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Mechanical properties of nanocrystalline nanoporous platinum

Ran Liu [a], Jacob Gruber [b], Dhriti Bhattacharyya [c], Garritt J. Tucker [b], Antonia Antoniou [a,*]

[a] The Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA
[b] Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA
[c] Institute of Materials Engineering, Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW 2234, Australia

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ABSTRACT

The mechanical behavior of nanocrystalline, nanoporous platinum (NP Pt) is investigated using a combination of experimental measurements and molecular dynamics (MD) simulations. The NP Pt considered in this work is characterized by an hierarchical internal structure with comparable characteristic strut thickness t and grain size D. The hardness of NP Pt with typical strut thickness $t = 2$–10 nm is measured by nanoindentation experiments to be $H_f = 0.2$–1.3 GPa. Using standard scaling assumptions, a characteristic individual strut strength can be estimated from the hardness measurements as $\sigma_s = 0.3$–2.5 GPa. These values compare reasonably well with the ones obtained from MD simulations of isolated struts, represented as nanowires with crystalline structure similar to the experimentally observed NP Pt. The findings suggest that for nanocrystalline NP structures with $t \sim D$ the strength of individual struts decreases gradually with decreasing strut size, so that the overall mechanical strength remains relatively high. The simulations provide insight into the underlying deformation mechanisms and behavior within the struts during mechanical loading. In particular, as struts decrease in size, they accommodate strain primarily through grain boundary plasticity, such as sliding. However, as strut size increases, dislocations begin to play a larger role in accommodating strain.

1. Introduction

Nanoporous (NP) metals often exhibit highly unusual mechanical, thermal, and electronic properties that are thought to originate from the abundance of nanoscale structure with typical internal scales in the range 2–100 nm [1–4]. Structurally, NP metals are open cell structures, i.e. they are an interconnected three-dimensional (3D) network of nm-sized struts and joints. These materials combine a high surface-to-volume ratio with many desirable properties of metals (e.g. electrical conductivity and strength), which makes them highly attractive in many applications. For example, NP metals have demonstrated great potential as catalysts [5], electrodes in electrochemical energy storage devices [6–8], sensors [3,9,10], nanoactuators [3,11], and biosensor platforms [12].

In this study we present a combined experimental and computational study of the mechanical properties of nanocrystalline nanoporous platinum (NP Pt). Platinum is a widely used catalyst in many important chemical reactions and nanoscale platinum containing structures that promise to provide compact, high-efficiency catalysts are particularly interesting [5,13–18]. The Pt considered in this work is synthesized by dealloying amorphous Pt–Si. The resulting NP Pt is nanocrystalline with comparable characteristic scales of the geometrical and material constituents (e.g. strut thickness comparable to a typical grain size $t \sim D$). This in contrast to NP metals most often considered in the literature (such as NP Au), which are characterized by $t \ll D$, i.e. individual struts that are effectively single crystalline [19]. Another distinguishing feature of the NP Pt described in this paper is that the average strut thickness is in the range $t = 2$–10 nm, substantially smaller than that considered in the majority of previous investigations. Existing studies of NP metals [20] typically infer that the strength of individual struts σ_s increases with decreasing strut thickness (e.g. as $\sigma_s \sim t^{-m}$, where m is a positive exponent), an effect that has been attributed to increasing role of surfaces in influencing defects (e.g. dislocations) as seen in other nanostructured systems [21–24]. The data presented here covers an important range of strut thicknesses, where such scalings have been relatively poorly explored. At the same time, some of the existing investigations found a characteristic change in the properties in the sub-10 nm range, such as global tension-compression asymmetry in MD simulations of NP Au [25].

We argue that from the perspective of the structure-property relation, nanocrystalline NP metals are a distinct class of materials, where *both* planar defects and free surfaces are volumetrically abundant and can influence processes of defect creation and annihilation. Understanding of the mechanical properties of such hierarchical [26] systems, where main structural elements (e.g. struts) are themselves nanostructured [27–29], is still lacking. At the same time,

* Corresponding author.
E-mail address: antonia.antoniou@me.gatech.edu (A. Antoniou).

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other nanostructured systems with overlapping geometrical length-scales and average grain sizes (e.g. nanowires and nanopillars) have attracted considerable interest [30–39].

In order to infer the influence of the nanoscale structure on the mechanical properties of NP metal from global mechanical tests, a typical analysis attempts to decouple the role of geometrical structure of the 3D network from the mechanical properties of individual struts and joints. To account for the former, one can utilize scaling relations characteristic of bulk porous media at larger scales (e.g. Refs. [40,41]), which leads to the following scaling for NP Pt hardness H_f (or, equivalently, strength σ_f) [42].

