different creep temperatures. Measurements of grain size showed that no grain growth occurred during the annealing and the creep tests.

3. Results

Figure 1 shows an example of creep strain-time ($\epsilon$–$t$) and strain rate-time ($\dot{\epsilon}$–$t$) curves of the nano-grained pure Cu. It can be seen that the creep contains the primary and steady state stages as usual, but the tertiary stage is very short. The strain-time ($\epsilon$–$t$) relation in the primary stage is found to obey the Andrade’s law [13]

$$
\epsilon = \epsilon_0 + \beta t^{1/3},
$$

where $\epsilon_0$ is the instantaneous strain, and $\beta$ is the slope of $\epsilon$–$t^{1/3}$ line.

In order to investigate the stress dependence of steady state creep rate (SSCR), we conducted a series of stress jump tests at different temperatures (i.e., 20 °C, 30 °C, 40 °C, and 50 °C). Each stress jump was carried out after the steady state had been reached for a sufficient time under the proceeding stress.

Figure 2 shows the SSCR as a function of applied true stress in respective steady state stage. One can see that the SSCR is linearly increased with increasing applied stress, and that there exists a threshold stress $\sigma_0$ at each test temperature. Accordingly the effective stress is

$$
\sigma_e = \sigma - \sigma_0,
$$

where $\sigma$ is the applied stress, and $\sigma_0$ is the threshold stress.

Figure 3 shows that the threshold stress $\sigma_0$ decreases with the increase of absolute temperature $T$. The relation between $\sigma_0$ and $T$ can be expressed as

$$
\sigma_0 = B_0 (1 - T/T_c),
$$
where $T_c$ is a critical temperature, and $B_0$ is a constant. From Fig. 3, we obtained that $T_c \approx 617$ K at which the $\sigma_0$ is expected to diminish, and $B_0 \approx 262$ MPa which is the expected value of $\sigma_0$ at $T = 0$ K.

After subtracting $\sigma_0$ from $\sigma$, all the straight lines in Fig. 2 will go through the origin, i.e., the SSCR is proportional to the effective stress $\sigma_e$. One can see also from Fig. 2 that the SSCR increases with increasing temperature. Hence the SSCR $\dot{\epsilon}$ can be expressed as

$$\dot{\epsilon} = \frac{A \sigma_e}{kT} \exp \left( -\frac{Q}{kT} \right),$$

where $A$ is a constant, $Q$ is the activation energy for the creep, $k$ and $T$ have their usual meaning.

With the values of the slopes of $\dot{\epsilon}/\sigma_e$ at different temperatures in Fig. 2, the parameter $kT \dot{\epsilon}/\sigma_e$ as a function of $1/T$ is plotted in Fig. 4. From the slope and the intercept of the straight line in Fig. 4, we obtain the activation energy $Q = 0.72 (\pm 0.05)$ eV and $A = 1.07 \times 10^{-22}$ m$^3$/s.

### 4. Discussion

The results indicate that the SSCR is proportional to the effective stress $\sigma_e$. The activation energy of the creep is measured to be 0.72 eV, which is obviously smaller than that of lattice diffusion (2.0 eV) and
grain boundary diffusion (1.08 eV) in coarse grained Cu [14], but is close to that of grain boundary
diffusion in nano-grained Cu (0.69 eV [14], 0.64 eV [15]).

The values of experimental SSCR are found to be of the same order of magnitude as those calculated
from the equation for Coble creep [16], i.e.,

\[
\dot{\varepsilon} = \frac{148D_b\delta\Omega\sigma_e}{\pi d^3 kT} = \frac{148D_{b0}\delta\Omega\sigma_e}{\pi d^3 kT} \exp \left( -\frac{Q_b}{kT} \right),
\]

where \(D_b\) is the grain boundary diffusion coefficient, \(D_{b0}\) is the pre-exponential factor, \(Q_b\) is the
activation energy, \(\delta\) is the thickness of grain boundaries, \(\Omega\) is the atomic volume, and \(d\) is the grain size.

In the calculation, the numerical values of the following parameters: \(d = 3 \times 10^{-8}\) m, \(\delta = 5 \times 10^{-10}\) m, \(\Omega = 8.78 \times 10^{-30}\) m³ and \(D_b = 3 \times 10^{-3}\exp(-0.64eV/kT)\) m²/s [15] were substituted into
Eqs. (5) and (6). We found that at the creep temperatures and the effective stresses in this study, the
calculated values of SSCR are larger than the measured values by a factor of about 5, but both the
calculated and measured values are in the same order of magnitude. For example, at \(T = 313\) K and
\(\sigma_e = 20\) MPa, the calculated SSCR is equal to \(5.3 \times 10^{-6}\) s⁻¹, while the measured value is \(1.1 \times 10^{-6}\)
\(\) s⁻¹ (see Fig. 2).

The existence of the threshold stress implies that the grain boundaries do not act as perfect sources
and sinks of atoms (or vacancies), as pointed out by Ashby [17], Arzt, Ashby and Verrall [18] and
Gleiter [19]. In such case, the rate of diffusion along grain boundaries will be limited by the emission
and absorption of atoms (or vacancies) at grain boundaries. The latter process needs an energy for the
emission and absorption of atoms (or vacancies) at grain boundaries, resulting in the threshold stress \(\sigma_0\).
Accordingly the creep can be attributed to the “interface controlled diffusional creep.” This terminology
was suggested by a number of scientists such as Arzt, Ashby and Verrall [18]. In the present case, the
creep can be attributed to the “interface controlled Coble diffusional creep.”

Gleiter [19] pointed out that the rate of emission and absorption of atoms (or vacancies) at grain
boundaries is dependent upon the boundary structure, and that the low energy grain boundaries can not
act as point defect sources or sinks below a threshold stress. The emission or absorption of point defects
at low energy grain boundaries will result in local increase of boundary energy. Consequently, the
applied stress must be high enough to supply the energy required for the local increase of boundary
energy. This stress is the threshold stress \(\sigma_0\) of a low energy boundary.
In fact, a high fraction of low energy grain boundaries in nanograined Cu was observed by Sanders et al. [7]. Hence we think that the existence of the threshold stress is possibly associated with the low energy grain boundaries. Nevertheless, the mechanism of the threshold stress \( \sigma_0 \) and its relation with temperature are to be further studied.

5. Summary and Conclusions

(1) Tensile creep of nano-grained pure Cu with an average grain size of 30 nm prepared by electrodeposition technique has been investigated at low temperatures (0.22–0.24 \( T_m \)). No grain growth occurred during the creep tests.
(2) The steady state creep rate is proportional to the effective stress \( \sigma_e = (\sigma - \sigma_0) \), where \( \sigma \) is the applied stress, and \( \sigma_0 \) is the threshold stress. The activation energy for the creep is measured to be 0.72 (±0.05) eV, which is close to that of grain boundary diffusion in nano-grained Cu. The experimental creep rates are of the same order of magnitude as those calculated from the equation for Coble creep.
(3) The existence of threshold stress implies that the grain boundaries of the nano-grained Cu samples do not act as perfect sources and sinks of atoms (or vacancies). Hence the rate of grain boundary diffusion is limited by the emission and absorption of atoms (or vacancies). The energy needed for the emission and absorption of atoms (or vacancies) results in the threshold stress.
(4) The results obtained suggest that the low temperature creep of nano-grained pure Cu in this study can be attributed to the “interface controlled diffusional creep.”

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References