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Morphological similarity and structure-dependent scaling laws of nanoporous gold from different synthesis methods

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ABSTRACT

Application of the foam scaling laws to the mechanical properties of nanoporous gold (np-Au) implicitly assumes geometrical similarity of structures of different relative density and synthesis methods. While the very few studies addressing the issue of geometric similarity during thermal coarsening show contradicting results, there are no studies covering np-Au from different synthesis routes. This paper performs quantitative morphological and topological comparison of np-Au of ca. 30% relative density synthesized by free and electrochemical corrosion methods, and thermally coarsened samples. Nanoindentation tests were performed to obtain elastic modulus and hardness. Uniaxial compression simulations of three-dimensional structures from FIB-nanotomography have been conducted using finite element analysis, and the results are compared with experiments. The three-dimensional np-Au structure has been quantified in terms of the ligament diameter and length distributions, ligament tortuosity, surface curvature distributions, structural anisotropy, nodal connectivity, and genus. Our results suggest that neither the synthesis route nor the thermal coarsening, to change length scale by up to a factor of 3, significantly altered the morphology and topology. The modulus and strength from both experiment and simulations exhibit a linear dependency on the scaled genus density, modifying the geometry-dependent prefactors in the Gibson and Ashby scaling relations.

1. Introduction

Nanoporous metals have attracted much attention in recent times due to their fascinating physical and chemical properties with potential for several functional applications [1]. This class of porous materials are in stark distinction from the conventional macroporous engineering foams in many respects. Due to nanoscale ligament dimensions, nanoporous metals exhibit size-dependent elastic modulus and strength [2–7]. Moreover, their relative density is quite high (25–50%) in contrast to the macroporous foams whose relative density is typically below 15%. The morphology of nanoporous metals is also significantly different from that of the conventional engineering foams. These peculiarities of the nanoporous metals pose challenges in characterizing their mechanical behavior, and raise the question of applicability of the cellular mechanics of low relative density macroporous foams to nanoporous metals. Early investigations have suggested modifications to the Gibson and Ashby (GA) foam scaling laws [8] to account for the size-dependent flow stress of the ligament material [5–7,9]. Although this refinement of the GA scaling laws can account for the order of magnitude variations in strength, this modification alone was found to be insufficient to fully explain the observed variation in the mechanical properties [2,10–13]. From molecular dynamics simulations on model spinodal structures, Sun et al. argue that there is significant contribution from the axial deformation of np-Au ligaments, which effectively lowers the scaling exponents [14]. On the other hand, a much larger scaling exponent for the macroscopic elastic modulus was found in np-Au when the relative density was increased by uniformly coating with Ag [15]. Saane et al. [16] have applied morphological erosion and dilation on a tomographically reconstructed nanoporous gold (np-Au) of 35% relative density—a method that is comparable with the uniform redeposition of Ag on dealloyed np-Au by Hodge et al. [15]—and conducted finite element analysis. Their results also suggest that the scaling exponents for elastic modulus and strength of such a porous material system are much larger than those in

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classical GA laws—although they are somewhat lower than those of Hodge et al. [15]. The unloading modulus during large-strain compression tests on np-Au has also been found to disagree with the classical GA scaling law exponent [12]. Several explanations for these discrepancies have been put forward: a change in the dominant deformation mechanism from bending to stretching as the relative density increases [14], a change in the relationship between the ligament thickness-to-length ratio and the relative density [17], changes in topological connectivity [2,13,16], early yielding due to surface stress-induced internal stresses [12], and morphological features such as material agglomeration at nodes, randomness, and nonlinear ligament profile [10,17–19]. Moreover, application of the GA scaling laws to np-Au of different relative density and synthesis methods, implicitly assumes geometric self-similarity of all these structures, which may not always be necessarily true. These observations emphasize the need to explicitly include the morphology and topology into the scaling laws in a general and experimentally quantifiable form. Although intuitively structural difference may be expected among nanoporous metals synthesized through different methods, they have not been quantified so far. This study addresses the issue of self-similarity and influence of morphology and topology on the mechanical properties of np-Au using nanoindentation and finite element (FE) modeling. We produce np-Au samples by two dealloying routes, namely free corrosion and electrochemical corrosion, and also by thermal annealing of the as-dealloyed samples. Nanoindentation is performed to obtain elastic modulus and hardness. Focused ion beam (FIB) nanotomography is used to reconstruct the three-dimensional structure of the samples, which will subsequently be used in quantitative morphological and topological characterization, and in FE analysis.

