Journal of Physics and Chemistry of Solids 74 (2013) 75–79

Contents lists available at SciVerse ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Grain size effects on the compressibility and yield strength of copper

Yuejian Wang [a,b,*], Jianzhong Zhang [b], Qiang Wei [b], Yusheng Zhao [b]

[a] Physics Department, Oakland University, 2200 North Squirrel Road, Rochester, MI 48309, United States
[b] Lujan Center, Los Alamos National Laboratory, Los Alamos, NM 87545, United States

ARTICLE INFO

Article history:
Received 29 November 2011
Received in revised form
2 July 2012
Accepted 5 August 2012
Available online 13 August 2012

Keywords:
A. Nanostructures
A. Metals
C. High pressure
C. X-ray diffraction
D. Mechanical properties

ABSTRACT

A comparative investigation on mechanical properties of micro- and nano-sized polycrystalline copper (Cu) under high pressure and temperature (high *P–T*) up to 9.1 GPa and 1150 K has been conducted in a single experimental run using *in-situ* synchrotron X-ray diffraction integrated with the high pressure technique. We derived the bulk moduli for both samples from the least-squares fitting of measured pressure-volume (*P–V*) data by a second-order Birch–Murnaghan equation of state (EOS). The results reveal that in the present study grain sizes negligibly affect the compressibility of Cu. Furthermore, we investigated the deformation of samples under high *P–T* conditions. At high pressure and room temperature, both local/micro and bulk/macro yielding points are observed in the elastic stage of nano-sized Cu. By contrast, micro-sized Cu demonstrates only a bulk yielding point over its entire elastic regime. At high temperature and fixed pressure, both samples exhibit stress relaxation, grain growth, and finally reach an identical status. Based on the peak-width analysis of diffraction profiles and subsequent graphic derivation, the yield strengths are determined to be 0.17 ± 0.05 GPa and 0.75 ± 0.07 GPa for micro- and nano-sized grains, respectively, which indicates a substantial enhancement of yield strength in Cu by nanocrystals.

1. Introduction

Because of its unique properties and potential for advanced applications ranging from aerospace exploration to human daily life [1], nanocrystalline material has attracted substantial interest in industry and scientific research. Nano, a dimension scale, is used in materials science to distinguish the materials with grain size no larger than 100 nm from conventional larger grain-sized materials [2]. In addition to the small grain size, what makes nanocrystalline material so appealing is its intrinsic structure and nature. As grain size decreases from micrometers or even larger into nanoregime, the related atom arrangement, lattice configuration, atomic interaction, as well as bonding energy also change into different ones compared to its larger grain-sized counterpart. Thus the unique atomic structures lead to many distinctive properties [2]. Several investigations, including both experiments and theoretical computations, have provided extensive evidences for the alteration of material properties as grain size diminishes [3–7]. However, the dependence of mechanical properties, such as compressibility and yield strength, on grain sizes still remains controversial and has not been well understood. Most of previous studies focused on nanocrystalline material only, and then compared the results with early-published data of larger grain-sized material to elucidate the size effects. In this regard, because of systematic errors associated with the experiments using different techniques, the conclusions derived from those studies may be inconclusive or even misleading. In the present investigation, we conducted *in-situ* high *P–T* synchrotron X-ray diffraction experiment on a pair of nano- and micro-sized Cu in a single experimental run. This comparative approach would eliminate/minimize systematic errors associated with instrument responses and pressure/stress determination and thus enable us to precisely measure the subtle distinction in mechanical properties between different grain-sized materials under high *P–T* conditions [8–13].

2. Material and methods

The starting materials of nano- and micro-sized Cu powders with grain sizes of 50–80 nm and 6–7 μm were purchased from Sigma-Aldrich. Both samples were observed under scanning electron microscopy (SEM), to study their morphology and size distribution. Fig. 1 shows that the nanograins with narrow size distribution have agglomerated into larger particles while micro ones are in loose form. The high *P–T* measurements were performed using a DIA type cubic anvil apparatus, which is coupled with synchrotron energy-dispersive X-ray radiation at

* Corresponding author at: Physics Department, Oakland University, 2200 North Squirrel road. Rochester. MI 48309, United States. Tel.: +1 2483703423; fax: +1 2483703408.
E-mail address: ywang235@oakland.edu (Y. Wang).

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http://dx.doi.org/10.1016/j.jpcs.2012.08.002

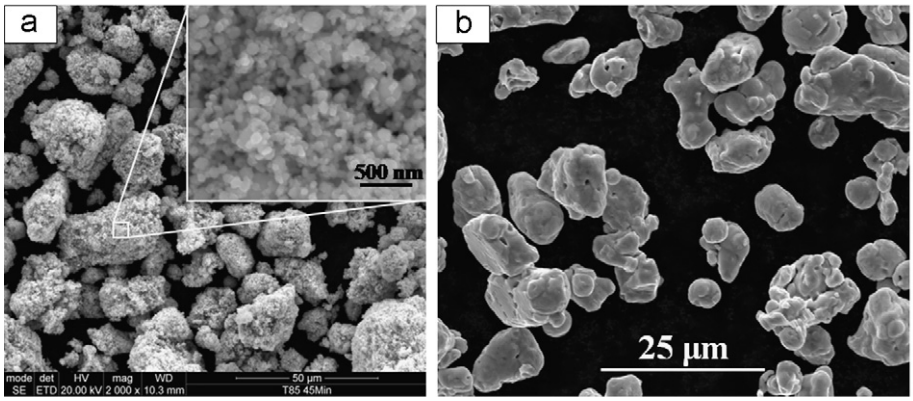

Fig. 1. SEM images of starting materials: (a) low-magnification SEM image of nano-sized Cu powders; the inset shows the high-magnification SEM image within the square area. (b) A typical SEM image for micro-sized Cu powders. Scale bars are shown for comparison.

