Hardness and strain rate sensitivity of nanocrystalline Cu

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Abstract

The measured hardness of nanocrystalline Cu with grain sizes ($d$) as small as 10 nm still follows the Hall–Petch relation. A rate sensitivity of $0.06 \pm 0.01$ and a flow stress activation volume of $8b^3$ were determined at $d = 10$ nm, suggesting grain boundary activities are enhanced but not yet dominant in the plastic deformation.

Keywords: Nanocrystalline Cu; Hall–Petch relation; Grain size; Strain rate sensitivity

1. Introduction

One of the crucial issues under debate for nanocrystalline (nc) materials is whether their plastic deformation is dominated by grain boundary (GB) activities (such as GB sliding or GB diffusional creep) once the grain size ($d$) is small enough. Molecular dynamics (MD) simulations [1] indicated that GB sliding dominates the plastic deformation in Cu with $d < 8$ nm. Another simulation [2] showed a maximum flow strength at $d = 10–15$ nm in Cu, corresponding to a shift in the microscopic deformation mechanism from dislocation-mediated plasticity to GB sliding. However, such a maximum strength or hardness has not yet been observed experimentally, at least in pure metals. Earlier experimental observations of the so-called inverse Hall–Petch (H–P) relation in Cu [3] may be attributed to the processing-induced flaws or porosities in the samples tested. Knapp and Follstaedt [4] found that the hardness of pulsed laser deposited nc Ni samples with a high density follows the empirical H–P relation even at $d = 10$ nm. For nc Cu samples the smallest $d$ ever reported for which the hardness data still fit the H–P plot is about 16 nm [3].

Two key signatures of deformation dynamics are strain rate sensitivity ($m$) and flow stress activation volume ($V^*$), which shed light on the thermally activated mechanisms contributing to plastic deformation processes in metals. The $m$ value of a material is expressed as [5]

$$m = \frac{\sqrt{3}kT}{V^*\sigma} = \frac{3\sqrt{3}kT}{V^*H},$$

where $k$ is Boltzmann’s constant, $T$ is absolute temperature, $\sigma$ is the flow stress, $H$ is hardness (usually assumed to be $3\sigma$) and $V^*$ is the activation volume, which is the rate of decrease of the activation enthalpy with respect to flow stress

$$V^* = \sqrt{3}kT \left( \frac{\partial \ln \dot{\varepsilon}}{\partial \sigma} \right),$$

where $\dot{\varepsilon}$ is the strain rate. For coarse-grained (CG) Cu, an increase in $m$ value from 0.004 to 0.0072 was observed as $d$ decreased from 90 to 12 $\mu$m [6]. When $d$ was reduced down to the submicron or nanometer regime, $m$ value increased further. For Cu with $d = 20$ nm, $m$ reached 0.035 [7,8]. Yet, this value is still far below that corresponding to the occurrence of GB sliding ($m = 0.5$) [9] or Coble creep ($m = 1.0$) [10].

Measurements of $d$-dependent mechanical properties down to 10 nm will be of great significance for understanding the deformation mechanism in nc materials. In this work, a series of Cu samples with $d$ ranging from 10 nm
to a few hundreds of nm were prepared by means of different techniques. Hardness, rate sensitivity and $I^*$ value, as well as their dependence of grain size, were determined by means of nanoindentation tests, in order to analyze the intrinsic deformation mechanism.

2. Experimental procedures

Three different techniques have been employed to synthesize the nc Cu specimens. Cu films (of about 600 nm thick) with grain sizes as small as 10 nm were prepared by means of magnetron sputtering using a pure Cu target (99.998% purity) on a pre-oxidized Si(111) substrate kept at room temperature (hereafter referred to as RTMS-Cu) and at liquid-nitrogen temperature (LTMS-Cu). Scanning electron microscopy observations indicated that the as-deposited films were continuous without any surface cracks or pores. Less than 200 ppm (wt.%) oxygen contamination was detected by Auger electron spectroscopy (AES) on the fresh surfaces of the as-deposited films.

A surface mechanical attrition treatment (SMAT) [11] was applied to synthesize a layer of nc Cu on a bulk Cu plate (99.998% purity). The processing details were reported in Ref. [11]. After the treatment, the surface layer of about 15 μm thick, in which grains are refined to the nanoscale, was removed from the Cu plate (referred to as SMAT-Cu) for the measurements.

Bulk ultra-fine grained (ufg) Cu samples (with grain sizes in the submicron regime) were prepared by using the equal channel angular pressing technique [12] (ECAP, referred to as ECAP-Cu). Bulk copper rods (99.998% purity) were pressed through a 90° die for eight cycles with the rod axis rotated through 90° clockwise and then 90° anticlockwise for each alternate pass.

