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Size dependence of effective Young's modulus of nanoporous gold

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Nanoporous gold (NPG) is a brittle, three-dimensional, random structure of Au with nanometer scale open porosity that is made by dealloying Au/Ag alloys in acid. In this work, Young's modulus of NPG with controlled porosity variation between 3 and 40 nm is determined by mechanical testing of ~100 nm thick, free standing, large-grained, stress-free films of NPG using a buckling-based method [C. Stafford *et al.*, Nat. Mater. **3**, 545 (2005)]. Results showing a dramatic rise in the effective Young's modulus of NPG with decreasing ligament size, especially below 10 nm are presented, and possible reasons for this behavior are discussed. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2436718]

Porous materials are used widely in sensing, catalysis, and other applications which benefit from their characteristic high surface area per unit volume. Nanoporous gold (NPG), one such material with a bicontinuous porosity tunable between 2 nm and 10 μm,[1] holds promise in several applications including, recently, proton exchange membrane fuel cells and substrates for biosensing.[2–5] Although gold is the most ductile element, nanoporous gold is macroscopically brittle. Li and Sieradzki attributed this to a microstructural length scale (ligament size) dependent ductile-brittle transition;[6] indeed, it has been shown that individual ligaments in brittle NPG exhibit ductile behavior characteristic of elemental gold.[7] The strong length scale dependence of the mechanical behavior of NPG makes it a particularly useful material to study nanoscale mechanics. It is conceivable, for instance, that at small enough porosity size, the increase in surface area (which scales inversely with ligament size) may allow surface properties such as surface stress to influence the overall mechanical response. Here we examine Young's modulus of freestanding, large-grained, and stress-free NPG thin films over a controlled range of ligament sizes by employing a version of a buckling-based metrology used recently to study the elastic response of polymers with high accuracy.[8] We compare our results to recent studies in which NPG of fixed ligament size was used,[9–11] and discuss possible reasons for our observed dramatic increase in modulus of ultrasmall ligament NPG.

Nanoporous gold is made by the dissolution in acid of silver atoms from a Au/Ag alloy; during dissolution, gold atoms in the lattice of the parent phase dynamically rearrange to form a three-dimensional crystalline random porous structure with uniform ligament size.[12] Application of anodic potential to the alloy in this dealloying process enhances the silver dissolution rate relative to the gold diffusion rate, leading to smaller ligament sizes. Samples for mechanical testing were made from commercially available "white gold leaf" (12 karat $Au_{35}Ag_{65}$ "Monarch" leaf, Sepp Leaf Products, New York) dealloyed in concentrated nitric acid (70%, Fischer Scientific). White gold leaf is polycrystalline with (001) texture and lateral grain size of order 10 μm owing to recrystallization as a result of the high degree of mechanical deformation from hammering.[2] For comparison, vapor deposited films of this thickness tend to possess lateral grain dimensions of order the film thickness (~100 nm here), so our grain boundary density is quite low. The leaf has a starting thickness ~100 nm which remains unchanged during porosity formation. While nanoporous gold leaf (NPGL) with ligaments 10–15 nm can be made by dealloying at open circuit potential (free corrosion), ligaments in the 3–10 nm range ("fine" porosity) can be obtained by dealloying under +1 V potential in a two electrode configuration using a graphite counterelectrode, and ligaments >15 nm ("coarse" porosity) can be formed by room-temperature coarsening in acid.[2] It is therefore easy to fabricate NPGL specimens of any desired ligament size greater than 3 nm. In the current work ligament size is varied only in the 3–40 nm range; given that the leaf itself is ~100 nm thick, ligaments >40 nm lead to a transition from a homogeneous three-dimensional to an inhomogeneous two-dimensional porosity. The crystallographic structure of the parent alloy is preserved in porosity formation during dealloying and coarsening,[12] so all NPGL samples have the same ensemble average grain structure, regardless of ligament size, as the starting white gold leaf, i.e., (001) textured, polycrystalline with grain size of order 10 μm. The effect of polycrystallinity on elastic modulus[13] of the samples is presumably the same for all samples and may therefore be ignored.

