Low temperature creep of nanocrystalline pure copper

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Abstract

Tensile creep of nano-grained pure Cu with an average grain size of 30 nm prepared by electrodeposition technique has been investigated in the temperature range 20–50°C (0.22–0.24 Tm). The steady state creep rate is found to be proportional to the effective stress σe = (σ - σ0), where σ is the applied stress, and σ0 is the threshold stress. The activation energy for the creep is measured to be 0.72 eV, which is close to that for grain boundary diffusion in nano-grained Cu. The creep rates are found to be of the same order of magnitude as those calculated from the equation for Coble creep. The existence of threshold stress implies that the grain boundaries do not act as perfect sources and sinks of atoms (or vacancies). The results suggest that the creep can be attributed to the ‘interface controlled diffusional creep’. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

There have been many investigations on the mechanical behaviour of nanocrystalline materials e.g. [1–7]. Nevertheless, the creep mechanism of nanocrystalline materials is not clear.

Sanders and coworkers [8] studied the creep of nanocrystalline Cu, Pd, and Al–Zr made by inert gas condensation and in situ compaction method over a wide temperature range. They suggested that the observed low creep rates are caused by the high fraction of low energy grain boundaries, together with the limitation on dislocation activity by the small grain sizes.

Wang and coworkers [9] investigated the room temperature creep behaviour of nanocrystalline Ni produced by electrodeposition technique. They pointed out that grain boundary sliding and the diffusion through intercrystalline regions are the major deformation mechanisms.

The high temperature creep of Ni–P and Fe–B–Si nanocrystalline alloys prepared by amorphous crystallisation method has been studied [10–13]. 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 (0.22–0.24 Tm, Tm is the melting point). The results suggest that the creep can be contributed to the ‘interface controlled diffusional creep’.

2. Materials and experimental procedure

The nanocrystalline Cu (here after, n-Cu) with purity of 99.995% was prepared by means of the electrodeposition technique with an electrolyte of CuSO4 and a substrate of Ti. The thickness of the n-Cu sheets was 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 cm−2, which is equivalent to 99.4% of the theoretical density for pure Cu. The full density of the as deposited n-Cu samples was also verified by position annihilation spectroscopy measurements, which confirm that the
sample contains no void-like (or vacancy-cluster like) volumes and no missing crystallites. The total oxygen content in the as deposited n-Cu was determined to be 24 (± 1) ppm by using LECO TC-436 oxygen/nitrogen determination analysis.

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 gage length and 1.0 × 0.7 mm² in cross section. The creep tests were performed on a miniaturised creep apparatus. The error of applied stress was within ± 0.1 MPa. The test temperatures were held constant to within ± 1°C.

The creep strain was measured by means of a differential transformer with high sensitivity of 0.27 µm, so that a low creep rate down to 2 × 10⁻⁷ s⁻¹ (this corresponds to an elongation 0.28 µm in a time interval 70 s) can be detected.

A series of annealing experiment 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 (0.22–0.24 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 difference creep temperatures. Measurements of grain size showed that no grain growth occurred during the annealing and the creep tests.

3. Results

Fig. 1 shows an example of creep curves of the nano-grained pure Cu. It can be seen that the creep curve contains the primary and steady state stages as usually observed in high temperature creep in coarse grained metals, but the tertiary stage is very short.

Fig. 2 shows the strain–time (ε–t) curves in the primary stage. One can see that the strain ε is linear with the cube root of time t¹⁄³. Hence the primary creep obeys the Andrade's law [14,15]

\[ \varepsilon = \varepsilon_0 + \beta t^{1/3} \]  

where ε₀ is the instantaneous strain, and β the slope of ε–t¹⁄³ 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, 30, 40, and 50°C). Each stress jump was carried out after the steady state had been reached for a sufficient time under the proceeding stress.

Fig. 3 shows the SSCR as a function of applied 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 σ₀ at each test temperature. The σ₀ obviously decreases with increasing temperature. The values of σ₀ at 20, 30, 40 and 50°C obtained from the extrapolation of the straight lines in Fig. 3 are 137, 134, 129, and 124 MPa, respectively. Accordingly the effective stress is

\[ \sigma_e = \sigma - \sigma_0 \]
Fig. 4 shows the SSCR as a function of effective stress $\sigma_e$. It can be seen from Fig. 4 that the SSCR is proportional to the effective stress and increases with increasing temperature. Hence the SSCR $\dot{\varepsilon}$ can be expressed as

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

(3)

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

With the values of the slopes of $\dot{\varepsilon}/\sigma_e$ at different temperature in Fig. 4, the parameter $kT\dot{\varepsilon}/\sigma_e$ as a function of $1/T$ is plotted in Fig. 5. From the slope and the intercept of the straight line in Fig. 5, we obtain the activation energy $Q = 0.72 (\pm 0.5)$ eV and $A = 1.07 \times 10^{-22}$ m$^3$ s$^{-1}$.

