Geometric characterization of nanoporous metals

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Abstract

Nanoporous metals made by dealloying possess significant geometric complexity—they are random, bicontinuous structures that also possess bubbles within ligaments, regions of very high negative, positive, and saddlepoint curvature, and significant polyfaceting. Here we introduce methods to geometrically quantify the structure of nanoporous metals employing simulated model nanoporous metals generated via large-scale kinetic Monte Carlo simulations as the basis of discussion. A method is introduced to transform these simulated structures into smooth triangulated meshes using new mesh-smoothing algorithms that hybridize mean curvature flow and signal processing approaches to mesh fairing. The technique is assessed by comparing the exact genus of high-genus meshes with the genus calculated via the Gauss–Bonnet formula, and works well to find the local curvature at all points of simulated surfaces of high topological genus. Specific geometric quantification of nanoporous metals is discussed for two quantities: (i) the relative surface area fraction of different crystal facets, which is important for catalysis; and (ii) the curvature distribution on the surface of porous metals, important for applications in which high curvature features are active (e.g. optical sensing).
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1. Introduction

In electrochemical dealloying for nanostructured materials synthesis, one component of a two-component crystal is electrochemically dissolved in an acid under conditions where the remaining component is allowed to diffuse along the growing acid–crystal interface [1,2]. Sometimes, when the etching rate is correctly balanced with the surface diffusion rate, the remaining material after much of the reactive component is dissolved is found to be porous, with a ligament and pore diameter as small as 10 atom near-neighbor distances. Structurally, the atoms of the crystals of interest typically sit on face-centered cubic (fcc) lattices that are randomly occupied by either element A or B (e.g. a well-studied system is A = gold, B = silver). With element B as the one that dissolves, the typical range of initial composition (atomic fraction) is 60–80% B. During dissolution of B, the occupancy of the lattice is transformed from 100% to 20–40%, depending on the initial parent composition. In principle, the remaining lattice sites are now uniformly vacant, but upon inspection, component A is found to have diffused along the metal–electrolyte interface and reorganized into locally dense ligaments. Fig. 1 shows an example of a material formed via this process, "nanoporous gold" (NPG), made by dealloying silver from a silver/gold alloy.

From the surface physics and chemistry standpoint, the structure evolution of nanoporous metals is a rich framework with which to study the driving forces for crystal surface morphological evolution, particularly when facilitated by surface diffusion (as opposed to bulk diffusion mechanisms such as vacancy diffusion that move material under the surface). Importantly, even with significant mass transport, the materials remain functionally single crystal because porosity forms at scales many orders of magnitude smaller than any grain size in the parent material. Surface diffusion occurs along different pathways, either along step edges, across flat area (terraces), i.e. along paths of different surface coordination (the number of bonds to the bulk). Study of the behavior of diffusing species along different

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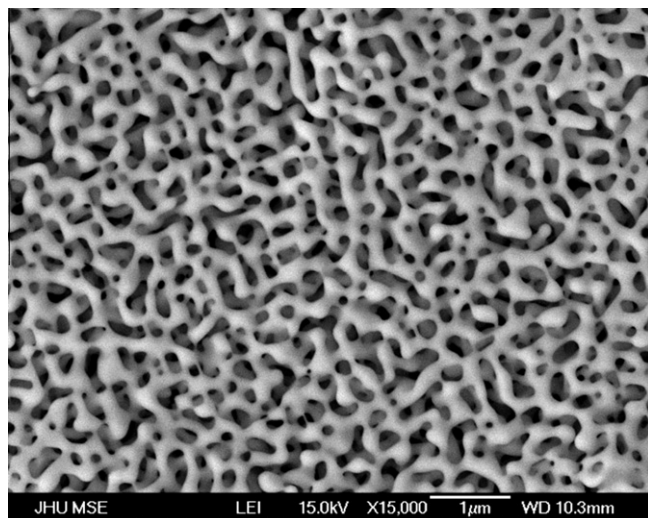 *E-mail address:* jonah.erlebacher@jhu.edu (J. Erlebacher).

