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Softening of nanocrystalline nanoporous platinum: A molecular dynamics simulation

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ABSTRACT

Spinodal decomposition and voronoi tessellation are combined for the generation of nanocrystalline nanoporous model with grain size corresponding to ligament diameter and randomly distributed crystal orientations. A series of large-scale molecular dynamics (MD) simulations were performed and utilized to research on the mechanical behaviors of nanocrystalline nanoporous platinum (nc-NPPt) undergoing uniaxial tension. The relation between relative density and mechanical properties, together with related atomistic deforming mechanisms of as-generated nc-NPPt were analyzed. It is found that the existence of nanocrystals and substantial surface may lead to decreased tensile strength and increased plasticity of nc-NPPt, and the plastic deformation scheme of nc-NPPt is dominated by grain boundary movements. The present results will provide atomistic insights for understanding deformation mechanisms of nanocrystalline nanoporous metals as well as future mechanical optimization of nanoporous metals.

1. Introduction

In the past decades, nanoporous metals have enjoyed numerous achievements in technological areas including, but not limited to, catalysis, sensing, actuation, fuel cells and microfluidic flow controlling [1–4], for possessing intriguing chemical and physical properties [5,6].

Synthesis of nanoporous metals includes the template method [7–9] and the dealloying method [10–12], to name a few. The former one is widely applied to fabricate replicable and regular pores and ligaments by removal of place-holding materials. The latter one is more likely to result in stochastic three-dimensional bicontinuous nanoporous structure with interpenetrating pores through atomic rearrangement of noble atoms in electrolyte. In many cases, the relative density of dealloyed nanoporous metals lies in the range of 20–60% [10,12–14]. The ligament diameter and relative density could be modified by alternative dealloying conditions and alloy constituents. It is observed that the micron-sized grains of the master silver-gold alloy tend to conserve in nanoporous gold samples through chemical dealloying [10]. Therefore, it is reasonable to assume a single-crystalline nanoporous structure within modeling range for nanoporous gold [15–19].

In experiments, apart from single-crystalline structure up to several micrometers, nanoporous metals with nanocrystalline structured ligaments can be observed occasionally [11–13,20]. Nanocrystals with grain size of 3–6 nm, comparable to ligament diameter were clearly observed in a high resolution transmission electron microscope image [11]. X-ray diffraction scans of a NPPt sample obtained from a co-sputtered Pt-Si alloy also present that the struct thickness t (e.g. ligament diameter) to the grain size D is $t/D \sim 1$ [12]. Liu et al. [13] fabricated nc-NPPt with relative density ranging from 40 to 55% and grain size of 5 nm by electrochemical dealloying of amorphous platinum silicide alloys. An average size approximately equals ligament diameter. Based on high resolution transmission electron microscope images, they deduced that there exists unique one grain along the struct diameter, in other words, the struct thickness to the grain size t/D is about 1. Also, nanocrystals can be observed in nanoporous metals on condition that the base metal is Pd [21], Ag [22] or Cu [23].

Currently, most MD works of nanoporous metals have focused on the mechanisms of single-crystalline nanoporous gold in consideration of tension [15], compression [16,17], and self-shrinkage due to surface stress [18]. For materials whose interatomic potentials exist, MD is suitable to provide reliable nanoscale simulations trough mean-field approximation. Generated by numerically solving the Cahn-Hilliard equation, three-dimensional bicontinuous single-crystalline nanoporous gold models with various ligament diameter and relative density are

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uniaxially stretched or compressed to figure out their mechanical properties [15]. On an attempt to understand the mechanical properties of nc-NPPt, multiple structs with different grain sizes ranging from 2 to 22 nm are used to obtain a more statistically relevant result of mechanical behaviors as $t/D \sim 1$ through MD simulations by Liu et al. [13]. But their simulations are conducted with nanocrystalline nanopillars under uniaxial tension/compression along the nanopillars. Three-dimensional bicontinuous nanoporous platinum with nanocrystalline structured ligaments has not been fully researched with the MD method in current research stage. Scaling laws and mechanical properties of nc-NPPt remain a challenge, and therefore it is of great necessity to research on the mechanical properties of nanoporous metals, which may be sensitive to grain size, especially when grain size is down to below 10 nm [24].

Having nanoscale grain sizes in bulk materials results in a departure of conventional Hall-Petch relation. A reason to this is that pile-ups of dislocations at small grain sizes cannot be well supported [25]. The portion of highly disordered atoms (~40% with grain size of 5 nm, as estimated in computer simulations) is considerably larger than that in single crystalline nanoporous metals. Therefore, grain boundary processes are expected to be important. It is reasonable to address whether the existence of substantial grain boundaries would have a positive influence on the Young's modulus, yield strength and ultimate strength of nc-NPPt.

In this work, spinodal decomposition and voronoi tessellation are combined to generate desired simplified nc-NPPt structure. Atomistic configurations of uniaxial tensile deformation of nc-NPPt are presented using MD simulations.

