Critical shear stress for onset of plasticity in a nanocrystalline Cu determined by using nanoindentation

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Abstract

The plastic deformation behavior was investigated by using nanoindentation in a magneto-sputtered nanocrystalline (nc) Cu film with an average grain size of 14 nm. The determined critical shear stress to initiate plasticity in the nc-Cu sample (about 8.3 GPa) is identical to that for nucleation of lattice dislocations in an annealed coarse-grained Cu (8.5 GPa), and both values are close to the theoretical shear strength in the dislocation-free single crystal. This observation, in agreement with the atomistic simulation results, supports the argument that the onset of plasticity of the nc-Cu is associated with initiation of dislocation activities at grain boundaries.

Keywords: Nanoindentation; Nanocrystalline copper; Plastic deformation; Dislocation

1. Introduction

On mechanical properties of nanocrystalline (nc) materials, one of the crucial points to be addressed is whether dislocation activities are suppressed by the ultrafine grains during plastic deformation. Molecular-dynamics simulations performed on "ideal" (fully dense, contamination-free, randomly distributed grains and grain orientations) nc fcc metals at room temperature have indicated that when grain sizes are small enough (e.g., 8 nm for Cu [1]), all plastic deformation is accommodated in grain boundaries (GBs) in the form of GB sliding. For larger grains, a transition appears from intergranular plastic deformation based on GB accommodation to a mixture of intergranular and intragranular processes with some GB dislocation activities [2].

Nevertheless, experimental results to verify this argument are still absent. In fact, experimental measurements to identify the intrinsic plastic deformation mechanism of nc materials at the atomic level are suffering from several major difficulties. On one hand, synthesis of the "ideal" nc bulk samples for conventional mechanical testing is still a challenge. Especially, stable nc pure metal samples with grain sizes around 10 nm are extremely difficult to prepare due to their poor thermal stability with high purities at room temperature. On the other hand, conventional mechanical tests (such as tensile and compression...
tests) provide an overall mechanical response of the tested sample. Identification of intrinsic deformation mechanism of the nanocrystallites and GBs at the nanometer scale is hardly feasible from those tests, in which various processing-induced defects (or artifacts) in the tested samples (such as porosity, inhomogeneous grain sizes, etc.) play a dominant role. Most existing data for mechanical properties of nc materials from conventional mechanical tests in the literature are very scattered, from which firm conclusions are difficult to make.

Recent development of nanoindentation offers an effective experimental technique to probe plasticity of materials at the atomic level. For example, the onset of plasticity in crystals is demonstrated by discrete bursts in the experimental load-displacement curves, which are attributed to the initial nucleation of individual lattice dislocations [3–6]. Moreover, samples used for nanoindentation tests can be very small in dimension. Synthesizing suitable nc samples for nanoindentation tests is much easier than that for conventional mechanical tests.

The objective of this work is to determine experimentally the critical shear stress to initiate plasticity in a fine-grained nc-Cu sample by means of nanoindentation. We synthesized a fully dense nc pure Cu film with an average grain size as small as 14 nm by means of the magneto-sputtering technique. In terms of the measured results and a comparison with the results of a coarse-grained Cu sample, the intrinsic plastic deformation mechanism in the nc-Cu sample is discussed.

2. Experimental

Nanocrystalline Cu films were fabricated by means of direct current (DC) magnetron sputtering using a Cu target with a purity of 99.999%. The substrate used is silicon (1 1 1). The base pressure in the deposition chamber is above $7.0 \times 10^{-5}$ Pa, and the working pressure of pure argon gas is about 1 Pa. Prior to deposition, the target was cleaned for 10 min by sputtering while the substrates were isolated from the plasma by a shutter. The thickness of the as-deposited nc-Cu film is about 2 μm determined by means of scanning electron microscopy (SEM) observations. Less than 200 ppm (wt.%) oxygen contamination was detected by Auger-electron spectroscopy (AES) on the fresh surface of the as-deposited Cu films.

