Mechanical Properties of Nanocrystalline Nanoporous Platinum

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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 $t = 2\text{-}10\text{ nm}$ is measured by nanoindentation experiments to be $H_f = 0.2\text{-}1.3\text{ GPa}$. Using standard scaling assumptions, a characteristic individual strut strength can be estimated from the hardness measurements as $\sigma_s = 0.3\text{-}2.5\text{ GPa}$. 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.

Keywords: nanoporous platinum, nanoindentation

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 $t = 2\text{-}10\text{ nm}$, 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, 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.[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. Section 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 procedure outlined by Oliver and Pharr[52, 53]. The reported NP Pt hardness is obtained from unloading curves by averaging the values measured at indent depths within 30% of the **porous film** thickness over a range of depths corresponding to two to five pore sizes. In that range of indentation depths both the effect of the substrate[54] and size effects due to limited contact with cell walls at shallow depths are minimized.

3. Results

3.1 Hierarchical Structure of the nanoporous platinum

Panels (a) and (c) in Fig. 1 show SEM plan views of typical morphologies of NP Pt with similar relative density (within 2%) but synthesized under different conditions. Samples shown in Fig. 1 (a)-(b) were synthesized from co-sputtered $\text{Pt}_{0.1}\text{Si}_{0.9}$ (atom percent) by electrochemical dealloying under an externally applied voltage of 0.6 V and 0.7 V respectively. The sample synthesized by dealloying vapor deposited $\text{Pt}_{0.2}\text{Si}_{0.8}$ at $V = 0.7$ V is shown in Fig. 1 (c). It is apparent that the geometrical structure of NP Pt can be manipulated by changing synthesis conditions. For example, the junction size increases as the externally applied voltage was increased from 0.6 to 0.7 for samples that were co-sputtered under identical conditions.

The grain structure of the sample shown in Fig. 1(c) is illustrated in Figs. 2 and 3. Figure 2(a) shows a bright field TEM image of a cross section of the sample. The selected area diffraction pattern of an area of size 470 nm^2 from the same image is shown in panel (b). Based on the images, the analyzed region consists of a large number of randomly oriented grains. Figure 3(a) shows a $30 \times 30 \text{ nm}$ High Resolution TEM (HRTEM) image with two struts each containing multiple grains, with their corresponding power spectrum found in the inset. Figure 3(b) shows the HRTEM image of multiple struts surrounded by epoxy (glue). The lattice planes of three grains are clearly visible (0.23 nm spacing) and their approximate boundaries are marked by the red, blue and green lines, respectively. Since the average grain size is of the same order as the strut diameter for several samples that were analyzed, we deduce that along the strut diameter there is only one grain, i.e. the ratio of strut thickness to grain size $t/D \sim 1$. This was also confirmed from the dark-field TEM views of several samples analyzed in this work. Both of these images show that there may be multiple grains along the strut. From the TEM analysis of multiple struts in the NP metal, it is observed that the ends of a strut (i.e. the joints) are mostly marked by grain junctions where struts with different orientations encounter each other. The Fast

Fourier Transform (FFT) of Fig. 2(b) shows a relatively continuous ring of $\{111\}$ spots. This implies that there is no preferential orientation, since this is a random cross-section. The $\{111\}$ planes may appear more easily in the high resolution images because of the large distance between them, which makes them easier to image even at tilts away from the exact zone axis orientation, and also because of the high structure factor and relatively high multiplicity factor (amongst the low index planes). Indeed, an X-Ray Diffraction (XRD) scan of the NP Pt shows near-random-orientation intensities of the different planes. Furthermore, XRD scans of a different NP Pt sample obtained from co-sputtered Pt-Si alloy also shows that the strut thickness to grain size $t/D \sim 1$ [5].