$$H_f = C\bar{\rho}^n \sigma_s, \quad (1)$$

where σ_s is the strength of the solid struts, $\bar{\rho}$ is the relative density, and C is a proportionality constant. Such scaling relationships have been verified experimentally for a wide range of ordered and disordered porous materials [42,43]. However, a distinctive property of NP metals relative to their larger-scale (bulk) counterparts is that the strut strength σ_s is itself a function of strut thickness and may also depend on the details of the internal microstructure (such as t/D and/or grain orientation). In low density bulk foams with the relative density $\bar{\rho} \lesssim 0.1$ the dominant deformation mode of struts is bending and $n = 1.5$ [42]. At higher relative densities ($\bar{\rho} \gtrsim 0.6$) theoretical arguments and experimental evidence suggest that the dominant deformation mode switches to axial strut yielding rather than bending [44], corresponding to $n \approx 1$ in Eq. (1). Average strut connectivity in the network is another important parameter that affects scaling Eq. (1) since in a highly-connected network the dominant deformation mode switches to uniaxial compression/stretching even at low densities, leading to significantly enhanced weight normalized stiffness and strength [40]. While the mode switch at lower densities is highly desirable, experiments and simulations have shown that random open cell, low density, isotropic foams are typically bending dominated (e.g. $n = 1.5$) due to the presence of defects such as missing cells, strut curvature, etc. that compromise overall mechanical properties [41]. Very few studies have attempted to directly verify applicability of Eq. (1) to NP metals. For example, a recent analysis of NP Au suggested $n \approx 3.5$ and $\sigma_s \propto t^{-0.6}$ [45].

It should be emphasized that Eq. (1) is best understood in the scaling sense. There exist significant uncertainties in the scaling and the value of proportionality constant in Eq. (1), so the inversion of Eq. (1) allows one to place bounds on the strut strength but not to pinpoint the precise value. Nevertheless, the estimates of strut strength obtained using this approach have proved useful in understanding the role of the microstructure. Here we apply this methodology to obtain estimates on the strut strength from nanoindentation measurements of hardness of NP Pt. Since NP Pt occupies an intermediate relative density regime [46], the deformation mode is expected to be a mix of bending and compression. In the absence of information on the exact scaling applicable to the NP Pt, we will use the pure bending ($n = 1.5$) and pure compression ($n = 1$) modes to obtain reasonable bounds on σ_s. The inferred strength is compared with MD simulations of single struts with aspect ratio and nanocrystalline microstructure similar to those observed experimentally. The simulations provide insights into underlying deformation mechanisms and how they change with strut thickness.

This paper is organized as follows: Section 2 is a description of the experimental and numerical protocol for the synthesis, mechanical testing of NP Pt, as well as molecular dynamics simulations of struts. Section 3 presents the experimental and atomistic simulation results, and provides an estimate of the strut strength. Sections 4 presents a summary of the work.

2. Experimental methodology

2.1. Sample synthesis

NP Platinum was synthesized by electrochemical dealloying of amorphous Pt–Si. First, an amorphous platinum silicide alloy (Pt_xSi_{1-x}, $x = 0.1–0.35$) was deposited on a silicon substrate (100) using sputter or vapor deposition. Due to mismatch strains that develop between the thin amorphous film and the silicon substrate, residual stresses can form in the film. For samples synthesized by sputtering, the deposition parameters were tuned so as to produce films with varying levels of residual compressive stress [47]. On the other hand, vacuum co-evaporated thin films of this system are almost always under tensile stress [48]. The calibration of the deposition conditions was performed by curvature measurements of the thin films on purposefully deposited cantilever silicon bars. These measurements indicated that the typical residual stress in the amorphous films is of the order of a few hundred MPa. A detailed description of the effect of residual stresses on synthesis of NP metals will be presented elsewhere.

The resulting amorphous alloy was electrochemically dealloyed in dilute hydrofluoric acid (3% in deionized water) under an externally applied potential in the range (0.3–0.9)V [29]. During the dealloying process, silicon was dissolved in the electrolyte while the platinum self-assembled into a three dimensional network of struts [49]. The residual stress enables crack-free assembly of NP metal during dealloying [50] and, together with dealloying parameters, enables a degree of control over the geometrical structure of NP metal [28,29].

2.2. Characterization

In this work we focus on mostly isotropic NP Pt with varying strut thickness, length and junction size. Each NP Pt sample was examined with a Scanning Electron Microscope (SEM) under plan and tilt views. Statistical information on the strut length, strut thickness and junction size was obtained by analyzing SEM images [51] and properly adjusted to account for the projection tilt views. For each sample, approximately 30 measurements of these parameters were made and the average values were used in the subsequent analysis. The distributions of the measurements of strut diameter and length within each sample are relatively narrow, with typical standard deviation approximately (10–20) % from the average value. The relative density for each sample was obtained from SEM stereographic projections using a procedure outlined in Ref. [46]. Here we define the relative density $\bar{\rho}$ as the ratio between the volume occupied by the solid to the total volume of the structure. Average strut thickness for all samples is in the 2–10 nm range, while the relative density is between 40 and 55%. A select number of samples were examined using Transmission Electron Microscopy (TEM). NP metal samples were encased in epoxy, cross-sectioned using a sandwich method, and thinned to electron transparency using a combination of mechanical polishing and ion milling techniques (Gatan PIPS™). The cross-section TEM samples were imaged using bright field, dark field and high resolution imaging using a Jeol 3000™ and Tecnai TF30™ TEM. TEM cross-section views of the initial platinum silicide alloy confirmed that it was amorphous [29].

2.3. Nanoindentation

The mechanical response of NP Pt samples was obtained from nanoindentation using a Hysitron Triboindenter equipped with a Berkovich tip with radius of 150 nm. Arrays of 25 indents were performed on each sample spaced 40 μm apart and the hardness was obtained from the unloading slope of each indent using the