Acta Materialia 119 (2016) 115–122

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Topology-dependent scaling laws for the stiffness and strength of nanoporous gold

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ARTICLE INFO

Article history:
Received 21 June 2016
Received in revised form
2 August 2016
Accepted 3 August 2016

Keywords:
Structure-property relations
Nanoporous gold
Morphological analysis
Topology
Spinodal structures
Gyroid

ABSTRACT

Nanoporous gold (np-Au) differs from its macroporous counterparts through its ligament and pore length scales, its high relative density, and its very distinct mesoscale cellular architecture. When reexamining the applicability of conventional macroporous foam scaling laws to np-Au, difficulties persist not only in determining the solid properties of nanoscale ligaments, but also because np-Au structure is not self-similar as the relative density changes. Thus, a clear distinction of the effects of relative density and structure is required. This paper aims to capture the role of topology and morphology into the scaling laws by comparing the overall mechanical response of real np-Au structures with the behavior of spinodal and gyroid structures. Quantitative morphological and topological characterization of these structures has been carried out and their role on the macroscopic elastoplastic response of np-Au has been studied using finite element (FE) simulations. The predicted elastic modulus of real np-Au structures from FE simulations is in remarkable agreement with the nanoindentation measurements, and validates the numerical simulations. Quantitative structural analysis reveals that np-Au and spinodal structures are topologically very distinct, but similar in their morphology. On the other hand, gyroids are both morphologically and topologically very distinct from np-Au. The results suggest that the macroscopic stiffness and strength are highly sensitive to the topology, while being relatively much less sensitive to the morphology. The effects of structural topology are captured into modified scaling laws where the geometric pre-factors for the stiffness and strength are found to vary linearly with the scaled genus.

1. Introduction

Nanoporous gold (np-Au) is a network of nanoscale gold ligaments forming an open porous structure. The abundance of surfaces and the nanoscale dimensions of np-Au impart remarkable functional properties, for which np-Au has attracted huge attention in the past decade with potential applications such as electrochemical actuators [1], catalysts [2,3], electrodes for fuel cells [4], biological sensors [5], etc. From the mechanical behavior point of view – an understanding of which is of course necessary for its applications – np-Au is viewed as an interesting model material to study small-scale mechanical behavior [6–13] and the associated defect structures [11,14–17] inside "non-regular" ligament geometries in contrast with the more widely investigated nanoparticles, nanowires, or nanoplates. For example, the flow stress of Au inferred from the measurements of the strength of np-Au has been shown to support the "smaller is stronger" trend down to characteristic length scales as small as 10 nm [6,7,18,19], which is not yet accessible for testing in the "regular" nanoscale geometries. Length scale dependency of the elastic modulus of metals has also been suggested in experiments on np-Au [9,13].

From the micromechanical tests on np-Au, the length-scale dependent properties of the ligament material are inferred from the effective properties of the np-Au supposing that it behaves as an open-cell foam. Thus, the scaling laws of Gibson and Ashby [20] originally proposed for macroporous cellular materials (e.g. metal foams and bone) have been borrowed, which then revealed size effects in elastic and flow properties [6,7,13,16,18,21–25]. These conventional scaling laws are of the form [20]:

$$\frac{E^*}{E_s} = C_E\left(\frac{\rho^*}{\rho_s}\right)^2, \tag{1}$$

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http://dx.doi.org/10.1016/j.actamat.2016.08.012
1359-6454/

and

$$\frac{\sigma^*_{pl}}{\sigma_s} = C_\sigma \left(\frac{\rho^*}{\rho_s}\right)^{1.5}, \quad (2)$$

where E^* and σ^*_{pl} are the overall foam elastic modulus and strength, E_s and σ_s are the elastic modulus and strength of the solid, and ρ^*/ρ_s is the relative density. The non-dimensional pre-factors, C_E and C_σ, are functions of the geometry of the foam. These factors depend on the shape, anisotropy, and size distribution of the cells, besides the ligament/strut morphology [20,26–28]. Fitting the scaling laws to a common pool of data from a wide range of low density foams, average values suggested for these pre-factors are $C_E = 1$ and $C_\sigma = 0.3$ [20]. Nevertheless, given the higher relative density and the distinct cellular architecture of the np-Au and other nanoporous metals, the direct applicability of these scaling laws (even after accounting for the length-scale dependency) has been widely debated [13,16,18,23,24,29,30].

Fig. 1 summarizes the literature measurements of the elastic modulus and flow strength of solid gold as a function of the average ligament diameter, d_{avg}. Here, the modulus and strength are normalized with the relative density raised to the power given by the foam scaling laws. While the size-dependent behavior of the elastic modulus has been reported to agree only qualitatively with the theory and atomistic simulations [30–34], the flow stress behavior is believed to be in fair agreement with size effects in gold in that the strength varies with the ligament size with an exponent close to −0.6 while approaching the theoretical limit for ligament sizes on the order of 10 nm [6,7,18]. The length scale dependence of the elastic modulus has been attributed to the effects of surface elasticity, surface stress, and nonlinear elasticity of the bulk [13,24,30–33]. The size-dependent flow stress has been explained in terms of source-limited deformation [7,35]. However, the problem with the data in Fig. 1 is the large (as much as an order of magnitude) scatter across various data sets for modulus and flow stress, which poses difficulties in arriving at predictive models describing the mechanical behavior of np-Au. This connects back to the primary question of whether or not the scaling laws from Equations (1) and (2) are applicable to np-Au.