The buckling-based method employed here is based on the following phenomenon: when a stiff thin film (such as NPGL) adhered to a thick compliant substrate is subjected to a compressive strain, a balance between the energy for bending the film and that required to deform the substrate causes a buckling instability in the film.[8,14] The underlying mechanics analyzed by several authors,[15–17] show that, assuming a smooth sinusoidal waveform of the buckles, the critical buckling wavelength λ is related to film thickness h and the elastic moduli E and Poisson's ratios ν of the film and substrate (denoted by subscripts f and s, respectively) as

$$\frac{E_f}{(1-\nu_f^2)} = \frac{3E_s}{(1-\nu_s^2)}\left(\frac{\lambda}{2\pi h}\right)^3. \quad (1)$$

This solution is valid for (1) $E_f/E_s \gg 1$, (2) low strain ($\varepsilon \ll 10\%$), (3) film thickness much smaller than substrate thickness, and (4) amplitude of buckles much smaller than their wavelength. This analysis is valid only within the elas-

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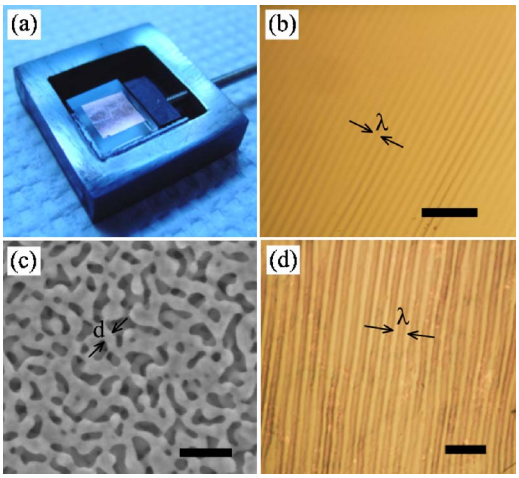

FIG. 1. (Color online) (a) Test jig is simply a rigid frame with a square recess machined out of graphite and a "piston" mounted on a fine-pitch screw to apply compressive strain. The sample is placed in the recess flush with a smooth sidewall and compressed; the magnitude of the strain is measured by noting the number of turns of the screw. (b) Optical image of the buckled surface of a Pt film (30 nm thick) on PDMS with buckling wavelength λ; scale bar 40 μm. (c) Scanning electron micrograph of nanoporous gold leaf with ligament size d=20 nm; scale bar 100 nm. (d) Optical image of the buckled surface of nanoporous gold leaf on PDMS; scale bar 40 μm.

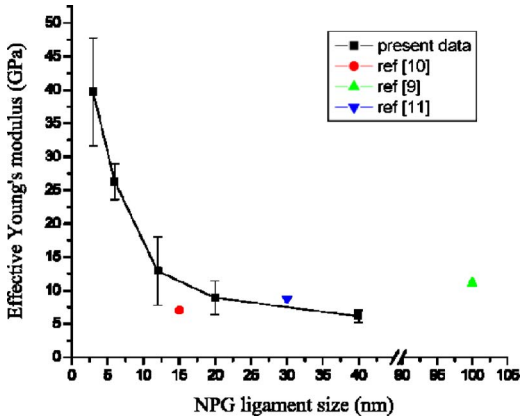

FIG. 2. (Color online) Plot of effective Young's modulus of nanoporous gold leaf as a function of ligament size. The modulus in GPa is plotted on the y axis and ligament size in nanometers on the x axis; error bars mark one standard deviation in the data. Data points for 100 and 15 nm ligament NPG from Refs. 9 and 10 are also marked.

tic limit prior to onset of yielding. For small increases in strain beyond buckling onset, the critical wavelength mode remains the lowest energy configuration so that λ remains constant and changes in strain are accommodated by variation in the amplitude of the buckles.[18]

Compliant substrates were made of 4 mm thick polydimethylsiloxane (PDMS) prepared as per manufacturer recommendations (Sylgard 184, Dow Corning) in a mixing ratio 10:1 base: curing agent, and cut into 1.5×1 cm^2 pieces with smooth vertical faces. The PDMS surface is hydrophobic, so the substrates were exposed briefly to an oxygen plasma (40 W) for 15 s to make them hydrophilic. We first determined Young's modulus of the substrate by buckling a film of known modulus (the inverse of the actual experiment with NPG): a 30 nm thick film of Pt was deposited on the substrates by magnetron sputtering and then subjected to compression in a simple winch-type compression testing jig fabricated for this purpose [Fig. 1(a)]. The Pt film promptly buckled [Fig. 1(b)] and the critical wavelength was measured by performing a fast Fourier transform (FFT) of the optical image. Using Eq. (1), where E_f=168 GPa (Ref. 19) and ν_f =0.38 for Pt, and ν_s=0.48 for PDMS, we found E_s =1.7 MPa, in excellent agreement with conventional tensile testing results in Ref. 14. A very thin, stiff layer of oxidized PDMS forms on the surface due to the short low-power plasma exposure,[20] but it does not affect our experiments and analysis, a hypothesis confirmed by the observation that the measured buckling wavelength of the Pt film was invariant for PDMS substrates with plasma exposures of different durations, from 5 to 45 s.

