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Mechanical properties of nanoporous gold in tension

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ABSTRACT

We report results of the tensile properties of nanoporous gold (NPG) as a function of the density and average ligament diameter. As-dealloyed tensile samples were thermally treated to coarsen the length scale of the NPG structure while increasing the sample density resulting from thickness reductions. The behaviors of samples with mean ligament diameters ranging from 30 to 750 nm and corresponding densities ranging from 0.30 to 0.57 that of bulk gold were examined. Digital image analysis was used to obtain ligament size histograms that were fit to the Weibull distribution. The Young's modulus was found to obey a power law, but with an exponent larger than that predicted by Gibson-Ashby scaling. The fracture behavior showed a brittle-ductile transition as a function of increasing ligament size. For samples characterized by a mean ligament diameter less than ~ 220 nm, the tensile behavior was linear elastic to sample fracture while samples with larger scale ligaments showed macroscopic yielding prior to fracture. These results are interpreted within the framework of extreme value statistics.

1. Introduction

Nanoporous gold (NPG) is typically made from a binary alloy such as Ag-Au within a compositional range of 60–80 at% Ag. The lower bound corresponds to the so-called parting limit for this binary alloy system below which it is not possible to electrochemically selectively remove Ag from the bulk of the alloy at ambient temperature [1,2]. Below this parting limit, only surface dealloying occurs during which the surface enriches in Au and eventually passivates. The upper bound is connected to the site percolation threshold for face-centered cubic systems [3,4]. Fully dealloying a silver-gold alloy with less than 20 at% Au results in mechanically disconnected regions yielding significant volume changes. The morphology of NPG is that of an isotropic interpenetrating solid/void composite where both the solid and void phase are continuous throughout the bulk of the solid. This structure is often characterized by a mean ligament and/or pore diameter. Nevertheless the structure is random in the sense that there is a distribution in ligament and pore size that can be expected to control many aspects of the mechanical behavior of NPG that depend on extreme values within this distribution.

High-rate dealloying often results in damaged NPG structures. This damage takes the form of cracks that form in order to accommodate the volume changes which can occur during dealloying. In parent-phase polycrystalline alloys, the cracks are predominantly intergranular. This damage, if severe enough, can certainly affect measurements of the elastic, plastic and fracture properties of NPG samples. In the past 10 years various experimental protocols have been developed in order to obtain so-called "crack-free" NPG samples and all of these involve low-rate dealloying [5–7]. Presumably, dealloying at low rates allows for surface diffusional accommodation of volume changes that would otherwise occur at higher dealloying rates.

Various aspects of the mechanical properties of NPG have been experimentally studied in bending [8,9], compression [10,11], tension [12,13], indentation [9,14] and non-contact ultrasonics [15]. Computational studies have used mechanics of materials approaches based on a "unit–cell" of the NPG structure [16–18], finite element methods (FEM) [16,19] and molecular dynamics (MD) [20–22]. The mechanics of materials models correspond to more detailed analyses but similar to the well-known Gibson-Ashby analysis which considers that a porous cellular solid can be represented by a unit cell of simply supported beams that respond to mechanical loading. In principle, such mechanics of materials based models can make accurate predictions for the elastic as well as the plastic behavior of porous solids so long as the degree of cell-to-cell randomness within the solid is not too large; in other words, so long as a useful representative volume element (RVE) can be identified. If on the other hand, there are significant levels of randomness (e.g., cell dimensions, beam dimensions comprising

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the cells, node points characterizing joints among beams, density fluctuations, etc.) within the porous solid then a suitable RVE may become difficult or impossible to identify. NPG solids likely correspond to this latter case. Both FEM and MD studies of NPG may suffer from this same limitation since in effect a RVE is always chosen for analysis. Nevertheless certain mechanical properties such as the elastic behavior of NPG may be accurately modeled using a suitable mean-field parameter such as the density. However, properties such as plastic yielding and fracture that depend on high order moments within the statistical distribution of ligament/pore sizes may not be accurately assessed using such approaches. These properties depend on the extreme values (e.g., the smallest diameter/length ligaments) within the tail of the distribution. In principle if one could experimentally characterize this region of the distribution, yielding and fracture behavior in these structures could be modeled. Ligament and pore size distributions of NPG can be determined with digital image analysis techniques, but even in this case one or many images of the structure that have been characterized in this way are likely not to yield sufficient information regarding the tail of the distribution. NPG morphologies have been produced with average ligament sizes ranging from about 5 to 1000 nm. If we consider a cube of NPG of dimensions 1 mm $\times$ 1 mm x 1 mm, such a cube will contain about 10^{15} and 10^{8} ligaments respectively. We know of no experimental approaches for characterizing the extreme values within a solid containing such large populations of ligaments. However, toy models can be constructed by assuming certain forms for the distribution and many realizations of populations within the distribution can be used to at least qualitatively elucidate the physics controlling the break down behavior of such solids [23,24].

