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Indentation size effect in nanoporous gold

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ABSTRACT

We find that hardness of nanoporous gold (np-Au) measured by nanoindentation tends to increase with decreasing indentation depth, similar to the indentation size effect (ISE) in solid materials. While ISE in solid materials is attributed to a local increase in density of geometrically necessary dislocations (GNDs), the origin of ISE in np-Au has not been studied systematically. We prepare four np-Au samples with ligament sizes of 26, 73, 126, and 630 nm by free corrosion dealloying and post heat treatments. For the normalized hardness (hardness/macroscopic hardness) vs normalized indentation depth (indentation depth/three times ligament size), we find that the ISE trends for three np-Au samples of ligament sizes 26, 73, and 127 nm are almost identical, while an enhanced ISE is shown for np-Au with greatest ligament size, 630 nm. We investigate ISE in np-Au based on nanomechanics model for nanoindentation on np-Au with a sharp indenter, uniaxial compression and pure shear testing for np-Au.

1. Introduction

Nanoporous gold (np-Au) has received significant attention for such possible applications as sensors, actuators, and catalysis due to its high specific surface area and chemical stability [1–14]. Studies on the mechanical properties of np-Au have been numerous because its fragility is critical in applications [15,16]. Previous research revealed that the strength of np-Au depends strongly on ligament size as well as relative density. Li and Sieradzki [17] suggested a ductile-brittle transition in three-point bending based on change in slope of the relation between fracture strain/stress and ligament size. Biener et al. [18] found that nanoindentation hardness depends on ligament size; hardness increases with decreasing ligament size. Using the Gibson-Ashby model on foam plasticity, they suggested that the ligament yield strength approaches the theoretical strength of Au that the yield strength of np-Au, evaluated from nanoindentation hardness, can be as strong as solid Au in spite of its porous structure. Volkert et al. [19] showed that the compressive strength of np-Au micro-pillars depends on ligament size rather than micro-pillar diameter, and that the strength of individual ligaments attains the theoretical strength of Au. They confirmed a distinction between elastic and plastic behavior of solid materials depending on sample size (diameter of single-crystalline nanopillars and ligament size in np-Au). They explained the trend in mechanical behavior of Au samples with external size ranging from 10 to 10^5 nm by the Gibson-Ashby model [20] estimated for np-Au, nanobox Au, and single-crystalline Au nanopillars. Yield strength is strongly dependent on external sample size below 50 μm, while elastic modulus is independent of sample size. Hodge et al. [21] showed that the mechanical behavior of np-Au is strongly dependent on ligament size, in contrast with previous studies finding that cell size, including ligaments and pores, had a minimal effect on mechanical properties in macrocellular materials of similar relative density. They suggested a modified scaling equation for the yield strength of np-Au as a function of ligament size and relative density by incorporating a Hall-Petch-type relation coefficient. They noted that np-Au follows the Gibson-Ashby model as ligament size approaches 1 μm from sub-micron size. From numerous experimental results, Briot and Balk [22] suggested a universal scaling law for yield strength of np-

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Au in which ligament size effect is significant only for ligament size smaller than 1 μm. Saane et al. [23] studied mechanical properties of np-Au using atomistic and continuum simulations; they found that elastic modulus depends strongly on relative density and crystallographic orientation, and yield strength depends on relative density. They found that the exponent in a scaling law determined from simulation results is higher than that using the Gibson-Ashby model, and explained this result by the loss of connectivity in np-Au.

The trend of nanoindentation hardness vs indentation depth for np-Au in previous studies is that hardness tends to increase with decreasing indentation depth, which is similar to indentation size effect (ISE) in solid materials. The ISE in solids is explained by saying that the density of geometrically necessary dislocations (GNDs) increases as indentation depth decrease, while density of statistically stored dislocations (SSDs) is independent of indentation depth [24–30]. The ISE in np-Au cannot, of course, be explained by this classical ISE mechanism. GNDs generated in ligaments of np-Au could easily escape at the free surface due to the typically sub-micron scale of ligament, and ligaments could collapse easily into the extensive neighboring free volume (pores), rather than undergoing plastic constraint as in solid materials. ISE in np-Au has not been studied systemically but could be critical, especially when indentation depth is limited to within the shallow indentation depth where ISE is pronounced.

Here we investigate ligament-size-dependent ISE in np-Au. To separate ISE elements coming from porous structure and ligament-size dependency, we used np-Au samples of four ligament sizes, 26, 73, 127, and 630 nm, to obtain the relation between normalized hardness – the ratio of hardness to macroscopic hardness (i.e., hardness at sufficient indentation depth – and normalized indentation depth (i.e., the ratio of indentation depth to length scale of one unit cell composed of one ligament and one pore assumed to be three times ligament size)). We find a clear transition in ISE in normalized hardness vs normalized indentation depth for our four np-Au samples: the trends in the ISE for the three np-Au samples of small ligament size (26, 73, 127 nm) are almost identical, but the ISE for np-Au with greatest ligament size (630 nm) is enhanced over the other three. To explain this result, we suggest a novel ISE model for np-Au in which during nanoindentation, initial plastic collapse of np-Au occurs at the contact boundary between nanoindenter and np-Au primarily by shear force, and the collapsed np-Au placed beneath nanoindenter expands primarily by compressive force. Using uniaxial compression and pure shear tests, we discuss the origin of ligament-size-dependent ISE in np-Au.

