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Size Effects on the Mechanical Behavior of Nanoporous Au

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ABSTRACT

Recent nanomechanical tests on submicron metal columns and wires have revealed a dramatic increase in yield strength with decreasing sample size. Here, we demonstrate that nanoporous metal foams can be envisioned as a three-dimensional network of ultrahigh-strength nanowires, thus bringing together two seemingly conflicting properties: high strength *and* high porosity. Specifically, we characterized the size-dependent mechanical properties of nanoporous gold using a combination of nanoindentation, column microcompression, and molecular dynamics simulations. We find that nanoporous gold can be as strong as bulk Au, despite being a highly porous material, and that the ligaments in nanoporous gold approach the theoretical yield strength of Au.

According to current models, the mechanical properties of foams can be described by scaling equations with the relative density of the material as the dominating parameter.[1] The mechanical properties of the foam ligaments (or struts), such as the yield strength, are assumed to be bulklike and size-independent, implying that the strength of foam materials always decreases with increasing porosity. On the other hand, recent nanomechanical measurements on submicron Au columns[2−7] and nanowires,[8] which closely resemble the ligaments in foams, have revealed a dramatic increase in strength with decreasing sample size. This leads to the question of whether the current models describing the mechanical properties of metal foams can be applied to foams with cell dimensions on the nanoscale. Indeed, we previously observed that the yield strength of nanoporous gold (np-Au) is higher than predicted by current models.[9,10] However, it remained unclear whether the higher-than-expected strength of np-Au is caused by the microstructure of the ligaments (as recently demonstrated of Ag nanowires[11]) or reflects the size-dependent mechanical properties of gold.

In this work we report on the ligament-size effects of mechanical properties of nanoporous gold (np-Au). The material exhibits a characteristic spongelike open-cell foam structure (Figure 1) which makes it an ideal candidate for such a case study for several reasons. First and foremost, the ligament size is (1) very uniform and (2) can be tuned from 10 nm to 1 micrometer without changing the relative density or relative geometry (connectivity, ligament shape, pore shape) of the material.[12−14] Second, monolithic millimeter-sized samples can easily be obtained by dealloying Ag−Au. Third, Au does not form an oxide layer. Furthermore, np-Au has recently attracted considerable interest fueled by its potential use in actuator,[15,16] sensor,[17−20] and catalyst[21] applications. However, despite these exciting prospects, the understanding of the mechanical behavior of metal foams at the nanoscale is still very much in its infancy.[9,14,22]

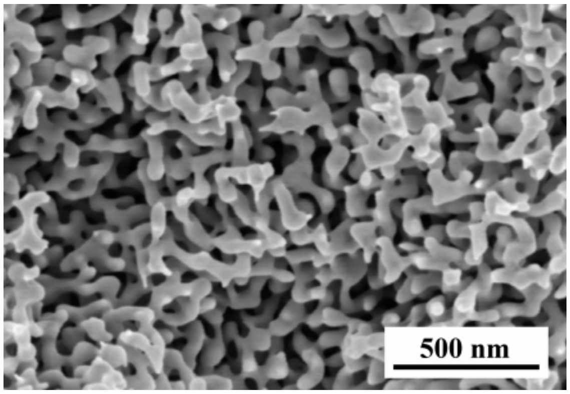

Figure 1. SEM micrograph showing the characteristic spongelike open-cell foam morphology of np-Au. The material is very homogeneous and exhibits nanometer-sized pores and ligaments, the latter with a length-to-diameter aspect ratio close to one.

Disk-shaped samples of np-Au (diameter, ∼5 mm; thickness, ∼300 μm) with relative densities of 0.25 and 0.3 were prepared by selective dissolution (dealloying) of $Ag_{0.75}Au_{0.25}$