3.2 Hardness of the nanoporous platinum

The hardness of NP Pt was found to be in the range of 0.2 to 1.3 *GPa* for samples examined in this work. The measurements of the hardness are summarized in Fig. 4, which shows the measured hardness as a function of average strut thickness t . The NP Pt with very thin struts $t < 4$ nm is characterized by lower hardness compared to the samples with thicker struts, but overall the correlation between hardness and strut thickness is rather poor. Overall, the relatively high hardness of NP Pt is quite remarkable, given that the hardness of nanocrystalline dense platinum with grain size 12 nm is approximately 3 *GPa*[39], while a typical value of hardness for bulk fully dense platinum is 0.7 *GPa*[55].

3.3 Molecular Dynamics Simulation of individual Struts

The mechanical strength of individual single-crystalline and nanocrystalline struts with similar geometrical size as seen experimentally was assessed using MD simulations. The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)[56] with a Pt embedded atom

method (EAM) interatomic potential[57] was used to uniaxially deform 2-25 *nm* diameter struts. Single-crystalline struts, with diameters of 2, 5, 15 and 25 *nm*, aligned along the crystallographic $\langle 100 \rangle$ and $\langle 111 \rangle$ directions were generated using LAMMPS. To create the nanocrystalline struts, bulk nanocrystalline structures were generated with grain size of 2.5, 5, 10, 15, and 22 *nm* using a modified Voronoi tessellation method that preserved the grain morphology/orientations and relative positions for all sizes. Five different cylindrical struts were then extracted from each bulk nanocrystalline structure with a diameter equal to the grain size – resulting in a total of 25 different struts (5 for each grain size). The resulting strength as a function of thickness behavior shown in Fig. 7 is averaged from 5 different nanocrystalline struts of each corresponding grain size. We used multiple struts of each grain size to get more statistically relevant results of the mechanical behavior, as different grain morphologies/orientations have a more significant effect on the strength as $t/D \sim 1$. Each strut was generated with an initial aspect ratio of 3:1. In all MD simulations, periodic boundary conditions were employed in the axial direction with free surfaces in the transverse directions. Prior to the imposed uniaxial straining, the energy of each strut was minimized by a conjugate gradient scheme with a convergence criteria of 10^{-12} and then equilibrated to 300K under isothermal conditions to achieve zero axial stress and surface relaxation. For the nanocrystalline samples, a 100 ps equilibration was used to allow the grain boundary structures and surface facets to relax into lower energy states. Each strut was deformed at a constant strain rate of 10^9 s^{-1} along the strut axis under both tension and compression at 300K. During straining simulations, atomic stress tensor calculations were performed and averaged over the entire structure to obtain a global stress-strain behavior, as shown in Fig. 7(b). The crystallographic identifier of each atom (e.g., FCC, HCP, non-12 coordinated) is based on

the coordination and structure of its nearest atomic neighbors. It was used to distinguish lattice and interface atoms.

To analyze the deformation behavior of the struts, we leverage post-processing algorithms that compute non-local estimates of the strain field around each atom, as outlined by Tucker et al.[58-60]. The initial atomic neighborhood of each atom is quantitatively tracked during deformation and an atomic formulation of various kinematic metrics and their application to nanoscale systems from continuum mechanics theory is obtained. In this work, we extend the formulation of the atomic strain tensor to include additional metrics such as the deviatoric and second invariant of the deviatoric strain tensor. The atomic strain tensor ($\mathbf{E}$) is obtained from the deformation gradient tensor ($\mathbf{F}$), as $\mathbf{E} = 1/2 [\mathbf{F}^T \mathbf{F} - \mathbf{I}]$, where $\mathbf{I}$ is the identity tensor. Once the atomic strain tensor ($\mathbf{E}$) is calculated for every atom with respect to its nearest neighborhood from the undeformed configuration, the atomic deviatoric strain tensor ($\mathbf{E}^*$) is calculated as $E_{ij}^* = E_{ij} - (E_{kk}/3)\delta_{ij}$, from the atomic strain tensor $\mathbf{E}$. The second invariant of the deviatoric strain tensor (e^*) is calculated from

$$e^* = (1/2)E_{ij}^*E_{ij}^* \quad (2)$$

providing an estimate of the effective shear strain in the neighborhood of each atom.