2. Methods

Nanoporous Au, with a nominal density of around 30% and ligament diameters between 20 and 40 nm, has been synthesized by dealloying a $Au_{30}Ag_{70}$ (at. %) precursor alloy by two methods. The first synthesis method involves dissolution of Ag from the alloy by free corrosion, while a second method uses a two-step electrochemical process. Two different starting materials with the same precursor composition were used for synthesizing nanoporous Au. For the free corrosion method, discs were cut by spark erosion from a 6 mm diameter cylindrical alloy rod (Wieland Dental + Technik GmbH & Co. KG, Germany) and then ground to a thickness of ~500 μm. The electrochemically dealloyed samples were $2 \times 2 \times 2$ mm^3 cubes obtained by cutting and grinding an alloy ingot (Kurt J. Lesker Company, Chicago, IL, USA). In electrochemical dealloying [20], the cube was first etched in diluted nitric acid (1:2, 70% assay) at a constant voltage of +1 V relative to a Pt wire counter electrode for 70 h. This step dissolved around half of the Ag, resulting in a weight loss of about a third. In the second step, undiluted nitric acid (70% assay) was used at the same potential for 24 h to dissolve the remaining Ag. In the free corrosion method, the disc-shaped samples were dealloyed in nitric acid (65%) without applying an external voltage [21]. This process is slower than the electrochemical dealloying process, leading to lower shrinkage, but typically results in a larger pore and ligament size. Samples of same relative density prepared following the same free corrosion synthesis protocol but at different locations—one in Göttingen, Germany and the other at Lawrence Livermore National Laboratories, USA—have been compared. The free corrosion samples prepared at Göttingen were split into two parts, and one of them has been thermally annealed at 500 °C for 2 h in an Argon-filled sealed glass tube placed in an oven. The sample is cooled in the tube to 100 °C, followed by air cooling to room temperature. In the following, we refer to these samples as “free corrosion S1” (LLNL), “free corrosion S2” (Göttingen), and “annealed S2” (Göttingen). Samples prepared at the University of Kentucky are referred to as “electrochemical corrosion” samples.

Berkovich nanoindentation tests are conducted using a MTS 200 Nanoindentor [22]. Berkovich indentation has been performed at a constant indentation strain rate (1%/s) with a superimposed small oscillatory signal (45 Hz, 2 nm) to allow determination of the modulus during indentation. The indentation hardness is converted to a yield stress using a Tabor factor of 2.7 [12,23]. Three dimensional structures of these samples (Fig. 1) are reconstructed by the FIB-nanotomography method presented in Ref. [21], and are used for quantitative morphological and topological characterization and subsequent FE analysis. Morphological and topological descriptors are computed using procedures described elsewhere [13,21].

In the FE simulations, the ligament material is assumed to be elastically isotropic, perfectly plastic material and obeys J_2-flow theory. For simplicity, we neglect the crystallographic nature of plastic yielding in the ligaments. We also assume that the elastic modulus and flow stress of the solid are independent of the local ligament diameter. We take $E_S = 79$ GPa for the elastic modulus, and $\nu_S = 0.42$ for the Poisson ratio for all samples, which are literature values for isotropic bulk gold. For the S1, S2, and electrochemical corrosions samples we use $\sigma_{YS} = 750$ MPa for the flow stress of the ligament material. This value is obtained by matching the 0.2% offset yield stress from uniaxial compression simulations on sample S1 with its the yield stress derived from nanoindentation hardness. These assumptions are reasonable since we limit our focus only up to macroscopic early yielding of np-Au and due to the fact that the orientation of ligaments results in isotropic elastic response independent of the shared crystallographic orientation [16,24]. However, such a yield stress matching exercise was not carried out in case of the annealed sample, since the tomographic reconstruction size is too small to be treated as a representative volume (see section 3). Hence, yield stress estimates from FE for the annealed samples are not available for the annealed sample. The gold volume is meshed using quadratic tetrahedral elements (of type C3D10 in ABAQUS). Uniaxial compression simulations have been performed in ABAQUS by prescribing normal displacements together with roller boundary conditions on one set of opposite faces. The macroscopic stress components on the sample are obtained by dividing the sum of the appropriate nodal reaction force components on each boundary by the corresponding boundary area (area of solid and pores).

For quantitative structural characterization, the tomographic reconstructions are processed to obtain skeletal representations, triangulated surface meshes, and voxel meshes. Skeletal networks are used to obtain the ligament length distributions and nodal connectivity. Surface curvature distribution, specific surface area, and genus are computed from the closed surface meshes. Voxel representations are used to compute pair correlation functions and pore-size distribution using the maximum sphere filling method. The reader is referred to Refs. [13,21] for a detailed description of these methods.

3. Results

The tomographic reconstructions of the four samples are shown in Fig. 1. Morphology of these structures is characterized in terms of ligament diameter and length distributions, specific surface area, interfacial shape distribution, and structural anisotropy. The topological descriptors include nodal connectivity and genus, which are measures of local and global connectedness of the structure, respectively. Several measures of ligament diameter have been