Transmission electron microscopy (TEM) experiments were conducted on a Philips EM420 microscope with an accelerating voltage of 100 kV. The thin film samples for TEM observations were prepared by means of dimpling and ion milling. Fig. 1(a) shows a plane view TEM image of the Cu film. It consists of uniformly distributed nanometer-sized grains, in which lattice dislocations are hardly observed as confirmed by high resolution TEM observations. The corresponding select area electron diffraction pattern (as in Fig. 1(b)) and the distinct contrast of the nanocrystallites indicate their random crystallographic orientations and high angle grain boundaries among the grains. According to a statistical analysis of TEM image for size distribution with totally about 720 grains (Fig. 1(c)), one may find the grain sizes range from 5 to 40 nm, with an average value of $14 \pm 5$ nm. X-ray diffraction analysis in terms of Scherrer equation indicates an averaged grain size of about 12 nm, which is close to the TEM observations. Furthermore, a (1 1 1) texture was detected in the Cu film with an X-ray diffraction peak intensity...
ratio of $I_{(111)}/I_{(200)}$ of 3.1 (with respect to 2.2 for Cu without preferred orientation), as usually observed in the sputtered thin film [7]. The estimated ratio of grain size along the $\langle 111 \rangle$ orientation to the averaged value with random orientations is about 2.

Surface morphology of the as-deposited Cu film was examined using atomic force microscope (AFM) Q-Scope 250 (Quesant Instrument Corp., USA) made at the contact mode. It shows clearly that the film was formed following a dominant mechanism of island growth. The average size of the islands in the nc-Cu film surface is about 150 nm, which is much larger than the tip radius of 50 nm.

The coarse-grained (CG) polycrystalline Cu sample was prepared by vacuum annealing a bulk Cu (with a purity of 99.999%) at 900 °C for 48 h. The resulting grains are equiaxial with an average size of 60 µm. The sample used for nanoindentation tests was mechanical polished followed by electro-polishing in a 2:1:1 solution of phosphoric acid, ethanol and distilled water at room temperature.

Nanoindentation experiments were performed using Nanoindenter XP™ (MTS, Inc., Tennessee, USA) with a diamond Berkovich indenter of size of 60 µm. The sample was prepared by vacuum annealing a bulk Cu (with a purity of 99.999%) at 900 °C for 48 h. The fitting of the measured indentation load, $P$, as a function of the penetration depth, $h$, for the bulk CG-Cu and the nc-Cu film. The $P$–$h$ curve of the CG-Cu exhibits multiple displacement bursts, separated by segments of positive slope. The initial curve prior to the first burst is well predicted with Hertzian elastic analysis [9] following

$$P = \frac{4}{3} R^{1/2} E^* h^{3/2},$$

where $R$ is the tip radius, $E^*$ is the reduced modulus which is defined as

$$E^* = \left\{ \frac{1 - v^2}{E_s} + \frac{1 - v_{ind}^2}{E_{ind}} \right\}^{-1},$$

where $E$ and $v$ are Young’s modulus and Poisson’s ratio, respectively, and the subscripts, ‘s’ and ‘ind’ refer to the sample and the indenter. The responses in between the bursts conform to the elastic relationship expected for a sharp Berkovich indenter [10], which is given by

$$P = 2.189 E^* h^2 \{1.00 - 0.21 v_s - 0.01 v_s^2 - 0.41 v_s^3\}.$$  

The elastic properties of Cu and indenter used in the prediction are as follows: $E_s = 1141$ GPa [11] and $v_s = 0.07$, $E_{ind} = 128$ GPa (bulk modulus for Cu with random grain orientations [6]) and $v_{ind} = 0.34$, respectively. $E^*$ is obtained, being 128.5 GPa. The displacements for different dashed lines are adjusted so as to make them coincide with the experimental $P$–$h$ curve.

Based on observations from a large number of repeated indentations on the CG-Cu sample, we found the first burst always occurs at a load of 0.016 ± 0.006 mN and a penetration depth of 8 ± 4 nm. The fitting of the measured $P$–$h$ curve with the Hertzian elastic response indicated that the Cu
sample underwent a purely elastic deformation prior to appearance of the first burst, which is an indication of the onset of plasticity. The discrete bursts were supposed to be the consequence of nucleation and movement of individual lattice dislocations, similar to those observations in a number of single crystals and polycrystals [3–6]. According to the relation for a spherical indenter [9], the critical shear stress for onset of plasticity, or the maximum elastic shear stress, \( \tau_{\text{max}} \), can be estimated by

\[
\tau_{\text{max}} = 0.31 \left( \frac{6PE}{\pi^3R^2} \right)^{1/3}.
\]

