**Superplasticity Extensibility and Deformation Mechanism of a Nanocrystalline Copper Sample**

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By means of the electrodeposition technique, a bulk sample of nanocrystalline (nc) copper was prepared with high purity and high density. An extreme extensibility (elongation >5000 %) without a strain hardening effect was observed when the nc Cu sample was rolled at room temperature. A detailed study on the microstructure evolution of the nc Cu during the cold-rolling process was examined by means of X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), and thermal analysis. It was indicated that the deformation process in the nc Cu sample is dominated by the grain boundary activity rather than lattice dislocation. This phenomenon agrees well with the observed mechanical behavior of the nc Cu sample.

1. Introduction

Owing to the ultrafine microstructure, the deformation mechanism of nanocrystalline (nc) materials may fundamentally differ from that in conventional polycrystalline materials.[1–3] Therefore, mechanical properties of nc materials have attracted considerable interests in the past decade.[4,5] For the conventional coarse-grained (cg) materials, it is known that the plastic deformation was predominated by the dislocation movement mechanism at relatively low temperature and by the diffusional creep mechanism at higher temperatures. According to the Coble creep equation, the diffusion creep rate ($\dot{\epsilon}$) is related to the grain size by:[6]

$$\dot{\epsilon} = \frac{B \Omega \sigma a d^2 D_{gb}}{d^3 kT}$$  (1)

where $\sigma$ is the tensile stress, $\Omega$ the atomic volume, $d$ the average grain size, $D_{gb}$ the grain boundary diffusivity. It is clear that the diffusional creep may be enhanced when the grain size is reduced and/or the grain boundary diffusivity is enhanced. Based on this mechanism, Gleiter et al.[4,7] predicted that a nc material would make it to high creep rates and a large scale deformation at much lower homologous temperatures, so that ductile ceramics and diffusional creep of pure metals would be possible even at room temperature.[7] Recent computer simulation results supported this expectation and indicated that plastic deformation of nc metals occurs by grain boundary sliding and motion with a minor lattice dislocation activity at low temperature,[8,9] which is in some ways similar to the way grain boundaries carry most of the deformation in superplasticity,[10] Softening with grain refinement in a nc Cu was seen in the simulation due to the dominant grain boundary deformation mechanism.[9]

Nevertheless, the progress is slow in experimental investigations on mechanical properties and deformation mechanism in nc materials. One of the major obstacles is the nc sample preparation from which various artifacts are introduced. These artifacts, such as porosity, contamination, residual stress, etc., have significant effects on the mechanical performance.[11] Therefore, it is always difficult to distinguish the intrinsic nanostructure effect on the mechanical properties as well as the underlying deformation mechanism from the observed mechanical performance in which those artifacts may play an important role. In order to identify the intrinsic mechanical properties of the nc materials and to exclude the influence of various artifacts, “ideal” nc samples are urgently needed.
needed, i.e., large sizes, free of porosity, contamination, and residual stress.

In this article we report our investigation on a bulk nc Cu sample with high purity (purity better than 99.993 at.-%) and high density, which was synthesized by means of the electrodeposition technique. The average grain (or crystalline domain) size of the as-deposited nc Cu specimen is about 30 nm and the mean microstrain is only 0.03 %. Plastic deformation of the as-deposited nc Cu specimen was carried out by using cold rolling at room temperature and a detailed study on the microstructure evolution during the cold-rolling process was investigated by means of X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and thermal analysis. The structural features indicated that the deformation process in the nc Cu is predominated by grain boundary activities rather than lattice dislocations.

2. Cold-Rolling Behavior of the nc Cu Sample

A piece of nc Cu sample (16 × 4 × 1 mm³) cut from the as-deposited sheet was rolled at room temperature using a twin-roller (with a diameter of 40 mm) apparatus. Cold rolling results in a continuous increase in the sample length in the direction of rolling while the sample width keeps unchanged. With the progress of repeated rolling, it is striking to find that the sample became longer and longer, as shown in Figure 1, eventually resulting in a uniform long thin ribbon (about 20 µm thick) with smooth surfaces and straight edges (without any cracks forming at the sample edges). The strain rate during rolling was controlled to be around 1 × 10⁻³–1 × 10⁻² s⁻¹. The total degree of deformation, \( e = (t_0 - t)/t \) (where \( t_0 \) and \( t \) denote thickness of the initial and the as-rolled samples, respectively), can be as large as 5100 %. Further cold rolling is still possible to extend the deformation.

Such an extreme extensibility has not been observed in the conventional coarse-grained (cg) polycrystalline Cu, which may break usually after an extension of about 800 %. The nc Cu was annealed at 500 °C for 48 h in vacuum (resulting in a much larger grain size of about 100 µm). Under the same circumstances, the as-annealed Cu sample was rolled and when the degree of deformation reached about 700 %, the sample remarkably hardened and cracks formed at the sample edges as is usually observed for conventional cg Cu. This observation implies that the extreme extensibility in the as-deposited Cu originates from the ultrafine-grained structures, while other effects, including the purity effect, can be ruled out.

