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Interpreting anomalous low-strength and low-stiffness of nanoporous gold: Quantification of network connectivity

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ABSTRACT

The strength and elastic modulus of macroscopic nanoporous Au samples are much lower than that predicted by using Gibson-Ashby scaling laws. Here we attribute this discrepancy to a lowered network connectivity in nanoporous structure, and propose to modify the scaling equations (for both strength and stiffness) by introducing a concept of effective relative density. It is presented that the effective relative density can be determined by measuring the elasticity of nanoporous Au; under this scenario, the corrected strengths of Au nano-ligaments agree (on the order of magnitude) well with the previous data for similar-sized Au nanowires or nanopillars, which confirms our hypotheses. This study also revealed a low power-law exponent of size-dependent strength for Au nano-ligaments ($\beta = -0.34$) compared with that of Au submicron-pillars machined by focused ion beam (FIB) ($\beta = -0.61$), which may be related to the critical roles of surface defects played in deformation. A ratio between effective relative density and relative density is suggested to quantify the network connectivity in nanoporous structure, which decreases rapidly during structure coarsening – it explains why most previous nanoporous Au samples, which more or less experienced coarsening, were unexpectedly soft. Current study also leads to some general strategies for syntheses of strong and stiff nanoporous metals.

1. Introduction

Due to the nanoscale open porous structure, extremely large specific surface area and macroscopic-scale sample dimensions, the nanoporous (np) metals fabricated by dealloying [1,2] have attracted great interests in the past decade for a variety of novel properties and applications [3–8]. The mechanical properties of this new type of nano-structured material are also interesting for two reasons. First, the np metals are supposed to be very strong, which might be beneficial for both mechanical and functional applications. Because of the well-documented "smaller is stronger" effect [9–13], the nano-scale ligaments (solid struts) in np metals are expected to gain GPa-scale strength as well as metal nanowires [14,15]. Therefore in theory, for np metals, the strengths of the solid phase and the macroscopic material would be higher than that of conventional foam metals by more than one order of magnitude. Second, np metals provide a unique opportunity to quantify the mechanical behavior of nm-sized solids by testing at macroscopic scale. A millimeter-sized (1 mm^3) np metal with ligament diameter at around 10 nm contains ~10^{15} nano-scale ligaments [16]. If the correlation between deformation of np metal and individual nano-ligaments can be established, the mechanical properties of the nanocrystal, which are averaged over the data of a huge number of individual nano-ligaments, would be obtained simply by few (or even one single) mechanical tests of macroscopic np metal.

As a most-widely investigated np metal, the np Au is often fabricated by dealloying (i.e., selective dissolution of Ag from) AuAg alloys [1]. Early mechanical tests [17–23] on np Au were mostly performed at *microscopic* scale, often in the region between native-cracks, by nano-indentation or submicron pillar compression tests. These studies suggested that the mechanical properties of the np metals may be well described by the Gibson-Ashby scaling laws [24], which were initially established for conventional low density, random, open foam materials whose feature sizes are at micron or millimeter scale. According to the scaling laws, the strength (σ) and elastic modulus (E) of the np metals can be related to that of the solid phase (e.g., nano-ligaments in np metals) by

$$\sigma_{np} = 0.3\sigma_{lig}\varphi^{3/2} \quad (1)$$

and

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$$E_{\mathrm{np}} = E_{lig}\varphi^2 \tag{2}$$

where φ is the relative density (volume fraction of the solid phase), and subscripts *np* and *lig* denote the nanoporous metal and nano-ligaments respectively. Most *microscopic* tests showed that both strength [17] and elastic modulus [19,21] of the np Au are consistent with the values predicted in terms of the Gibson-Ashby scaling equations, where σ_{lig} takes the values of the Au nanowires [11–15] (and even theoretical strength of Au [18]) and E_{lig} equals to that of bulk Au.

However, when crack-free millimeter-sized np Au samples became accessible [31,16] and the mechanical tests at *macroscopic* scale became viable, the experiments showed that the strength [16,25] and elastic modulus [32] of np Au are significantly lower than that obtained in *microscopic* tests, and certainly are much lower (even by more than one order of magnitude) than the theoretical predictions. It is still unclear what is responsible for the discrepancies between *microscopic* and *macroscopic* tests. Nevertheless, the anomalous low strength and low stiffness have been repeatedly confirmed in *macroscopic* np Au samples by different research groups using different testing and simulation methods [16,25–28], and have become real obstacles to applications (such as actuation [6,7,29,30]) where the material requires to bear considerable load.