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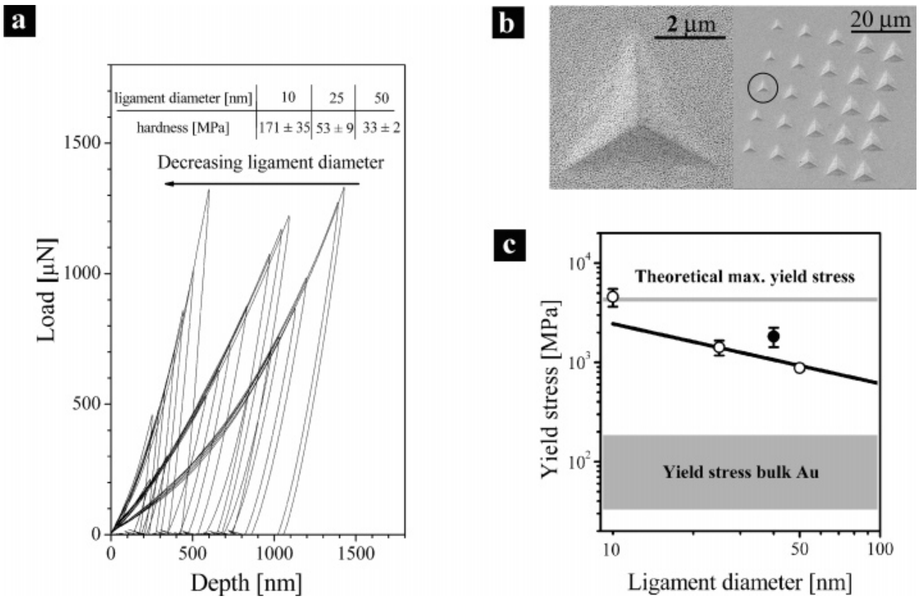

Figure 2. Nanoindentation experiments on np-Au with a relative density of 0.25 as a function of ligament diameter: (a) series of load versus displacement (*P-h*) curves using a Berkovich tip. The shift of the *P-h* curves toward lower depths indicates that the indentation hardness and therefore the yield strength of np-Au increases with decreasing ligament diameter. (b) SEM micrograph of the residual impressions of an array of indents and a close-up of the marked indent are shown. Note that the plastic deformation is confined to the area under the indenter. (c) Plot of yield strength of Au ligaments versus ligament diameter (open circles) is shown. Also shown is a data point obtained by a linear compression test using micrometer-sized columns of 30% np-Au (filled circle) as well as a linear extrapolation of the yield strength data obtained from single-crystal Au columns (solid line).[7] Note, that the yield strength values shown in Figure 2c are corrected with respect to density by applying eq 1.

and $Ag_{0.7}Au_{0.3}$ alloys, respectively. This corrosion process generates a nanoporous metal foam of almost pure Au.[23,24] Details of alloy preparation and dealloying procedures can be found in the literature.[9] In short, np-Au with 25 and 50 nm ligaments were prepared by free corrosion, that is, emersion in concentrated nitric acid (70%), and the pore size was adjusted by the immersion time (typically between 2 and 5 days). Nanoporous Au with 10 nm ligaments was prepared by electrochemically driven dealloying, that is, by applying a potential of ~1 V measured versus a Ag pseudoreference electrode in a 1 M HNO_3 + 0.01 M $AgNO_3$ electrolyte. The complete removal of Ag was verified by energy dispersive X-ray spectroscopy, and pore/ligament size was measured by scanning electron microscopy (SEM).

The mechanical properties of 25% and 30% relative density np-Au were tested by conventional load-controlled nanoindentation using a Berkovich tip with a radius of curvature of ~200 nm (Figure 2). Indentations were performed on polished surfaces (polished before dealloying) using a constant loading rate of 500 μN/s with loads ranging from 200 to 1800 μN. Note that the experiments do not test the mechanical properties of individual ligaments but sense the mechanical response of an ensemble of ligaments and pores which is a necessary prerequisite to characterize the strength of foams by indentation.[25] Subsequent inspection of the residual impressions by SEM revealed that plastic deformation is predominately confined to the area under the indenter since the adjacent areas are virtually undisturbed (Figure 2b).

Figure 2a shows three sets of nanoindentation load-displacement (*P-h*) curves obtained from three different np-Au samples, all with a relative density of 25% but with different ligament dimensions (10, 25, and 50 nm). The overlapping loading sections of each data set demonstrate the excellent reproducibility of the measurement. More importantly, the shift of the *P-h* curves toward lower displacement values with decreasing ligament diameter indicates that the strength of np-Au increases with decreasing ligament diameter. This result is in contradiction to the vast body of data on macrocellular foams which unequivocally shows that the strength is a function of the relative density and, to some extent, of the cell geometry, but *not* of the cell size.[1] Standard analysis of the *P-h* data shown in Figure 2a reveals that the indentation hardness (or contact pressure), and thus the yield strength,[26] increases from ~33 to ~171 MPa as the ligament diameter decreases from 50 to 10 nm. This result has to be seen in context of bulk Au for which we determined a yield strength of ~150 MPa,[27] in agreement with literature (the yield strength of bulk Au depends strongly on the sample history and can vary between 10 and 200 MPa[28,29]). This means that np-Au with 10 nm ligaments and a porosity of 75% is stronger than bulk Au.