The microstructures of the nc Cu samples were characterized by means of X-ray diffraction (XRD) on a Rigaku DMAX/2400 diffractometer with CuKα radiation and transmission electron microscopy (TEM) on a JEM 2000 EX with an accelerating voltage of 200 kV. Nanoindentation was used to measure the hardness and rate sensitivity values of the samples. The indentation method for rate sensitivity measurements can be found in Ref. [13]. In the indentation process, the material underneath the indenter can be likened to an expanding cavity with a hydrostatic core and an expanding elastic/plastic boundary. The creep process is believed to depend upon the rate at which the elastic/plastic boundary can proceed into the material. For a geometrically similar indenter the instantaneous displacement rate of the indenter divided by the instantaneous displacement is typically defined as the indentation strain rate, which can be approximated as a steady-state strain rate from uniaxial tests.

The indentations were performed on a Nanoindenter XP with a Berkovich tip. Nanoindentation tests at constant strain rates in ranges of about $10^{-2} \sim 10^{-3}$ s$^{-1}$ and $10^{-3} \sim 10^{-5}$ s$^{-1}$ were performed for the nc Cu samples and other Cu specimens, respectively. For example, the specimens were loaded at a constant strain rate of $2.5 \times 10^{-2}$ s$^{-1}$ to a maximum depth of about 50 nm for the film specimens and 1000 nm for bulk samples and held constant for 15 s. Then specimens were unloaded to 10% the maximum load and held constant for 20 s for thermal drift calibration. For the film samples, the as-deposited surfaces were used for indentation of which the root mean square (RMS) roughness was less than 3 nm. The bulk samples were electro-polished before testing, resulting in stress-free surfaces with an RMS roughness of several tens of nm (as listed in Table 1).

3. Results and discussion

Figs. 1(a) to (c) show plan-view TEM images of the LTMS-Cu sample, in which uniformly distributed nanosized grains are seen. The selected area electron diffraction (SAED) pattern (Fig. 1(c)) indicates random crystallographic orientations of the tiny grains. Quantitative analysis of a number of dark-field TEM images showed that the plan-view grain size of the sample ranges from 2 to 18 nm, with an average value of $d_0 = 6 \pm 3$ nm (as shown in Fig. 1(d)). This value is comparable to that derived from quantitative XRD analysis according to the Scherrer equation (about 4 nm). XRD analysis substantiates a clear (111) texture in the sample with a peak intensity ratio ($I_{(111)}/I_{(200)}$) of 3.1 as compared to 2.2 for the texture-free Cu. Considering the columnar-shaped grains in the as-deposited sample and that dislocations glide mainly in the inclined {111} planes, one may approximate the effective $d$ of the film samples as the dimension of the inclined {111} plane, being $\sqrt{3}d_0$. Hence, the effective average $d$ for LTMS-Cu sample and RTMS-Cu samples can be derived as $10 \pm 5$ nm and $31 \pm 12$ nm, respectively. The average grain sizes of other Cu samples were determined similarly using TEM and XRD analysis. The results are listed in Table 1.

The hardness of various nc Cu samples was determined by using nanoindentation. The measured hardness of the LTMS-Cu sample with $d = 10$ nm was as high as 3.02 GPa, which was the highest hardness for all known Cu, nc or otherwise, prepared via the different approaches. Hardness of the SMAT-Cu was about 1.75 GPa, which agrees with the previous tensile test data [14]. For the ECAP-Cu hardness was about 1.67 GPa, consistent with the previously reported data [12]. Fig. 2(a) plots hardness vs. $d^{1/2}$ using our measured data and those reported in

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Purity (wt.%)</th>
<th>RMS roughness (nm)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTMS-Cu</td>
<td>[O] &lt; 200 ppm</td>
<td>2.4</td>
<td>10 ± 5</td>
</tr>
<tr>
<td>RTMS-Cu</td>
<td>[O] &lt; 200 ppm</td>
<td>2.8</td>
<td>31 ± 12</td>
</tr>
<tr>
<td>SMAT-Cu</td>
<td>99.99+%</td>
<td>36</td>
<td>42 ± 15</td>
</tr>
<tr>
<td>ECAP-Cu</td>
<td>99.99+%</td>
<td>22</td>
<td>190 ± 80</td>
</tr>
</tbody>
</table>
Fig. 1. Plan-view bright-field (a), dark-field (b) TEM images and a corresponding SAED pattern (c) of the LTMS-Cu sample. (d) Plan-view grain size distribution determined from dark-field TEM images.

Fig. 2. (a) Variation of hardness with $d^{-1/2}$ for various Cu samples. Literature data on hardness [3,15–17] (solid symbols) and yield strength (multiplied by 3) from compression tests [3,16,19–22] (empty symbols) are also included. (b) Variation of tensile yield strength with $d^{-1/2}$ for various Cu samples reported in the literature [3,12,15,19,22–26]. The straight lines represent the H–P relation extrapolated from the CG-Cu [18].
the literature [3,15–17,19–22]. For comparison, Fig. 2(b) plots the tensile yield strength (multiplied by 3) vs. \(d^{-1/2}\) for various Cu specimens [3,12,15,19,22–26]. Attention should be paid to the following features.