Current understanding is far from complete regarding the origin of the anomalous low strength and stiffness in macroscopic np Au. On one hand, the Au nano-ligaments may have been weakened by some "surface effects". Recent reports on electrochemical tuning of strength [31], stiffness [32], creep [33] and fracture [34] of np Au have confirmed the significant roles of the surface played in deformation of nano-ligaments, although most of these surface modifications led to "strengthening" or "stiffening". The surface stress, in particular, could impose axial compressive and shear stresses on nano-ligaments, which increase inversely with decreasing ligament diameter, may decrease the (compressive) strength of nano-ligaments and even lead to spontaneous contraction [33,35] of np Au samples. Ngô et al. [27] suggested that the surface-induced stress could be so large that the nonlinear elasticity may be activated and some ligaments could be brought to a shear-unstable state, which may account for the anomalous compliance of np Au. But most likely, these "weakening" mechanisms operate and become dominant only if the ligament diameter is very small, say, well below 50 nm.

On the other hand, it has been observed that the strength [16,25], and particularly the stiffness [26,28] of the np Au samples are still much lower than theoretical predictions when their ligament diameters were coarsened to well above 50 nm – under this circumstance, the above-mentioned weakening mechanisms are either inoperative or ineffective. These observations strongly suggest that the anomalous mechanical behavior of np metals might root in their "weakened" network structure, rather than (or on top of) the "weakening" of individual nano-ligaments. Some previous studies have attempted to model the network structure of np metals and modify the scaling equations [26,36,37]. But the new equations are often complex, and/or involve (more than one) additional fitting parameters whose physical meanings and feasibility are under debate. These modeling can successfully reproduce some, but not all essential deformation features of the np metals.

The anomalous low-strength and low-stiffness have evoked some discussions over evolution of network connectivity in np metals [28]. Indeed, both strength and stiffness would be decreased if a good number of ligaments in np metals are "broken" and the network structure is less connected compared with conventional foam materials. But the questions then arise as to how the network connectivity parameter can be defined and experimentally measured in the np metals, and how it can be correlated to the material's mechanical properties. In a recent review paper [28], Mameka et al. proposed a connectivity parameter, c_c, which is essentially a ratio between the diameter of the unit cell of nanoporous structure and the diameter of the closed rings in a network of load-bearing paths. The c_c value and other parameters of this kind may be quantified by direct stereological analysis of reconstructed np structure [38–41]. But such analyses would require sufficiently large (size and number of) representative reconstructions units, which is challenging for current 3D reconstruction methods.

In this paper, we propose to modify the scaling equations by introducing a concept of effective relative density, and suggest quantifying network connectivity of np structure by a ratio between the effective relative density and the real relative density. It is demonstrated in this paper that the effective relative density (and thus the network connectivity) can be experimentally determined by the macroscopic mechanical test of elastic modulus, instead of the stereological analysis of local np structures. The validity of our hypotheses and the modified scaling equations were assessed in np Au samples with different annealing and deformation histories, by systematically examining their strength and stiffness.

2. Effective relative density and network connectivity in np structure

From a typical scanning electron microscopy (SEM) image of np Au as shown in Fig. 1a, one could easily identify some ligaments (in the interior) that are dangling in the air, and obviously, could not sense and respond to the external load applying on the macroscopic np sample. Apparently, these broken/dangling ligaments, as schematically depicted in Fig. 1b, could not contribute to the instant strength and stiffness of the macroscopic material. Removing these broken/suspending nano-ligaments would lead to a "mechanically equivalent" network structure that consists only of load-bearing backbone-like ligaments (see also Fig. 1b) – a structure whose instant strength and stiffness are identical to that of the initial structure. The relative density of this "mechanically equivalent" structure, which is defined for convenience as the effective relative density (φ_{eff}), is lower than that of the initial structure (φ). If this "mechanically equivalent" structure behaves similar to conventional open cell foams, then the scaling equations (for real np metals) become

$$\sigma_{np} = 0.3\sigma_{\mathrm{lig}}\varphi_{eff}^{3/2}, \tag{3}$$

and

$$E_{np} = E_{lig}\varphi_{eff}^{2}. \tag{4}$$

Here the effective relative density is a structure parameter, whose experimental determination is challenging by direct stereological analysis of the np structure. But for np Au samples with ligament diameter larger than 30 nm, its values may be determined in terms of eq. (4). The elastic modulus of Au is insensitive to size when larger than 30 nm [14,42] and can take the value of the bulk Au ($E_{\mathrm{Au}} = 79$ GPa). The elastic modulus of the np Au sample, E_{np}, can be measured experimentally. Thus, the effective relative density can be determined as

$$\varphi_{\mathrm{eff}} = \left(E_{np}/E_{lig}\right)^{1/2}. \tag{5}$$