Figures 5 and 6 show the deformed state of nanocrystalline struts tested in tension using MD simulations. In each figure panels (a) and (c) show struts where atoms are colored according to their computed potential energy from the interatomic potential to highlight the higher energy regions within the microstructure, while in panels (b) and (d) the coloring of atoms corresponds to calculated effective shear strain e^* defined in Eq. (2) to highlight shear strain. The initial location of the grain boundaries in each strut are shown by the dotted white lines in (a) and (c).

The activation of dislocations in the larger nanocrystalline Pt struts is seen in Fig. 6(d) as the thin light blue/green planes, whereas deforming grain boundaries are highlighted by thicker red regions. The deformed struts in Fig. 5 (a),(b) and 6(a),(b) have $t = 5 \text{ nm}$ and struts in Fig. 6(c),(d) have $t = 15 \text{ nm}$. All modeled struts have approximately 1 grain across the strut thickness $t/D \sim 1$ and $t/l = 1/3$. Each strut was uniaxially strained up to 10% until extensive inelastic deformation had occurred. The effective shear strain e^* shown in Fig. 5(b),(d) and 6(b),(d) highlights regions where the greatest shear has occurred after tensile or compressive straining. The majority of strain accommodation has occurred within the necked region and along grain boundaries within the struts seen in Fig. 5, as highlighted by the higher calculated atomic shear strain. The observed high strain regions correspond to deformation mechanisms of grain boundary sliding, atomic reordering, and local dislocation slip along the interface planes to accommodate the macroscopic imposed strain from the simulation conditions. It is interesting to note that negligible strain accommodation has occurred outside the necked region when tested under tension, especially within grain boundaries aligned vertically (parallel to strut axis). This is true for both the $t = 5 \text{ nm}$ and $t = 15 \text{ nm}$ struts. In the $t = 15 \text{ nm}$ strut, there is also evidence of local dislocation plasticity within the necked region and next to the highly strained grain boundaries (light blue/green atomic planes). The same nanocrystalline struts tested under compression are shown in Fig. 6. As compared to the resulting deformed nanocrystalline struts under tension, the struts under compression do not display the same localized strain regions. Under compression, the shear strain appears to be accommodated along several unconnected grain boundaries throughout the sample. In addition, the $t = 15 \text{ nm}$ strut also shows evidence of higher dislocation plasticity, as compared to under tension, within numerous grains. Once again, grain boundaries that are more vertically aligned with the deformation axis show negligible strain accommodation. These same

strain accommodation trends were observed in the other 4 nanocrystalline struts at each grain size as well.

Figure 7 shows the strength as a function of strut thickness for each set of nanocrystalline and single-crystalline struts tested in both tension and compression. Errors bars show the standard deviation after averaging. The strength in the nanocrystalline struts was the averaged stress between 6 and 10 percent uniaxial imposed strain, while in the single-crystalline struts it was measured as the peak stress just following the elastic regime. Due to the high strain-rate requirement of these MD simulations, the calculated strength values of the struts are probably slightly higher than those that would be obtained from experiment on individual struts. However, the trends seen in the strength data provide insight into the deformation and mechanics of the individual struts, as well as correlating mechanical response with size. Figure 8 shows the strength asymmetry in tension and compression for the same struts. The asymmetry is large when struts are very small in diameter ($t = 2 \text{ nm}$) but decreases as the strut diameter is increased. For the case of $t = 5 \text{ nm}$, nanocrystalline strut strength is nearly equal in tension and compression. The strength of the nanocrystalline struts decreases gradually with decreasing t in compression. In contrast, the variation in strength in tension with t is relatively small. This trend is more pronounced in the single-crystalline nanowires, of $\langle 100 \rangle$ axial orientation, as displayed in Figure 7. Therefore, the single-crystalline struts with small values of t are characterized by more significant tension-compression asymmetry than struts of larger diameters as well as nanocrystalline struts. We note that the orientation of the single-crystalline struts plays a crucial role in determining their mechanical properties and the degree of tension-compression asymmetry. The $\langle 100 \rangle$ oriented struts exhibit a higher peak stress in tension than in compression, and the reverse is true for the $\langle 111 \rangle$ oriented struts. Both axial orientations of the

