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Nanoporous Au: Statistical analysis of morphological features and evaluation of their influence on the elastic deformation behavior by phenomenological modeling

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Abstract—This work investigates the relationship between the morphology of nanoporous (NP) Au metal foams and their response to elastic deformation. A detailed statistical analysis of scanning electron micrographs has been performed to obtain a quantitative description of ligaments and nodes in terms of characteristic lengths. The thickness of ligaments is shown to vary along their length according to a quadratic function. The relatively broad distribution of ligament length and thickness indicates that local structures can be significantly different from each other. Invariably, nodes are quite massive. Based on this experimental evidence, a phenomenological model of the NP Au structure has been developed to describe its mechanical response within the elastic deformation range. The elementary structural unit consists of a cubic node connecting with six half ligaments with a square cross-section and a parabolic thickness profile. The model predicts that the bending behavior is restricted to the central portion of the ligaments, the effective response being modulated by the ligament characteristic lengths. Model predictions are found to agree fairly well with experimental data.

Keywords: Porous material; Nanostructured material; Metals and alloys; Elastic behavior; Modeling

1. Introduction

Nanoporous (NP) metal foams exhibit a disordered three-dimensional (3-D) open-cell structure formed by pores percolating through a network of ligaments interconnected by relatively massive nodes [1,2]. Pores and ligaments have characteristic lengths in the range between 2 and 100 nm, which result in unusually high surface-area-to-volume ratios [1,2]. These morphological features give NP metals a set of unique physical and chemical properties that not only pose challenging questions concerning the fundamental structure–property relationships, but also show considerable promise for application in different areas of science and technology. Structural materials [1–3], catalysis [4], sensing [2,5,6] and energy-oriented electrochemistry [7–9] are just a few examples.

At present, NP metal fabrication mostly relies upon chemical and electrochemical de-alloying, which allows the preferential, selective dissolution in aqueous medium of one or more elements from a parent alloy [10–13]. The dissolution, involving individual atoms or small clusters, is accompanied by a reconstruction of solid–liquid interfacial regions mediated by surface mass transport phenomena [1]. A connected porosity progressively develops inside the residual alloy, which finally consists of a disordered network of relatively thin ligaments [13]. Thermal treatments can be used to relax internal stresses arisen because of the volume shrinkage upon dissolution [14], or to coarsen the structure [15].

Although the apparent simplicity makes it attractive, de-alloying suffers from various limitations. For example, it can be hardly applied to alloys containing non-noble metals, which restricts the range of NP metals that can be effectively fabricated [1]. In addition, it is typically performed in aqueous solution, which excludes its use for metals prone to oxidation [1,9]. Finally, it depends on experimental variables that can be only partially determined, which results in a scarce control of atomic-scale mechanisms [16]. Thus, developing innovative synthetic routes to NP metals is a necessary task. The detailed characterization of the geometrical features defining the morphology of pores, ligaments and nodes is a pre-requisite to assess the validity and versatility of any given fabrication method.

Nevertheless, achieving the capability of fine-tuning the structural features via a refined manipulation of matter on the nanometer scale is only one of the crucial steps on the way to practical exploitation of NP metal foams. Another is gaining a deeper understanding of the relationship between structure and properties, which would enable a rationale design of NP metals.

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In this regard, mechanical properties represent a paradigmatic case. On the finer scale, the deformation mode of individual ligaments depends on material properties, characteristic lengths, aspect ratio and configuration of local mechanical stresses [11–14,17]. On a coarser scale, the overall mechanical response of the NP metal is a complex function of its morphology, averaged over the entire arrangement of ligaments and pores [11–14,17,18]. The disorder inherent to the NP structures inextricably links local and global deformation mechanisms to each other, making a comprehensive model for describing the mechanical properties particularly difficult to develop.

A model proposed by Ashby and Gibson in 1980s within the context of studies on mesoscopic foams provided the first conceptual framework to connect mechanical properties with morphological features [19]. The model describes the porous structure as a regular and periodic 3-D arrangement of connected cylindrical beams [19]. Beams are assumed to exhibit large aspect ratios [14,20]. This allows modeling beams as thin flexural components with three-point bending as the dominant deformation mode, which finally results in a simple power-law relationship between mechanical quantities and relative density [21]. Whereas this prediction is widely supported by experimental evidence in the case of mesoscopic foams [19], its validity for NP metals is still debated.