2. Experiments

Four np-Au samples of ligament sizes 26 (±4.0), 73 (±8.8), 127 (±12.8), 630 (±61.4) nm were prepared as shown in Fig. 1(a)–(d). To prepare the precursor alloy of Au 30 at.% and Ag 70 at.%, Au (99.99%) and Ag (99.99%) pellets were melted together by plasma arc-melting in an Ar environment, held at 800 °C for 72 h in a tube furnace under N_2 environment for homogenization, and slowly cooled to room temperature in the furnace. The spherical samples were compressed into round disks using universal mechanical tester (Instron 5982). Both sides of the alloys were gently mechanically polished down to 0.25 μm diamond suspension. The precursor alloys were round discs of diameter ~8 mm and thickness ~1 mm. The samples were annealed in a tube furnace under N_2 environment at 800 °C for 24 h to homogenize them further and to release any residual stress induced during mechanical compression and polishing.

The np-Au samples were prepared from the precursor $Au_{30}Ag_{70}$ alloys by free-corrosion dealloying. To control ligament size, dealloying was carried out in nitric acid solutions under different conditions: in mixture of 2:1 70% concentrated nitric acid to DI water at 20 °C for 72 h, resulting in ligament size (l) 26 nm (hereafter called sample #1 ($l = 26$ nm)), in mixture of 1:1 of 70% concentrated nitric acid to DI water at 50 °C for 72 h, resulting in ligament size 73 nm (hereafter called sample #2 ($l = 73$ nm)), and in mixture of 1:1 of 70% concentrated nitric acid to DI water at 80 °C for 72 h, resulting in ligament size 127 nm (hereafter called sample #3 ($l = 127$ nm)). These dealloying conditions were based on the authors' previous work [31]. Through additional heat treatment of sample #3 ($l = 127$ nm) at 600 °C for 2 h, np-Au samples of ligament size 630 nm were obtained (hereafter called sample #4 ($l = 630$ nm)). The np-Au samples were examined in field emission scanning electron microscopy (FE-SEM, FEI Nanonova 230). Ligament sizes were evaluated by thickness of necks at the ligament center, their thinnest part, from at least 100 measurements in SEM images. Since homogeneity in ligament size distribution could affect ISE in np-Au, we measured ligament sizes for cross sections prepared by focused ion beam (FIB, Quanta 3D FEG) milling as shown in Fig. 1(e)~(h). Fig. 1(i) shows that ligament size normalized by average ligament size measured for top SEM images is almost one throughout the nanoindentation loading direction from the free surface, which indicates that the size of ligaments corresponding to volume from free surface to maximum indentation depth is uniform for samples #1~#4.

Nanoindentations using three-sided Berkovich indenter were performed on samples #1 through #4. For each sample, at least 12 reproducible nanoindentation force-depth curves were obtained. Maximum indentation depths for each sample were determined as 40 times of their ligament size, where cell size D is composed of one ligament and one neighboring pore, assumed here to be three times ligament size, $3l$ as shown in Fig. 6(f); that is, intended maximum indentation depth = $13.3D = 40l$. Indented volume by this maximum indentation depth approximately contains 27000 cells, and we confirmed that convergent trend in hardness with increasing indentation depth is well-described up to this maximum indentation depth. Continuous stiffness measurement (CSM) nanoindentations were carried out by XP and DCM II modules with maximum load capacity 500 and 30 mN in a G200 nanoindenter (Keysight Co.), respectively. All nanoindentation tests were conducted at constant indentation strain rate 0.05 s^{-1}, with allowable thermal drift limit of 0.05 nm/s. Relative densities of the samples were evaluated from measurements of external volume and sample weight. Np-Au cuboids of dimensions 0.8 mm × 0.8 mm × 1.2 mm for testing in both uniaxial compression and pure shear were prepared. Compression and shear tests were performed at constant displacement rate of 0.05 s^{-1} using a micro universal testing machine (Instron 5948). For each sample, at least 4 reproducible force-displacement curves were obtained for compression and shear tests.

3. Results and discussion

3.1. ISE in np-Au

Fig. 2 shows typical indentation force-depth curves and hardness as a function of indentation depth for four np-Au samples. Fig. 2(a)–(d) show that greater force is required to attain same indentation depth as ligament size decreases, which is in line with the higher hardness found for smaller ligament size in previous researches [21]. Fig. 2(e)–(h) show an increase in hardness with decreasing indentation depth for all np-Au samples, i.e. an ISE in np-Au. A convergent hardness value as indentation depth increases is measured by averaging hardness values between indentation depths $30l$ and $40l$, the maximum indentation depth. This