3. Mechanical Property

Microhardness measurements showed a slight hardness increase in the as-deposited nc Cu induced at the initial stage of rolling, from 1.05 GPa (as-deposited) to 1.20 GPa (\( e = 800 \) %), as shown in Figure 2, and no strain hardening effect was seen with further rolling (\( e > 800 \) %). This is in contrast with the evident strain hardening effect in conventional cg Cu, from 0.6 GPa (initial state) to 1.57 GPa (\( e = 800 \) %, with crack formation) and in as-annealed Cu from 0.51 GPa (initial state) to 1.45 GPa (\( e = 650 \) %, with crack formation), both effects are shown in Figure 2. It is clear that the hardness variation tendencies differ fundamentally between the nc and the cg Cu samples, indicating different underlying deformation mechanisms.

4. Structure Characterization

Figure 3a displays the average grain size (determined from XRD result) of the as-rolled nc Cu specimens as a function of the degree of deformation in the cold rolling process. It is seen that the average grain size of the nc Cu samples remains unchanged during the whole rolling process, being about 30 nm. However, the microstrain in the cold rolled nc Cu samples varied significantly. Figure 3b shows the mean microstrain (\( \varepsilon \)) and the microstrains in (111) and (100) planes (\( \varepsilon_{111} \) and \( \varepsilon_{100} \)) for the nc Cu samples as a function of the degree of deformation. During the cold rolling process, \( \varepsilon_{111} \) increases slightly from 0.06 % to 0.1 % when the sample was deformed to 500 % and then dropped down to zero. The vanishing microstrain in the (111) plane during deformation may be attributed to the easy dislocation sliding in the (111) plane.

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**Fig. 1.** The nc Cu specimens before and after cold rolling at room temperature with different amounts of deformation degree (e) as indicated.

**Fig. 2.** Microhardness variation with the deformation degree of cold rolling for the as-deposited nc Cu specimen, the conventional cg polycrystalline Cu, and the as-annealed cg Cu as indicated.
in Cu with a fcc structure. Little change was found in the $\varepsilon_{100}$ when $\varepsilon < 500 \%$. When $\varepsilon > 500 \%$, $\varepsilon_{100}$ increased slightly from 0.12 $\%$ to 0.16 $\%$ and then tended to a saturated value of about 0.16 $\%$ (when $\varepsilon \geq 1000 \%$). The mean microstrain increased gradually from 0.03 $\%$ to 0.16 $\%$ and saturated at about 0.16 $\%$.

HRTEM observations indicated that the average grain size of the as-deposited Cu sample is about 20 nm, which is close to the XRD result. Most of the nanometer-sized crystallites (or domains) in the as-deposited nc Cu specimen are separated by small-angle grain boundaries and the misorientation angle is in a range of 1–10°. After the cold-rolling process, it is found that the dislocation density increased. The misorientation angle of the nanocrystallites increased evidently to 6–18° in the as-rolled nc Cu specimen with a deformation degree of 2300 %. The mean misorientation angle (statistic result) is about 13°. This means that when the as-deposited nc Cu was rolled, the small angle grain boundaries evolved to different grain boundaries with a much larger misorientation, while the average crystallites size remains unchanged. Or in other words, a major observed effect results from the cold-rolling treatment of the nc Cu sample is the obvious increment of the grain boundary misorientation angle, or the grain boundary dislocation density, which might be correlated with the obvious increase in the mean microstrain determined from XRD.

5. Thermal Analysis

The thermal effects in the nc Cu samples with various degrees of deformation were measured in differential scanning calorimetry (DSC) at a constant heating rate. When the as-deposited nc Cu sample was heated, a rather weak exothermal signal was observed in the DSC curve at about 150°C ($T_p$), which originated from the microstrain release process. For the as-rolled nc Cu samples, a clear exothermal peak was observed, with an increase of the degree of deformation, the exothermal peak of the as-rolled nc Cu sample shifts to lower temperatures. The exothermic peak for the as-rolled ones may be attributed to the microstrain release process and the grain growth process as well, which was confirmed by XRD results. The observed thermal effect in the as-rolled nc Cu is much different from that in the deformed cg Cu. When the as-rolled cg Cu sample with the same degree of deformation was heated, no thermal effect can be detected in the measured temperature range. It is evident that the stored energy in the nc Cu induced by plastic deformation is larger than that in the cg Cu specimens.

The variation of the characteristic temperature as a function of the degree of deformation in the nc Cu is shown in Figure 4a. It can be seen that both the peak and onset temperatures decrease significantly with an increase of the degree of deformation, and tend to saturation values of 140°C to
120 °C, respectively. The total decrease is as large as 50 °C for the peak temperature and 35 °C for the onset temperature. Such a large difference in the instability temperature implies a remarkable change in the microstructure of the as-rolled nc Cu samples. The saturating instability temperatures indicated that, when \( \varepsilon > 1000 \% \), the microstructure of the as-rolled nc Cu specimens tends to a stable state during the cold-rolling process. No further structural evolution may be activated by plastic deformation.