For the CG-Cu with \( E = 128 \) GPa, \( \tau_{\text{max}} = 8.5 \pm 1.1 \) GPa is obtained. This value is very close to the theoretical shear strength of Cu, \( \tau_{\text{th}} \), approximately \( \tau_{\text{th}} = \frac{\mu b}{2l} \) (where \( \mu \) is the shear modulus, \( \mu = E/(1+v) \), \( b \) is the Burgers vector and \( l \) is the interplanar spacing between close packed planes, for an fcc Cu in \{111\} \{112\} shear with \( E(111) = 191.1 \) GPa [12], \( \tau_{\text{th}} = 8.0 \) GPa). Such an agreement means the onset of plasticity of the CG-Cu occurs accompanied with nucleation of lattice dislocation when the maximum shear stress beneath the indenter reaches the theoretical shear strength of Cu. The slight difference between the \( \tau_{\text{th}} \) and the measured \( \tau_{\text{max}} \) might be ascribed to many factors, such as the experimental scatter, model approximation, complexity of the stress state, grain anisotropy and the surface roughness. Suresh et al. [6] measured the maximum elastic shear stress and obtained a much larger value (20.88 GPa) for a Cu thin film with an average grain size of 500 nm. The difference between their results and the present work may originate from the different grain size and thermal history of the samples, as well as definition of the first burst in the \( P–h \) curve.

For the nc-Cu thin film, however, no obvious displacement burst was detected in the \( P–h \) curve, which shows a continuous increase with the penetration depth up to 50 nm. It is noted that the \( P–h \) curve is calibrated from the original measurement data by subtracting the effect of the thin porous oxide layer (a few nm thick) on the sample top surface due to the enhanced chemical reactivity of the nc-Cu. Although the \( P–h \) curve of the nc-Cu is obviously different from that for the CG-Cu, a close observation (insert in Fig. 2) revealed that the initial part of the \( P–h \) curve for the nc-Cu also fits the Hertzian response when \( h < 5 \) nm. With increasing depth, the \( P–h \) curve deviates gradually from the Hertzian prediction, indicating the onset of plasticity in the nc-Cu sample. This behavior differs remarkably from that observed in the CG-Cu sample in which onset of plasticity is manifested by an abrupt displacement burst.

More than 50 repeated indents on the nc-Cu sample were performed in order to determine the load at which the initial departure from the elastic deformation occurs, i.e., the critical load for the onset of plasticity. Consistent measurement results showed that the onset of plasticity always appears at a load of about \( 0.015 \pm 0.007 \) mN and a displacement of about \( 6 \pm 2 \) nm. Fig. 3 summarizes the distributions of the measured critical load, \( P^* \), and displacement, \( h^* \), for onset of plasticity in the CG-Cu and the nc-Cu film, respectively. It is clear that the critical loads and displacements for both samples are approximately identical. Similarly, the critical shear stress for onset of plasticity in the nc-Cu sample is obtained, being \( \tau_{\text{max}} = 8.3 \pm 1.3 \) GPa. This value is as high as that for nucleation of

![Fig. 3. Distributions of the measured critical load \((P^*, a)\) and the displacement \((h^*, b)\) at which the first displacement burst occurred in the CG-Cu sample. Distributions of the measured critical load \((P^*, c)\) and the displacement \((h^*, d)\) at which the \( P–h \) curve deviates from the Hertzian elastic response in the nc-Cu.](image-url)
lattice dislocations in the CG-Cu, and both values are very close to the theoretical shear strength for Cu.

According to classical dislocation theory, one knows that the grain size in the present nc-Cu sample (average 14 nm) is smaller than the critical size for formation of lattice dislocations at Frank–Read sources [13], and is also smaller than the critical size for lattice dislocation pile-ups (about 20 nm for Cu) [14]. Therefore, nucleation and movement of lattice dislocations are expected to be inhibited by the ultrafine grains during plastic deformation of the present nc sample. Or in other words, plastic deformation of the nc-Cu sample is not likely to be accommodated by lattice dislocation activities.

In terms of computer simulation studies [1], alternative deformation mechanisms associated with GB activities are possibly responsible for deformation in nc-Cu sample with such small grain sizes at room temperature. For grain sizes small enough, plastic deformation may be completely accommodated in GBs with many small GB sliding (GBS) events controlled by grain boundary diffusion [1]. The deformation rate for GBS is given by [15],

$$\dot{\epsilon}_{\text{GBS}} = 2 \times 10^5 D_b \frac{\mu b}{kT} \left( \frac{b}{d} \right)^3 \left( \frac{\sigma_s}{\mu} \right)^2.$$  \hspace{1cm} (5)

Here $\sigma_s$ is the applied stress, $d$ is grain size, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $D_b$ is grain boundary diffusivity, which is defined as

$$D_b = D_{b0} \exp \left( -\frac{Q_b}{kT} \right).$$  \hspace{1cm} (6)

Here $D_{b0}$ and $Q_b$ are the pre-exponential factor and the activation energy for GB diffusion.