One of our main motivations for this work was to characterize the elastic properties of NPG as a function of the density and the ligament size. In previous work Li and Sieradzki [8] were not able to get reliable results for the elastic properties because digital image correlation techniques were not as well developed and readily available as they are today. Additionally owing to the great improvements in the resolution of scanning electron microscopes in the past 25 years we were motivated to closely examine ligament size distributions in NPG structures and connect these to fracture behavior.

2. Brief review of research aimed at understanding the mechanical properties of NPG

Here we describe a set of experiments aimed at measuring the mechanical properties of NPG in tension as a function of the density and the average ligament/pore size. In order to place this work into context, we present a brief and by no means comprehensive review of the different experimental and computational approaches that have been employed to elucidate the mechanical properties of NPG. We focus on work that intersects with the experiment and analysis presented in sections 3 and 4.

2.1. Experiment

One of the most reliable methods for the determination of the elastic properties of a solid is through the measurement of the longitudinal and shear-wave velocities and using well-known relationships to calculate the elastic constants. Ahn and Balogun made such measurements using a laser-based ultrasonic technique [15]. For NPG samples with an average ligament size, $\mathscr{L}$, in the range of 30 – 50 nm, they obtained values of Young's modulus, E^{NPG}, in the range of 2.6 – 2.9 GPa and Poisson's ratio in the range of 0.21 – 0.24. They were also able to fit their results for E^{NPG} to the Ashby-Gibson scaling form, $\left(E^{NPG}/E^{\circ}\right) \sim \left(\rho^{NPG}/\rho^{\circ}\right)^{n}$ and obtained values of n in the range of 2.5 – 3.0. Here, E^{o} and ρ^{o} correspond respectively to the Young's modulus and density of bulk gold. Briot et al. reported on tensile test results for single crystal NPG with mean ligament size in the range of 32 – 60 nm [12]. Within this range in ligament size, they found an average value of E^{NPG} equal to 4.5 GPa and Poisson's ratio of 0.22 ± 0.06. They reported that there was no obvious correlation between the ligament size and the elastic properties. In these same tests they measured the coincident yield and fracture stress and reported and an average value of 25.2 MPa. Mather and Erlebacher used a thin film technique involving the compressive deformation of 100 nm thick NPG leaf adhered to a thicker more compliant substrate [25]. An applied in-plane compression results in a buckling instability of fixed wavelength from which E^{NPG} was determined. In this manner, they measured E^{NPG} as a function of mean ligament size. As the ligament size increased from 3 to 40 nm, E^{NPG} decreased from about 40 to 6 GPa. One parameter that enters into the calculation is the thickness of the NPG leaf and they attributed potential errors in their measurements to errors in the thickness measurements. Li and Sieradzki examined the fracture behavior of 2 mm $\times$ 2 mm x 30 mm NPG beams in three-point bending as a function of mean ligament/pore size [8]. The NPG length scale was varied by thermally coarsening the as-dealloyed morphology. The main result of this investigation was the observation of a brittle to ductile transition with increasing mean ligament size. This transition occurred for a mean ligament size of ~ 250 nm. Below this size the samples were macroscopically brittle and above this size the samples were ductile.

2.2. Computational modeling

Farkas et al. used a phase-field model to generate a bicontinuous NPG structure characterized by an average ligament size, $\mathscr{L}$, of 1.8 nm and $\left(\rho^{NPG}/\rho^{\circ}\right) = 0.25$ [21]. They modeled atomic scale interactions with a Johnson Embedded Atom Method (EAM) potential. Simulations were performed using periodic boundary conditions at a temperature of 300 K. They obtained a value of E^{NPG} of 3.70 GPa, a yield stress of 175 MPa in tension and 25 MPa in compression. This tension-compression asymmetry in yielding was attributed to surface stress effects. Ngo et al., used MD to study Young's modulus and yielding of NPG in compression and compared these results to their own experiments [22]. They used a Monte Carlo scheme simulating spinodal decomposition to evolve a NPG structure, with $\mathscr{L}$ = 3.15 nm, and initial value of $\left(\rho^{NPG}/\rho^{\circ}\right) = 0.30$. A standard EAM potential was used to model the atomic scale interactions at 300 K. In analogy with experiments, they performed a series of load/unload sequences and determined E^{NPG} and yield behavior as a function of the degree of densification. Prior to densification they found a value of Young's modulus in compression of 280 MPa that increased significantly with densification. The MD simulations mirrored their experimental results, however, it is important to note that while the relative density of the NPG in the experiments was similar to that in their simulation, the mean ligament size in experiment was ~ 40 nm. After ruling out a number of explanations for the anomalously low initial compliance of NPG in compression, the authors focus on surface stress induced bulk shear stress in the smallest ligaments within the distribution which they argued might result in a vanishing low shear modulus. In a latter paper from this same group they speculate that the anomalous compliance in compression may result from unconnected or dangling ligaments within the porous structure effectively reducing the load bearing components in the structure [26]. They acknowledge that a high population of dangling ligaments would be required in order to explain the low