According to the standard model of foam plasticity developed by Gibson and Ashby, the relationship between yield strength (σ) and the relative density (ρ^*/ρ_s) of a foam material is given by

$$\sigma^* = 0.3\sigma_s(\rho^*/\rho_s)^{3/2} \qquad (1)$$

where $*$ and s denote foam and bulk properties, respectively.[1] It is important to notice that the model contains no explicit length scale dependence and assumes that the material properties of the ligaments such as the yield strength (σ_s) are size-independent and equal to the bulk value. However, recent nanomechanical tests have revealed a strong sample size effect at the submicrometer length scale.[2−8] Therefore, in order to apply the scaling equation to nanoporous metal foams, the yield strength should be considered as a variable of the ligament size. In this case, eq 1 can be used to back-calculate the yield strength of Au ligaments (σ_s) from the load-displacement data shown in Figure 2a. This interpretation of the data reveals that the yield strength of nanometer-sized ligaments increases from ~880 MPa to 4.6 GPa as the ligament diameter decreases from 50 to 10 nm (Figure 2c). Remarkably, the yield strength of the smallest ligaments reaches the theoretical shear stress $G/2\pi$ for Au (4.3 GPa).[29]

The high yield strength of the ligaments of np-Au is consistent with recent uniaxial compression tests on submicron-sized Au columns,[5−7] which have shown the general trend that "smaller is stronger". Specifically, the yield strength data of 10−50 nm ligaments are in excellent agreement with an extrapolation of the size dependence reported by Volkert and Lilleodden,[7] who observed that the yield strength of submicron Au columns follows the power low d^{-n}, where d is the column diameter and n is 0.6 (Figure 2c). Thus, the constant σ_s in eq 1 should be replaced by a function $\sigma_s(d)$ which depends on the ligament diameter. Several important results emerge from this discussion. First, nanoindentation is a simple and straightforward method to measure the yield strength of nanoporous materials. Second, the yield strength of the ligaments in np-Au increases with decreasing ligament dimensions, which is consistent with the sample size effect previously reported for submicron Au columns and wires.[2−8] Third, the ligament size dependence observed in the present study suggests that the scaling equations have to be modified in order to account for this size-scale effect on plasticity. However, this is beyond the scope of the current study and will be discussed in a future publication. Finally, using np-Au as a sample, considerably extends the range of column dimensions for mechanical tests as the smallest diameter accessible by the FIB micromachining technique is about 100 nm.

To further validate our test method and the interpretation of the results, we performed uniaxial compression tests on micrometer-sized nanoporous Au columns[10] using the methodology developed by Uchic et al.[2] Briefly, freestanding micrometer-sized columns with an aspect ratio (height-to-diameter) of ~2 were machined into the surface of np-Au (Figure 3a) and mechanically tested using a MTS nanoindenter equipped a flat diamond punch. Details of both fabrication and testing can be found elsewhere.[7,10] These microcompression tests confirm the very high yield strength values revealed by conventional nanoindentation. Figure 3b shows a typical stress−strain curve obtained from np-Au with a relative density of 0.3 and a ligament diameter of 40 nm (this material was used for the microcompression tests because it is more uniform and easier to handle than 25% relative density np-Au). The stress−strain curve shows a linear-elastic regime followed by a plateau indicating plastic collapse. The elastic−plastic transition is observed around 90 MPa at 2.5% strain, in good agreement with nanoindentation experiments on 30% np Au ($\sigma \approx 70$ MPa). The long plateau of the stress−strain curve reveals that the high stress levels observed in the nanoindentation experiments (Figure 2) cannot be explained by densification, at least not at strain levels below 15%. Most importantly, it should be emphasized that the mechanical behavior of np-Au columns is controlled by the ligament size as an internal length scale[10] rather than by the physical dimensions of the columns as observed for fully dense single crystalline materials.[2−7]