Firstly, the hardness data follow the H–P line even when \(d\) is as small as 10 nm, indicating that grain refinement hardening is still valid as long as \(d\) is larger than 10 nm for Cu, in contrast to the MD simulation results that show softening appears at about 10–15 nm [2].

Secondly, both the hardness and tensile strength for the ufg Cu samples (with \(d\) in the submicron regime) are obviously higher than the H–P line. Note that most ufg samples were prepared via severe plastic deformation, in which dense dislocation walls, tangles, cell walls, or even subgrain boundaries are formed. These are barriers to dislocation motion and hence strengthen materials. The deviation of experimental hardness and strength data from the H–P line seems to diminish when \(d\) is smaller than 100 nm, which may correspond to a critical crystallite dimension below which the presence of substructures like dislocation cells become unlikely.

Thirdly, it can be found that some measured data of tensile yield strengths are obviously lower than the H–P line when \(d < 100\) nm (as seen in Fig. 2(b)). This was attributed to the effect of residual porosities [3]. For the porosity-free SMAT nc Cu samples [24] and the porosity-free ufg Cu sample with nanoscale twins [23], the tensile data fit the H–P line very well.

Fig. 3 shows a comparison of typical double logarithmic curves of hardness vs. indentation strain rate for the nc Cu samples with those for CG (with grain sizes larger than 100 \(\mu\)m) and single crystal Cu(123) samples. Evidently, the rate sensitivity \((m)\) values of the nc Cu samples are much larger than those of the CG counterparts. The statistical distributions of measured \(m\) values (from 50 repeated indents each) for various specimens were presented in Figs. 4(a) to (f). For the single crystal CG-Cu and Cu(123) samples, \(m = 0.009 \pm 0.002\) and \(0.006 \pm 0.001\), respectively, which are consistent with the literature data determined from tensile or compression tests \((m = 0.004–0.007)\) for CG-Cu [6,27] and \(m = 0.006\) for Cu(431) single crystal [28]). The \(m\) value of the ECAP-Cu sample is \(0.020 \pm 0.007\), which is comparable to the reported data \(m = 0.009–0.029\) [7,20,29]. For RTMS-Cu and SMAT-Cu, with similar \(d\), the \(m\) values are comparable, being \(0.038 \pm 0.006\) and \(0.032 \pm 0.003\), respectively. \(m = 0.06 \pm 0.01\) was found for LTMS-Cu sample, which is about 10 times higher than...
that of Cu(123). The agreement between the measured results in the present work and the literature data indicates that the nanoindentation technique employed has a satisfactory accuracy in determining rate sensitivity. The scattering of \( m \) values might be attributed to the inhomogeneity of \( d \) distribution, surface roughness and possible presence of oxides at sample surfaces. Here we ignored the effect of grain growth induced by the large deformation (high stress) under the indenter on the measured \( m \) values, as observed by Zhang et al. [30].

Fig. 5 presents the variation of \( m \) as a function of \( d \) for nc Cu including the literature data from various testing methods [6–8,20,27–29]. Despite some inconsistency in the absolute values obtained using different synthesis techniques or different testing methods, a consistent trend is clear: \( m \) values increase slightly with a decreasing \( d \) from the macro to the submicron scale (from 0.006 to about 0.02), while an obvious “take-off” appears when \( d \) is reduced below 100 nm or so. The \( m \) value increases from about 0.02 at \( d = 100 \text{ nm} \) to 0.06 at \( d = 10 \text{ nm} \). Such a transition in the \( m-\) variation tendency may imply a change in the plastic deformation mechanism.

Fig. 6 presents the correlation between \( V^* \) and \( d \) for Cu samples together with some literature data [7,13,27,29,31]. Our results on single crystal, CG and ufg samples are consistent with those reported in the literature [7,27,29,31]. With a decreasing \( d \), \( V^* \) falls drastically from a few thousand \( b^3 \) to about 50\( b^3 \) in the submicron regime. Further decreasing \( d \) leads to a slight decrease in \( V^* \), to about 8\( b^3 \) when \( d \) approaches 10 nm. Extremely small \( V^* \) values in nc samples were also observed in nc Cu–Ni–P alloy samples with \( d \) varying from 33 to 7 nm, in which a single solid solution face-centered cubic (fcc) structured nanophase is formed [13]. And \( V^* \) of the alloy falls to about 8\( b^3 \) for \( d = 7 \text{ nm} \).