Figure 4b shows the measured heat release (\( \Delta H \)) as a function of the degree of deformation in the nc Cu. It is obvious that the heat release increases significantly at the initial stage of rolling and tends to a saturated value of about 0.94 J/g when \( \varepsilon > 1000 \% \). It is clear that the heat release in the nc Cu specimens is only a small fraction of the heat of fusion (\( \Delta H_f \)) (about 0.45 % \( \Delta H_f \) for the as-rolled nc Cu with \( \varepsilon \geq 1000 \%) . This value is much smaller than those reported in the literature: \( \Delta H \) is about 2 % \( \Delta H_f \) for the consolidated ultrafine nc Cu powders\(^{[14]} \) and sub-microcrystalline Cu produced by means of severe plastic deformation,\(^{[15]} \) and about 39 % \( \Delta H_f \) in the ball-milling nc Cu.\(^{[16,17]} \) The difference between our measured results and the literature data may be attributed to the following two reasons: i) The difference in grain boundary structures. In either the consolidated nc samples or the samples made by means of ball-milled or severe plastic deformation, high-angle grain boundaries with random crystallite orientations and a high density of grain boundary defects are formed during the procedure process. While for our nc Cu samples, most grain boundaries are of small-angle, therefore, these grain boundaries have a small excess enthalpy. ii) Measurement accuracy. Checking the measurement procedures and results in the literature, e.g., for the ball-milled nc Cu specimens, a very large heat release that was calculated from the integration of the area under the large exothermal peak in the DSC (100–500 °C) was assumed to be the grain boundary excess enthalpy only. This procedure is questionable as the nc Cu may be easily oxidized in this temperature range, especially when the temperature exceeds 250 °C. The heat effect due to oxidation of Cu (which is also exothermic) might contribute a major part of the total measured heat release. In our experiments, oxidation of the nc Cu sample surface was strictly controlled. The oxidation of nc Cu is negligible.

### 6. Grain Boundary Enthalpy

Supposing the grain boundary enthalpy \( \gamma \) keeps unchanged during the grain growth process, one may get the grain boundary enthalpy from the heat release during the grain growth process by:

\[
\gamma = \frac{\Delta H_{gb}}{\Delta S_{gb}}
\]

where \( \Delta S_{gb} \) is the total grain boundary area in the nc sample from an initial grain size of \( d_0 \) to a final size of \( d_f \).

XRD results indicated that, during the grain growth process, the average grain size of nc Cu samples was increased from 30 nm to about 80 nm.\(^{[13]} \) Figure 5 shows the resultant grain boundary enthalpy for the nc Cu samples as a function of the degree of deformation. It is obvious that the grain boundary enthalpy of the as-deposited nc Cu is small, only about 0.012 J/m². The grain boundary enthalpy increased gradually during the deformation process and tended to a saturated value of about 0.27 J/m² when \( \varepsilon > 1000 \% \).

It is known that the mean misorientation angle of the crystallites in the as-rolled nc Cu increases to about 13°, which is still in the range of the small-angle grain boundaries. Based on the tilt dislocation model, the small-angle grain boundary (\( \theta < 15° \)) energy (\( \gamma_{gb} \)) is related to the misorientation (\( \theta \)) by:\(^{[18]} \)

\[
\gamma_{gb} = E_0 \theta (A_0 \ln \theta)
\]

where \( \theta \) is the misorientation angle of the crystallites, \( E_0 \) and \( A_0 \) are constants that are related to the elastic strain energy.

Taking the relevant parameters from the literature for Cu,\(^{[19]} \) one may get an estimated value of grain boundary energy of 0.30 J/m² for \( \theta = 13° \). This value is rather consistent with our measured grain boundary enthalpy of 0.27 J/m² from the DSC experiments.

From the variation tendencies of grain boundary enthalpy (as shown in Fig. 5) and the microstrain (Fig. 3b) with the degree of deformation in the nc Cu, one may find that the cold-rolling process can be divided into two stages in which the deformation mechanism may be proposed.

Stage I: \( \varepsilon < 1000 \% \). In this stage, the deformation process seems to be dominated by dislocation activities (probably in large grains or at the grain boundaries). Generation and motion of dislocations may result in a substantial increase in the density of defect (i.e., the microstrain) and in the misorientation between neighboring grains due to the pile-up of dislocations at grain boundaries. Hence the grain boundary energy increases in this stage. This tendency can also be verified by the hardness measurement results that show a slight hardening effect during this stage (as seen in Fig. 2).

Stage II: \( \varepsilon \geq 1000 \% \). The microstrain, grain boundary enthalpy, and grain boundary structure, as well as the grain size remain unchanged in this deformation stage. Also, the hardness of the nc Cu sample becomes a constant when \( \varepsilon \geq 1000 \% \).
(Fig. 2). This implies that the lattice dislocation activity is no longer a dominating mechanism in the deformation. Instead, grain boundary activities (grain boundary sliding or grain boundary diffusional creep) may be activated and become dominant in the deformation as the grain boundary structure evolves to be of higher energy (with a higher density of defects). When the deformation is controlled by grain boundary activities, strain-hardening effects disappear, and the grain boundary structure as well as the dislocation density tend to be saturated.