At least three broad sets of experimental observations suggest that the Ashby and Gibson model provides an oversimplified description of the mechanical behavior of NP metal foams. First, scanning electron microscopy (SEM) images clearly show that NP metal structures are quite far from an ordered arrangement of beams [20]. Second, a close inspection of SEM micrographs points out a significant agglomeration of mass at ligament junctions and relatively low aspect ratios for ligaments, which are predicted to significantly affect the bending behavior of individual ligaments [22–24]. Third, accurate mechanical tests on NP Au show that deformation does not depend exclusively on the relative density, but also on the ligament size, which requires adding terms to the Ashby and Gibson equations to satisfactorily interpolate the experimental data [22,25,26]. Overall, it appears that more refined modeling approaches are needed to progress in the field.

The present work aims exactly at providing an improved description of the relationship between morphological features of NP metals and mechanical response to elastic deformation. First, a statistical analysis of SEM images is carried out to quantitatively estimate size and shape of ligaments and nodes in terms of characteristic lengths. Then, a mathematical model of the bending behavior of individual ligaments is developed, taking into due account the experimental observations.

Statistical analysis of morphological features and comparison of model predictions with experimental data have been performed for NP Au, the NP metal for which more literature is available. However, methodology and model can be in principle applied to any possible NP metal foam.

2. Statistical analysis of morphological features of NP Au

The available literature on NP metal foams, and NP Au in particular, is plentiful of SEM micrographs showing the particular structure of these materials. SEM observations clearly point out two fundamental aspects: first, the variability affecting size and shape of individual ligaments and pores within any given sample; and second, the impossibility of distinguishing NP metal structures with different characteristic lengths based only on the morphology emerging from SEM micrographs. Ligaments and pores exhibit indeed almost the same topology and morphology at different characteristic length scales.

Despite the wealth of SEM observations, and the importance of characterizing the structural features of NP metal foams in detail, the statistical investigations of characteristic lengths are surprisingly rare [6,20,27]. Definite indications on the bi-continuous structure of NP Au have been obtained by transmission electron tomography [20]. The 3-D reconstruction of the structural arrangement indicates that ligaments and pores are topologically and morphologically equivalent [20]. They share similar distributions of length and diameter, which suggests that they form a complementary pair of interpenetrating networks that are the inverse of each other [20]. Accurate studies on the NP Au specific surface area have also shown that single gyroids are satisfactory approximants of the 3-D morphology [13,28]. This hypothesis has received further support from a kinetic investigation of the de-alloying processes involving Au–Ag alloys to finally produce NP Au [13]. Indeed, the experimental findings indicate that also the intermediate porous structures formed at different stages of de-alloying exhibit topological and morphological features similar to the ones of single gyroids [13]. In this respect, it is also worth noting that gyroidal geometries perfectly agree with the evidence that mass agglomerates at the ligament junctions, as demonstrated by a combination of stereographic projections and Rutherford back-scattering for NP Au and NP Pt [22].

The present study exploits the analysis of morphological features as emerging from SEM micrographs to provide the necessary details for enabling a quantitative description of the geometrical aspect of individual ligaments. In this regard, it is here worth noting that, in principle, SEM and transmission electron microscopy (TEM) micrographs cannot univocally probe the internal microstructure of NP metals. SEM and TEM micrographs provide indeed only a planar view of the NP metal foam microstructure via a two-dimensional (2-D) projection of the 3-D arrangement of pore and ligaments in the neighborhood of free surface. Therefore, local morphological information is lost due to the lack of satisfactory depth of field. This limitation can be suitably tackled by using transmission electron tomography, which allows a 3-D reconstruction of the NP metal microstructure [20,29,30]. The results obtained are definitely encouraging, and it can be reasonably expected that this method will progressively replace the present ones. However, it must be also noted that transmission electron tomography is still far from reaching a level of availability comparable with SEM and TEM, which negatively affects at present its impact on the field. In addition, SEM and TEM micrographs of fracture surfaces, as well as 3-D models obtained by transmission electron tomography, clearly indicate that conventional SEM and TEM micrographs satisfactorily represent the 3-D structure of NP metal foams. Clear examples in such sense can be found in the available literature [17,20,31–34].

The errors and uncertainties introduced in this work by not correcting SEM observations for the 3-D character of