NPGL specimens of ligament size 3, 6, 12, 20, and 40 nm floating on clean water [Millipore Milli-Q, 18.2 MΩ, 2 ppb (parts per billion) total organic content] were mounted on the PDMS substrates simply by catching them from below and lifting them off the surface of the water. A typical scanning electron micrograph (SEM) of NPGL is shown in Fig. 1(c). Prior to mounting, a "test coupon" of each sample was collected on a Si substrate for cross-sectional thickness measurement. The NPGL/PDMS samples were placed vertically and left to dry in air for 1 h. Surface tension of water evaporating through the pores presses the NPGL on the PDMS, so that dry NPGL adheres extremely well to the substrate and cannot be removed by reimmersion in water. The dried samples were subsequently placed in the testing jig and subjected to a small compressive strain which induced the NPGL to buckle [Fig. 1(d)]; the buckling wavelength was determined by an FFT of the optical image.

Owing to the $E_f\sim(\lambda/h)^3$ dependence, results for NPGL modulus are particularly sensitive to measurement errors in λ and h. Unfortunately, the NPGL thickness h, measured by viewing film cross section in SEM (JEOL 6700F), was found to vary over a given specimen, sometimes by as much as 20%. To minimize the error in analysis, we used measurements of λ and h averaged over multiple spots on each sample. For each ligament size, six NPGL specimens were tested. A minimum of three optical images (200×200 μm^2 scan size) were taken on each sample to arrive at a mean λ, while h was averaged over ten cross-section points of each sample, so that a reasonably accurate value for $\bar{\lambda}/\bar{h}$ was determined. Nevertheless, a significant spread in results for E_f is inevitable in this approach. Additionally, we point out that the average ligament size of a sample is determined by a visual assessment of SEM micrographs and is not a mathematically precise measure, so that a "3 nm" sample may actually have ligament size nearer to 2 or 4 nm. This binning of data is convenient because we avoid complicated analyses to determine the precise ligament size, but it does contribute to larger error bars on a plot.

Results for E_f of NPGL of ligament sizes from 3 to 40 nm are plotted in Fig. 2 (assuming Poisson's ratio for NPGL ν_f=0.2). The error bars mark one standard deviation in the data. A trend is clear. For ligaments >12 nm, NPGL modulus is found to lie in the 6–12 GPa range, which compares very well with values measured by nanoindendation and compression testing.[9–11] However, for ligaments 12 nm and smaller the modulus increases rapidly, going up nearly four times to 40 GPa for 3 nm NPGL.

The dramatic rise in modulus of fine NPGL is surprising. Since NPGL is free of residual stresses that may otherwise cause stiffening, suspicion initially fell on the possible pres-

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ence of a stiff thin layer of gold oxide formed during electrochemical dealloying.[21] To test this possibility, electrochemically dealloyed NPGL was subjected to a brief cathodic bias in nitric acid (−0.5 V for 5 s) to reduce any surface oxides. However, the mechanical response of this "clean" NPGL was statistically identical to other NPGL data.

It was recently reported that dealloying under potential leads to macroscopic reduction in volume of NPGL,[22] and therefore, a concomitant increase in density. Nanoporous gold can be modeled as an open-cell foam so that its modulus E_{np} increases rapidly with density:[9] $E_{np}=E_0(\rho_{np}/\rho_0)^2$, where E_0 is Young's modulus of bulk Au and ρ_{np}/ρ_0 is the relative density of NPG. However, a 20% decrease in volume as reported in Ref. 22 accounts for only a 56% increase in modulus, much smaller than the 300% change observed in experiment.

Surface stresses in thin flat films (<5 nm) can significantly affect their apparent elastic properties[23] and an increased effect of surface stress in fine NPG is indeed expected. But the nature of this effect, given the complicated morphology of NPG, is unclear. Even so, the scale of any surface stress induced stiffening is expected to be small compared to the large change observed here.