Fig. 1. SEM micrograph of nanoporous gold, a nanostructured material with a complex, open porosity. This particular sample has been thermally coarsened according the recipes in [2] to make the ligaments bigger and easier to image. Notice the similarity of this real structure to the simulated structure shown in Fig. 6.

paths, and the ramifications for the morphological stability of nanostructured materials, is very important for many areas of technology—as a mundane example, if an interconnect wire in a computer chip is only a few tens of atoms wide, can we expect it to keep its shape over a useful time period?

In models of the morphological evolution of nanostructure crystal surfaces, the driving force for diffusion is associated with gradients in local surface free energy, themselves associated with local surface curvature. This is the so-called Gibbs–Thomson (GT) effect. The GT effect leads to a difference $\Delta\mu$ between the local chemical potential μ on a point on surface with mean curvature and the chemical potential of a point on a flat surface with $\kappa = 0$. Thermodynamics tells us this difference is equal to $\Delta\mu = \gamma\kappa\Omega$, where γ is the local surface energy and Ω is the atomic volume [3]. In the earliest one-dimensional continuum models of surface diffusion, the flux of surface diffusing surface atoms is given by $J = -\frac{DC}{k_B T}\nabla_s\mu$, where D is the diffusion coefficient, C is the concentration of diffusers, k_B is Boltzmann's constant and T is the temperature [4–6]. Later models have attempted to account for anisotropic surface energy, non-equilibrium concentrations of diffusers, the effect of discrete steps and terraces, and other higher order effects, but they all require an understanding of the local gradients in surface curvature (see e.g. see Ref. [7] and references therein).

A number of attempts have been made to model porous crystal morphological evolution computationally. Eilks and Elliott, for instance, have used an interface evolution equation based on variations of the continuum equations above [8]. To help assess the validity of the continuum equations, their results need to be compared to the results of microscopic atomistic models. The kinetic Monte Carlo (KMC) technique has been useful in this regard. In KMC,

a discrete lattice of atoms is generated computationally, and allowed to evolve according to stochastic rate laws for diffusion and dissolution. There has been considerable success in using KMC to model the morphological evolution of nanoporous materials [9,10] but what has been lacking in this area is a methodology to compare the simulated morphological evolution of discrete-atom systems to continuum models based on curvature gradients. In this paper, we develop some prerequisites to any detailed analysis of the kinetics of nanoporous crystal evolution. First, we demonstrate computational methods that translate the discrete lattice of simulated atoms into smooth meshes from which valid curvature gradients can be computed. Although characterization of nanoporous metals is the motivating application to which the fairing method described here will be applied, the methods presented here should be applicable to any structure of high genus and a wide dispersion of principal curvatures. Second, we quantify the baseline morphology and geometry of simulated dealloyed nanoporous metals in two respects: using a dataset of simulated nanoporous metal nanoparticles coarsening toward the Wulff shape from Ref. [10], we (i) determine the distribution of surface normals to estimate which surface orientations dominate the porous metal at various periods during the morphological evolution; and (ii) determine how the curvature distribution (the "interfacial shape distribution") changes as porous metals coarsen. Ref. [10] uses results of the analysis presented in this work to inform how the kinetics of morphological evolution of nanoporous metals during coarsening decrease the topological genus of the material, as a result of surface diffusion-driven "inverse" Rayleigh instabilities.

On the more technical level, concepts and techniques developed in the meshing and fairing (mesh smoothing) literature were used here to develop a hybrid procedure in which one starts with a porous structure on a lattice, transforms the structure into a triangulated mesh, and then fairs (smoothens) the mesh into a structure from which relevant curvature gradient information can be gleaned. This procedure is outlined in Fig. 2. From the topological perspective, these structures are interesting because (i) they have a high genus (the "number of handles" in a structure); (ii) they have a primarily open porosity but still contain some voids; (iii) the local principal curvatures relative to the inverse mesh node spacing can be quite high; and (iv) the range of these local curvatures can span the inverse system size to the inverse mesh spacing (within an order of magnitude). We show that good fairing of these complex structures can be achieved via a hybridization of the mean curvature flow algorithm of Desbrun et al. [11] with the $\lambda|\mu$ method of Taubin [12]. When the local mean curvature is calculated by polynomial fitting following Goldfeather and Interrante [13], good results are found as quantified by a reasonable match between the topological genus independently calculated by the Poincaré formula (which generalizes the famous Euler–Descartes formula), which gives an exact measure of the genus, and the genus calculated by numerical application of the Gauss–Bonnet formula.