The GB sliding may be triggered by uncorrelated shuffling and to some extent by stress-assisted diffusion at GBs. For the GB accommodation mechanism with GB diffusional creep, the creep (or Coble creep) rate can be expressed by [16]

$$\dot{\epsilon} = \frac{148\sigma_s \Omega \delta D_b}{\pi d^3 kT}. \hspace{1cm} (7)$$

Here $\delta$ is the width of grain boundary, $\Omega$ is the atomic volume and the other parameters are specified in Eq. (5).

Based on the above equations, one may estimate the strain rates of the two processes (GB sliding and GB diffusional creep) at the maximum elastic stress for the nc-Cu sample by using the available data for GB diffusion in Cu [17]. Calculation results showed that the strain rates at room temperature are $6.0 \times 10^{-4}$ s$^{-1}$ for the GB sliding controlled by grain boundary diffusion and $2.3 \times 10^{-6}$ s$^{-1}$ for Coble creep, respectively. Obviously, these strain rates are several orders of magnitude smaller than the applied indentation strain rate ($2.5 \times 10^{-2}$ s$^{-1}$) used in the present study. Therefore, any of these GB accommodation mechanisms alone does not seem to be dominant in the present case.

As indicated by computer simulations, all plastic deformation can be accommodated by GB mechanisms only when the grain size is small enough. For larger grains (still in the nanometer regime), meanwhile GB accommodation mechanisms might remain dominant, dislocation activities are necessary for facilitating the GB motion, e.g., emission of partial dislocations at GBs [1,18]. The coincidence of the maximum elastic shear stress for the nc-Cu sample with the critical shear stress to initiate nucleation of lattice dislocations may imply that the onset of plastic deformation in the nc-Cu is somehow associated with initiation of dislocation activities. These activities may include nucleation or emission of dislocations at GB regions or formation of stacking faults depending upon the strain and the orientation of grains, as well as the stacking fault energy.

Recently, atomistic simulations of nanoindentation in nc Au and in a single crystal Au were performed [19]. It was found that the onset of plasticity in the nc Au samples with two different grain sizes (12 and 5 nm) is identical to that for the Au single crystal. This behavior is in agreement with our experimental observations in the present study despite of the difference in the indenter size. The simulations showed that the onset of plasticity in both cases originates from dislocation emission under the indenter. This is in account with our measured results that the maximum elastic shear
stress for the nc- and the CG-Cu samples is close to the theoretical shear strength for initiation of lattice dislocations. Although it is difficult to identify the location of dislocation nucleation in the nc-Cu sample in terms of our nanoindentation measurement results, the atomistic simulations demonstrated that GBs in the nc samples act as efficient sinks for dislocation nucleation under the indenter and intergranular sliding was observed when the indenter size and the grain size are comparable [19].

The comparable shear stress for onset of plasticity in the present nc-Cu sample with that for the nucleation of lattice dislocations also indicated that the grain refinement induced softening (or the reverse Hall–Petch relation) [20] has not been reached down to a mean grain size of 14 nm for pure Cu. Softening due to fully GB accommodation mechanisms might be possible for even smaller grain sizes or at elevated temperatures, providing the nc samples with stable grain sizes are feasible. The critical shear stress to initiate the GB accommodation process can be determined with such samples, which may exhibit improved ductility, as dislocation activities may not be involved.

4. Concluding remarks

Nanoindentation measurements indicated a high critical shear stress for onset of plasticity in the nc-Cu sample with an average grain size of 14 nm, which is close to the theoretical shear stress for nucleation of lattice dislocations in the dislocation-free Cu(1 1 1) crystal. The high indentation elastic strength of the nc-Cu sample may originate from the suppressed lattice dislocation activities by the ultrafine crystallites, and at the same time, the inactive GB accommodation mechanism at room temperature. Our experimental results, in agreement with the atomistic simulations of the nanoindentation in nc gold samples [19], support the argument that the onset of plasticity of the nc-Cu is associated with initiation of dislocation activities at GBs.

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