Fig. 6 shows the threshold stress $\sigma_0$ as a function of the absolute temperature $T$. The relation between $\sigma_0$ and $T$ can be expressed as

$$\sigma_0 = B_0 \left(1 - \frac{T}{T_c}\right),$$

(4)

where $T_c$ is a critical temperature, and $B_0$ is a constant. From Fig. 6 we obtained that $T_c \approx 617$ K at which the $\sigma_0$ is expected to diminish, and that $B_0 \approx 262$ MPa which is the expected value of $\sigma_0$ at $T = 0$ K.

4. Discussion

The results indicate that the SSCR is proportional to the effective stress $\sigma_e$. The activation energy of the creep 0.72 eV is obviously smaller than that of lattice diffusion (2.0 eV) and grain boundary diffusion (1.08 eV) in coarse grained Cu [16], but it close to that of grain boundary diffusion in nano-grained Cu (0.69 eV [16], 0.64 eV [17]). Hence, the creep is likely to be associated with grain boundary diffusion.

The values of experimental SSCR are found to be of the same order of magnitude as those calculated from the equation for Coble creep [18], i.e.

$$\dot{\varepsilon} = \frac{148D_b\delta \Omega \sigma_e}{\pi d^3 kT},$$

(5)

with the grain boundary diffusion coefficient

$$D_b = D_{b0} \exp\left(-\frac{Q_b}{kT}\right),$$

(6)

where $D_{b0}$ is the pre-exponential factor, $Q_b$ the activation energy, $\delta$ the thickness of grain boundaries, $\Omega$ the atomic volume, and $d$ 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, $\Omega = 8.78 \times 10^{-30}$ m and $D_{b0} = 3 \times 10^{-9} \exp(-0.64$ eV $k^{-1}$ $T^{-1}$) m$^2$ s$^{-1}$ [17] were substituted into Eqs. (5) and (6). We found that at the creep temperatures and the effec-

Fig. 4. Steady state creep rate as a function of effective stress $\sigma$ for nano-grained pure Cu at different temperatures.

Fig. 5. The parameters $kT\dot{\varepsilon}/\sigma_e$ as a function of $1/T$ for nano-grained pure Cu.

Fig. 6. The threshold stress $\sigma_0$ as a function of temperature $T$.

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

We did several tests at stresses below $\sigma_0$, no visible creep strain was detected in a reasonable period, confirming the existence of the threshold stress.
tive 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 $\sigma_0 = 20$ MPa, the calculated SSCR is equal of $5.3 \times 10^{-6}$ s$^{-1}$, while the measured value is $1.1 \times 10^{-6}$ s$^{-1}$ (see Fig. 4).

It is noted that the grain boundary diffusion coefficient $D_b$ used for the above estimation is based on the data measured by tracer diffusion experiments in nano-grained Cu with average grain size 8 nm [17], while in our experiments, the average grain size is 30 nm. It is possible that the $Q_b$ increases and the $D_b$ decreases with increasing grain size. If we substitute a larger $Q_b$ and hence a smaller $D_b$ into Eq. (5), a better agreement between the calculated and the measured creep rates could be reached.

From the intercept of the ordinate of the straight line at $1/T=0$ in Fig. 5, we have $148D_b\partial\Omega/\pi d^3 = 1.07 \times 10^{-2}$ m$^3$ s$^{-1}$, hence the value of $D_{b0}$ can be estimated to be $1.4 \times 10^{-3}$ m$^3$ s$^{-1}$. If we adopt this $D_{b0}$ value and the activation energy $Q_b = 0.72$ eV, the calculated values of SCSR of the nano-grained Cu according to Eqs. (5) and (6) would be coincident with the measured values.

The existence of the threshold stress implies that the grain boundaries do not act as perfect source and sinks of atoms (or vacancies), as pointed out by Ashby [19], Arzt, Ashby and Verrall [20], Gleiter [21], Balluffi [22] and Poirier [23]. 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 energy for the emission and absorption of atoms (or vacancies) at grain boundaries, resulting in the threshold stress $\sigma_0$.

Based on the aforementioned analyses, one may suggest that the low temperature creep of the nano-grained pure Cu in this study is controlled by not only the diffusion along grain boundaries, but also the emission and absorption of atoms (or vacancies) at grain boundaries. In other words, 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 [20]. In the present case, the creep can be called ‘interface controlled cable creep’.

Gleiter [21] 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 act as point defect sources or sinks only above a threshold stress. In fact, a high fraction of low energy grain boundaries in nano-grained Cu was observed by Sanders et al. [8]. Hence 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 studied further.

The primary creep as demonstrated in Figs. 1 and 2 is possibly corresponding to the transient period for the establishment of steady state condition of diffusional fluxes [24].

5. Conclusions

Tensile creep of nano-grained pure Cu with an average grain of 30 nm prepared by electrodeposition technique has been investigated at low temperatures (0.22–0.24 $T_m$). The creep curves contain the primary and steady state stages. The strain–time relation in the primary creep obeys the Andrade’s law.

The steady state creep rate is proportional to the effective stress $\sigma_e = (\sigma - \sigma_0)$ where $\sigma$ is the applied stress, and $\sigma_0$ the threshold stress. The activation energy for the creep is measured to be 0.72 ($\pm$ 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.

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. The mechanism of the threshold stress and its relation with temperature are to be further studied in connection with the microstructure of grain boundaries.

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’, more exactly the ‘interface controlled Coble creep’.

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