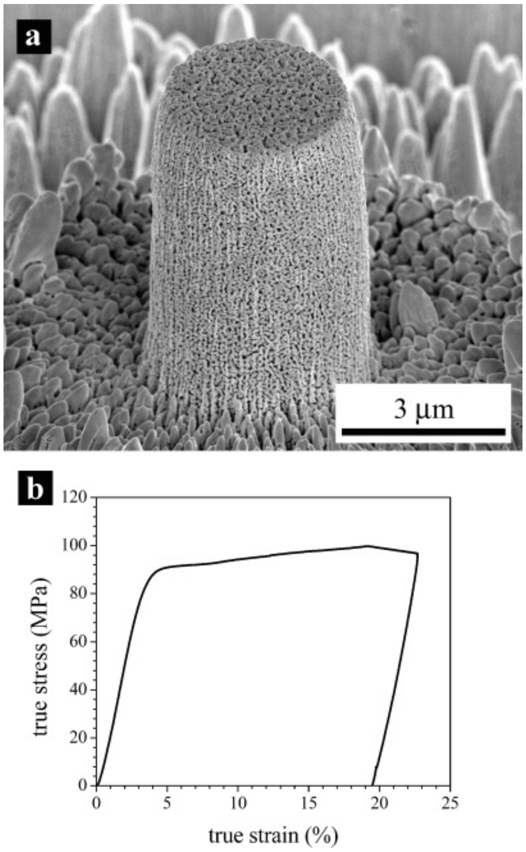

Figure 3. Uniaxial microcompression tests of np-Au: (a) SEM micrograph of a 4 μm-diameter np-Au column with an aspect ratio of ~2:1 prepared by FIB micromachining (after compression testing). Note that the characteristic pore structure of np-Au survives the FIB micromachining. Panel b shows the stress−strain curve of a np-Au column. Note that despite this high porosity np-Au is as strong as bulk Au (10−200 MPa).

To extend our study beyond the length scale accessible by experiments, we performed molecular dynamics (MD) simulations of gold columns. Recently, MD simulations have been used to study the mechanical behavior sub-10-nm Au nanowires.[30−32] Here we focus on length scales overlapping with our experiments (10−50 nm). All simulations were performed on [001]-oriented cylindrical systems with diameters ranging from 4 to 50 nm and a constant height-to-diameter aspect ratio of 2. The columns were initially equilibrated to zero pressure at 30 K for several picoseconds. Uniaxial compression tests were performed along the z-direction (001 orientation) using free boundary conditions in all three directions and strain rates ranging from 2×10^7 to 1×10^9 s^{-1}. Our MD simulations confirm the high yield strength of nanometer-sized Au ligaments, but fail to reproduce the experimentally observed size dependence (smaller is stronger). Instead, we observe that the strength of defect-free, single crystalline Au columns increases with increasing diameter. The MD result can be qualitatively understood in terms of the 1/diameter dependence of the surface-stress-induced compressive stress reported previously.[32] This leads to the important conclusion that the experimentally observed size dependence (smaller is stronger) seems to be linked to the presence of defects along the following line: the larger the ligament is, the larger the dislocation source is which can be accommodated, and the lower the stress required to initiate yield is. Indeed, preliminary simulations show that it is difficult to incorporate a stable dislocation source (such as a Frank−Read source) in ligaments with a diameter less than 20 nm. In this "defect-free" length scale regime, the column/ligament strength should decrease with decreasing diameter as predicted by our MD simulations. In the context of np-Au, this line of argument suggests that decreasing the feature size beyond 10 nm should weaken the material instead of further increasing its strength, similar to the reverse Hall−Petch regime predicted for nanocrystalline materials.

In conclusion, we have demonstrated that the recently discovered sample-size effect in plasticity can be utilized to improve the strength of metal foams by reducing the length scale of ligaments and pores. The ultimate strength in nanoporous metals can be reached when the ligaments attain the theoretical strength or, according to MD simulations, by reducing the ligament diameter to approximately 10 nm. Furthermore, we have shown that the scaling equations, originally developed for macroscopic foams, can be applied to nanoporous metals by incorporating the sample-size effect.

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