A third explanation may arise from a structural consideration of nanoporous gold. If NPG microstructure is approximated as a truss composed of identical "beams" (ligaments), it is conceivable that finer NPGL with a large number of thin beams has a greater moment of inertia than coarse NPGL with fewer but thicker beams, making the finer NPGL stiffer in bending. Since the buckling method used here relies on film bending energy to determine Young's modulus, finer NPGL may therefore demonstrate a higher effective modulus. This appears to be a probable mechanism; however, further analysis is necessary to probe the magnitude of this effect.

In conclusion, we report a marked increase in effective Young's modulus of nanoporous gold with decreasing ligament size <10 nm. We speculate that the cause of this anomalous rise may lie in a combination of factors that include density increase, a rise in surface stress effects, and, perhaps, a higher bending stiffness owing to microstructural aspects.

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[1] Y. Ding, Y. J. Kim, and J. Erlebacher, Adv. Mater. (Weinheim, Ger.) **16**, 1897 (2004).
[2] Y. Ding, M. Chen, and J. Erlebacher, J. Am. Chem. Soc. **126**, 6876 (2004).
[3] R. Zeiss, A. Mathur, G. Fritz, J. Lee, and J. Erlebacher, J. Power Sources (doi: 10.1016/j.jpowsour.22006.12.007).
[4] F. Yu, S. Ahl, A.-M. Caminade, J.-P. Majoral, W. Knoll, and J. Erlebacher, Anal. Chem. **78**, 7346 (2006).
[5] S. O. Kucheyev, J. R. Hayes, J. Biener, T. Huser, C. E. Talley, and A. V. Hamza, Appl. Phys. Lett. **89**, 053102 (2006).
[6] R. Li and K. Sieradzki, Phys. Rev. Lett. **68**, 1168 (1992).
[7] J. Biener, A. M. Hodge, and A. V. Hamza, Appl. Phys. Lett. **87**, 121908 (2005).
[8] C. Stafford, C. Harrison, K. L. Beers, A. Karim, E. J. Amis, M. R. Vanlandingham, H.-C. Kim, W. Volksen, R. D. Miller, and E. E. Simonyi, Nat. Mater. **3**, 545 (2005).
[9] J. Biener, A. Hodge, A. Hamza, L. M. Hsiung, and J. H. Satcher, Jr., J. Appl. Phys. **97**, 024301 (2005).
[10] C. A. Volckert, E. T. Lilleodden, D. Kramer, and J. Weissmuller, Appl. Phys. Lett. **89**, 061920 (2006).
[11] D. Lee, X. Wei, M. Zhao, X. Chen, S. C. Jun, J. Hone, and J. W. Kysar, Modell. Simul. Mater. Sci. Eng. **15**, 5181 (2007).
[12] J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, and K. Sieradzki, Nature (London) **410**, 450 (2001).
[13] J. G. Berryman, J. Mech. Phys. Solids **53**, 2141 (2005).
[14] E. M. Wilder, S. Guo, S. L. Gibson, M. J. Fasolka, and C. Stafford, Macromolecules **39**, 4138 (2006).
[15] H. G. Allen, *Analysis and Design of Structural Sandwich Panels* (Pergamon, New York, 1969), p. 135.
[16] A. L. Volynskii, S. Bazhenov, O. V. Lebedeva, and N. F. Bakeev, J. Mater. Sci. **35**, 547 (2000).
[17] J. Groenewold, Physica A **298**, 32 (2001).
[18] X. Chen and J. W. Hutchinson, J. Appl. Mech. **71**, 597 (2004).
[19] A. M. James and M. P. Lord, *Macmillan's Chemical and Physical Data* (Macmillan, London, 1992), p. 20.
[20] N. Bowden, W. T. S. Huck, K. E. Paul, and G. Whitesides, Appl. Phys. Lett. **75**, 2557 (1999).
[21] N. A. Senior and R. C. Newman, Nanotechnology **17**, 2311 (2006).
[22] S. Parida, D. Kramer, C. A. Volckert, H. Rosner, J. Erlebacher, and J. Weissmuller, Phys. Rev. Lett. **97**, 035504 (2006).
[23] F. H. Streitz, R. C. Cammarata, and K. Sieradzki, Phys. Rev. B **49**, 10699 (1994).

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