beamline $X_{17}B_2$ of National Synchrotron Light Source, Brookhaven National Laboratory. The detailed description of experimental approach has been reported elsewhere [14]. In the present study, the incident X-ray beam was perpendicular to the compression direction of sample, and the diffracted X-rays were recorded by a multi-element detector at a fixed Bragg angle of $2\theta=6.4900^{\circ}$. Two samples of nano- and micro-sized Cu, separated by a NaCl layer, were loaded into a cylindrical container made from boron nitride. Here, NaCl also served as an internal pressure standard. At each experimental condition, the sample pressure was determined from NaCl diffraction profiles using the Decker scale [15]. Temperatures were measured by a W/Re25–W/Re3% thermocouple that was in direct contact with samples.

3. Results and discussion

The bulk modulus of both samples at ambient temperature and high pressure were obtained by fitting the *P–V* data to a second-order Birch–Murnaghan EOS [8],

$$P=3f(1+2f)^{5/2}K_0, \tag{1}$$

where $f=1/2[(V/V_0)^{-2/3}-1]$, K_0 is the bulk modulus at ambient conditions, and V_0 represents the unit-cell volume at atmospheric pressure and temperature. The unit-cell volumes were determined by least-squares fits of diffraction lines of 111, 200, 220, 311, and 222 for both samples. A second-order instead of third-order EOS was used because the limited pressure range in the current investigation prohibits an accurate constraint on the first pressure derivative of bulk modulus, K_0'. As shown in Fig. 2, the least-squares fits yield $K_0=143\pm4$ GPa, $V_0=47.06$ Å^3 for micro-sized Cu and $K_0=140\pm2$ GPa, $V_0=47.12$ Å^3 for nano-sized Cu with K_0' fixed at 4. The uncertainties in K_0 are those of the least-squares fits, and they do not include the uncertainties in *P–V* measurements. Within the experimental uncertainties, there is no measurable distinction in the bulk modulus of copper when grain size is reduced from 6–7 μm to 50–80 nm. Our determined K_0 is consistent with previous measurements using ultrasonic approach [16] and synchrotron X-ray diffraction in a diamond anvil cell [17].

The peak-width analysis of diffraction profiles has been widely used to determine materials' yield strength under compression or extension conditions [6,10–12,18–25]. Compared to conventional indentation or tensile test, this approach eliminates the effects of the sample's porosity and impurity on the determination of yield strength. The width of X-ray diffraction peak is a convolution of functions related to instrument response, grain-size distribution, and crystal lattice deformations along the diffraction vector. In non-hydrostatic high-pressure experiments, the loading force

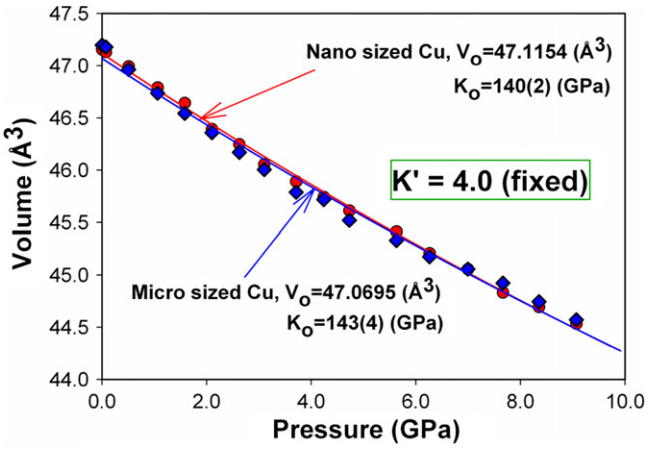

Fig. 2. The measured *P–V* data of Cu. The solid red and blue curves represent the least-squares fits using a second-order Birch-Murnaghan for *P–V* data of nano- and micro-sized Cu, respectively. The ambient unit-cell volumes (V_0) and bulk moduli (K_0) are obtained from the *P–V* fits. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

applied at grain-to-grain contacting areas induces local stress concentration, which in turn leads to peak broadening of the X-ray diffraction patterns. Therefore, we can evaluate the evolution of sample stress under compression through peak profile analysis. Fig. 3 shows the peak (1 1 1) for nano-/micro-sized Cu at selected *P–T* points along the experimental pathway. The top panels demonstrate that the peaks of nano-sized Cu become broader with pressure up to 2.1 GPa, and the further pressure causes the peak slightly shrinking instead of widening, which suggests that stress developed inside the sample under compression leads to plastic yielding in the vicinity of 2.1 GPa and then enters into the work softening stage. For the micro-sized Cu, the peak also broadens under pressure, but its increment is really small. The bottom panels show the variation of peak width of two samples under high temperatures at a fixed pressure of 9.1 GPa. The grain growth and strain/stress relaxation induced by high temperature narrow the gap between the peak widths of two samples, and eventually turn into the similar peak width and shape beyond 673 K.

There are two different approaches to test the material's strength. One is to derive the overall macrostrain data by monitoring and recording the shifts of the diffraction peak positions during the compressive or tensile test [26–28]. Through this method we can build the constitutive equations of materials and thus get knowledge on how crystal lattice responds to externally applied force (compressed or elongated) in the macro perspective. Before