2. Methodology

2.1. Sample preparation

In order to get ideal bicontinuous nanoporous structures with sufficient randomness, spinodal decomposition whose evolution can be described by the Cahn-Hilliard equation [26] is adopted. The classical Cahn-Hilliard equation demonstrates the phase separation during the cooling process of a binary alloy. Ligament morphology and connectivity of samples generated from the Cahn-Hilliard equation are in good agreement with experimentally obtained nanoporous metals [15–18,27]. The formula of the Cahn-Hilliard equation is:

$$\frac{\partial u}{\partial t} = \nabla^2 \left[\frac{\mathrm{d}f(u)}{\mathrm{d}u} - \theta^2 \nabla^2 u \right] \tag{1}$$

where $u(-1 \leqslant u \leqslant 1)$ is the phase concentration whose extreme values of ±1 correspond to pure component, $f(u)$ is the free energy function, t is the evolutionary time and θ is the width of the component transition region. Here, we use the double-well potential $f(u) = \frac{1}{4}(u^2 - 1)^2$ as a replacement of $f(u)$ [15–18,27]. Finite difference method (FDM) with a second order central difference scheme is used to numerically solve the Cahn-Hilliard equation. We discrete a large enough system with $100 \times 100 \times 100$ grids and set θ, mesh size and time step to be 0.1, 0.1 and 0.0001 in reduced units, respectively. The initial state of the whole discrete system is randomly chosen between $[-10^{-4}, 10^{-4}]$. Periodic boundary conditions are adopted. Models of time step up to 150,000 are calculated with system status conserved every 1000 time steps to get adequate models. Grids with values smaller than a certain value are removed to form pores and the remaining structure represents a three-dimensional bicontinuous nanoporous structure.

The relative density is defined by the ratio of ligament atoms to atoms of full dense with the same volume. For ligament diameter detection, Douglas et al. [28] described the chord length distribution of ligaments from nanoporous model generated from the Cahn-Hilliard equation as a normal distribution, coincident with their small-angle neutron scattering data. Nevertheless, if we see ligament morphology of a NPM as circular cylinders with finite length l_0 and diameter d_0, the length of chords that are randomly oriented distributes with 2 probability peaks which appear at l_0 and d_0, respectively [29]. The higher extremum corresponds to the cylinder diameter, and the lower one corresponds to the cylinder length. The statistically obtained distribution of chord length within a nanoporous structure generated from Cahn-Hilliard equation is slightly different from the analytical result originated from integration of chord length possibility within an ideal circular cylinder and exhibits a two-bell-shaped modality (see Fig. 1). The lower extremum submerges in the higher peak if the length of the cylinder approximates the diameter. Therefore, it is reasonable to adopt the summation of two normal distributions as a compromised fitting pattern of statistically obtained chord length distribution. The chord length that corresponds to the maximum probability in the fitting curve is regarded as the nominal ligament diameter d.

Generally, the nanocrystalline feature of a simulated structure could be achieved by two means in MD simulations. The first one is to imitate three-dimensional voronoi tessellation with stochastically oriented grains [30], resulting in mainly high angle grain boundaries, or likewise with controlled grain boundary angles. The second one is to solidify a liquid phase by quenching in the presence of fixed nuclei [31] yet with a serious drawback of substantial defects. In analogy with voronoi tessellation, random dots in a particular number within the ligament as nuclei of the grains are generated at first. Assuming nanocrystals in ligaments to be cylinder with diameter and height equivalent to nominal ligament diameter d, the number of nuclei n can be calculated by the relative density as $n = [\frac{4V\nu}{\pi d^3}]$, where V is the system volume, ν is the relative density, d is the nominal ligament diameter and [] is the rounding function. Then topological atoms starting from nuclei are generated in fcc scheme. Atoms of distance with nearest ligament grids no more than $\frac{\sqrt{3}}{2}L_0$ (L_0 denotes mesh size which is also the lattice constant, and the lattice constant is 0.392 nm for fcc platinum at 300 K) are remained to form ligament atoms. The orientation of each grain is randomly selected. Topological atoms are likely to stretch across pores on condition that nuclei are too close to pore grid. Therefore, nuclei which have distances with the nearest pore grid smaller than a certain value (2 times the lattice constant in our

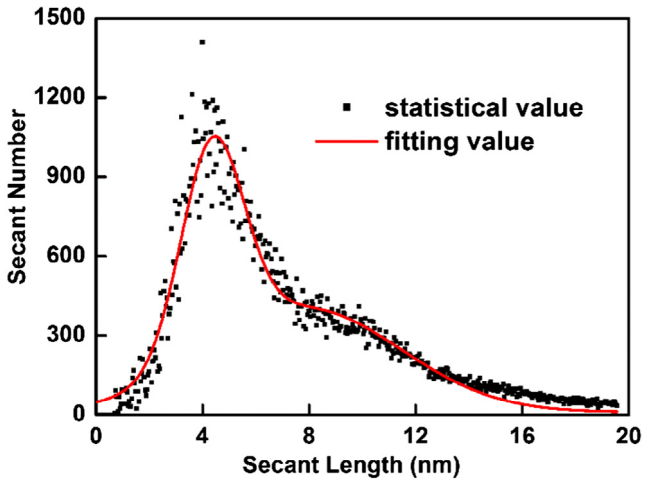

Fig. 1. Secant length distribution of a nanoporous structure obtained from the Cahn-Hilliard equation, showing a two-bell-like modality and its fitting value of a double normal distribution. The nominal ligament diameter is 4.7 nm.