The overall rate-dependence of a material is influenced by dislocation activities, GB diffusion and lattice diffusion [32]. Generally the contribution of lattice diffusion is negligible at RT. For CG fcc metals, forest lattice dislocation dominates the plastic deformation, resulting in weak strain rate sensitivities and high \( V^* \) values (~1000\( b^3 \)). With a decrease in \( d \) to the submicron regime, the forest cutting mechanism is suppressed because of the large amount of GBs and/or subgrain boundaries which serve as significant obstacles to dislocation motions. Hence, \( m \) value increases and \( V^* \) drops.

When grains of fcc metals are further refined into the nanometer regime, the plastic deformation is still dominated by dislocation activities, as indicated by experimental results for hardness as shown in Fig. 2(a), as well as the MD simulations [33]. For extremely small \( d \) values, the continuous nucleation of lattice dislocation from Frank–Read sources and their pile-ups in the grain interior are not valid any longer. It was suggested by MD simulations that the most possible sites for dislocations nucleation are GBs, and most dislocations that would not be trapped inside the lattice would terminate at the opposite GBs [33]. Therefore, it is supposed that the plastic deformation mechanism of nc Cu samples is dominated by dislocation–GB interactions while the forest cutting dislocations in lattice play a negligible role. The highly localized dislocation activities at the GBs would contribute to an extraordinary rate sensitivity and a small \( V^* \). The transition in the plastic deformation mechanism in Cu from forest cutting to the dislocation–GB interaction may correspond to a transition in the \( m-\) and the \( m-\) correlations as observed experimentally.

A mechanistic model for nc metals has been developed by Asaro and Suresh [5] in terms of the emission of dislocations at a stress concentration at GBs. They observed that \( V^* \) decreases monotonically with a reduction of \( d \) and tends to a value of 3–10\( b^3 \) with \( d \) of a few nanometers. The extremely small value of \( V^* \) coincides with our measured data (8\( b^3 \)) in the nc Cu alloy samples [13]. In fact,
for nc samples with $d$ of a few nanometers, both the dislocation length and its travel distance are extremely small, hence an extremely small $V^*$ is anticipated.

Cheng et al. [34] recently presented a similar summary of Cu behavior, including its tensile strength and strain rate sensitivity as a function of grain size down to 20 nm. The elevated strain rate sensitivity and the small activation volume were explained using a model considering the length scales in nc grains during grain boundary–dislocation interactions. Their results indicated the grain boundary diffusion mediated mechanisms are not yet dominant over dislocation-based processes for the grain sizes studied, which is consistent with our present result.

Although the $m$ value of Cu in our study is enhanced by one order of magnitude when $d$ is reduced to 10 nm, it is still much smaller than that expected for the plastic deformation process controlled by GB sliding or Coble creep. The strain rate of GB sliding in polycrystalline materials is related to $d$ by [9]

$$
\dot{\varepsilon}_{\text{GBS}} = 2 \times 10^5 \frac{D_b}{kT} \left( \frac{b}{d} \right)^3 \left( \frac{\sigma_e}{\mu} \right)^2,
$$

where $\mu$ is the shear modulus, $\sigma_e$ is the effective stress and $D_b$ is the GB diffusion coefficient. Taking the parameters for Cu [32], the estimated $\dot{\varepsilon}_{\text{GBS}}$ is $\sim 10^{-5} \text{s}^{-1}$ at RT even at $d = 10$ nm, much smaller than the measured rate ($10^{-3} \text{s}^{-1}$). This means that the observed plastic deformation in the nc Cu sample is unlikely to be dominated by GB sliding. Similarly, the GB diffusion related Coble creep rate can be estimated, being $\sim 10^{-7} \text{s}^{-1}$ at RT for Cu with $d = 10$ nm, about 3–4 orders of magnitude below the measurement rate. Hence, Coble creep can be also ruled out from dominating the plastic deformation of the nc Cu. These analyses mean the plastic deformation for Cu with $d$ as small as 10 nm at RT is not yet dominated by GB diffusion or Coble creep.

It is noted that the critical $d$ values predicted from computer simulations (8 nm [1] or 10–15 nm [2]) differ from our measurement results. The difference is understandable as atomistic simulations were performed at extremely high strain rates ($>10^7 \text{s}^{-1}$), several orders of magnitude higher than that experimentally accessible, and plastic deformation in nc materials is more strain rate sensitive as compared with the CG counterparts.

4. Conclusions

Our experimental results showed that for pure Cu with grain sizes as small as 10 nm, hardness still follows the classical H–P relation, and the rate sensitivity value is one order of magnitude higher than that for CG-Cu. The flow stress activation volume for nc Cu with $d = 10$ nm was about $8b^3$. This experimental evidence indicates that GB diffusion related activities are much enhanced with grain refinement in the nanometer scale, but are not yet a dominating mechanism in plastic deformation of nc Cu sample even with $d$ values as small as 10 nm.

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