Experimental investigations so far of the power law exponents in the above equations appear to be inconclusive since structures with different relative density are morphologically and topologically distinct [36–38], indicating that the geometry dependent pre-factors in the scaling laws may also vary simultaneously. A few previous numerical studies have attempted to idealize the structure of np-Au as gyroids [30] or diamond-cubic networks [39] to investigate relative density scaling. Interestingly, gyroid networks were found to agree well with the power law exponents of Equations (1) and (2) over a wide range of relative densities [30,40], supporting the validity of the scaling. Other studies have approximated the np-Au structure with very similar looking spinodal structures [16,17,41,42]. However, the predicted effective modulus of the spinodal structure is quite low (0.5 GPa [17]), while that of the gyroids is very high (6.9 GPa [30]). The fact that the measured modulus of np-Au falls between these two limits suggests that (i) neither of the two model structures is a good approximation for np-Au, and (ii) structural differences in np-Au can potentially lead to large variations in properties. Hence, validation of the applicability of scaling laws requires quantifying and incorporating the structural information into the scaling laws, which forms the central goal of this paper.

We conduct a detailed quantitative morphological and topological characterization of (i) tomographic reconstructions of two np-Au samples, (ii) a spinodal structure, and (iii) a gyroid structure (Fig. 2). Since we focus exclusively on the role of structure on the mechanical properties, we consider structures with a constant relative density equal to ~0.32. Finite element (FE) simulations are carried out on these structures assuming an isotropic elastoplastic solid. Assuming isotropic elasticity for the solid is fully justified since the overall elastic modulus of np-Au has been shown to be independent of the shared crystallographic orientation of the np-Au ligaments in both experiments and simulations [30,43]. FE simulations are validated by comparing the predicted elastic moduli of tomographically reconstructed np-Au structures with experimental measurements from nanoindentation. By comparing the microstructural descriptors and the overall elastic modulus and strengths of these three types of structures, dominant microstructural parameters are identified and structure-dependent scaling laws are obtained.

The following section describes briefly the experimental methods of synthesizing, tomographic reconstruction, and mechanical testing of np-Au (Section 2.1), generation of spinodal

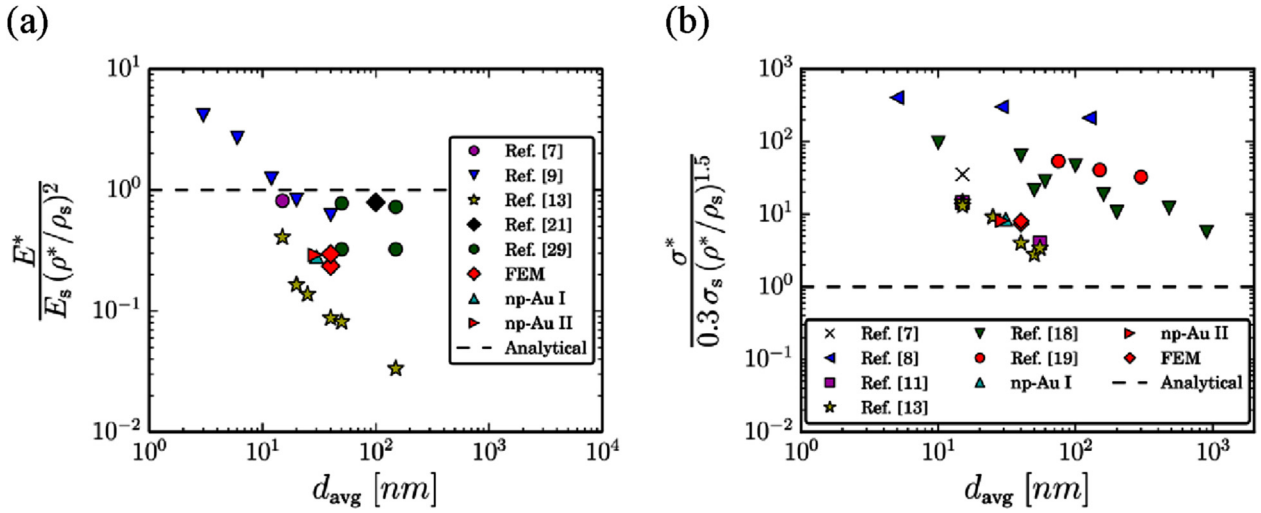

Fig. 1. Variation of normalized modulus (a) and flow stress (b) of nanoporous gold with average ligament diameter d_{avg}. Experimental measurements from this study for the two nanoporous gold samples are denoted as "np-Au I" and "np-Au II" and those from the simulations are labeled "FEM". The dashed line represents the Gibson and Ashby law with $C_E = 1$ and $C_\sigma = 0.3$ along with bulk gold properties. For normalization, we take $E_s = 79$ GPa and $\sigma_s = 50$ MPa corresponding to bulk polycrystalline gold.