single-crystalline struts tested in tension exhibit an increase in the peak stress when t decreases below 5 nm. Above $t = 5$ nm the peak stress in tension is relatively constant. However, when those identically oriented struts were tested in compression they exhibit a weakening with decreasing t . The observed behavior of strength, as a function of thickness, is likely influenced by the initial core and surface stress of the struts. For example, the surface is under a state of tension, while the core is under a state of compression prior to straining. With increasing thickness, the compressive stress within the strut steadily reduces. Therefore, at smaller thicknesses, the compressive strength will be reduced and the tensile strength will increase to overcome the initial stress state within the struts. This behavior is true for both single-crystalline orientations, but as Figure 7 (a) shows, there is a strong influence of orientation on the relative strength under compression and tension. We note that the nanocrystalline simulations show a much higher strength than predicted by a model previously proposed for nanocrystalline platinum nanopillars[18] at $t/D \sim 1$. Moreover, in contrast to predictions of the model proposed in Ref. [18], the simulations demonstrate gradual decrease in strength with decreased thickness for a fixed $t/D \sim 1$. Further research will be performed to fully understand the behavior of these struts at small sizes.

Figure 9 shows the fraction of uniaxial and volumetric strain accommodated by lattice atoms, grain boundary atoms, and dislocations as a function of strut diameter, for both tension and compression. For very small thickness ($t = 2$ nm), strain is accommodated by grain boundaries and the grain interiors as elastic lattice strain. As the thickness increases beyond $t = 10$ nm, the majority of strain is still primarily accommodated by grain boundaries and lattice atoms, but dislocations start to become increasingly relevant in accommodating strain. This suggests a more complicated cooperation/competition of various nanoscale mechanisms in strain accommodation

in larger nanocrystalline struts under compression. In summary, plastic deformation occurs in large struts through combined dislocation operation, grain boundary plasticity, and lattice elastic strain while in small struts, grain boundary plasticity (such as sliding, atomic reordering/shuffling, and free volume migration) is the dominant mechanism.

Furthermore, the mechanisms of uniaxial strain accommodation are highly asymmetric between tension and compression. This points to the importance of both structural and loading orientation on the mechanics and deformation of nanostructured materials, such as nanocrystalline struts. It is also important to note the effectiveness of grain boundary sliding during strut stretching under tension. These strain accommodation mechanisms are highly dependent on the grain boundary orientation as well as the individual properties of the boundaries, such as structure and atomic order. This implies that in order to successfully model the behavior of nanocrystalline NP metals, we must move beyond models that assume strut homogeneity and the independence of strut strength on thickness.

3.4 Estimates of strut strength obtained from experimental data

As described in the introduction, the hardness measurements can be used to estimate the strength of individual struts using Eq. (1). A summary of this analysis is demonstrated in Figure 10, which shows strut strength σ_s as a function of t obtained from the experimental dataset by inversion of Eq. (1) under various assumptions. Panel (a) corresponds to the case where the dominant deformation modes is assumed to be bending, corresponding to $n=1.5$ in Eq. (1), while panel (b) of Fig. 10 shows the same data under the assumption of the dominant deformation mode being compression (corresponding to $n=1$ in Eq. 1). Also shown on both panels is the strut strength under compression from the MD simulations (black data points for nanocrystalline; red

and green for single crystal struts). The dotted line corresponds to the prediction from a model developed for nanocrystalline Platinum nanopillars[39]. The error bars in the inferred strength are determined by the uncertainty in the proportionality constant C , which can be written as $C = C_H C_G$, where C_H relates porous metal strength to hardness and C_G is a constant that relates porous metal strength to its relative density. For indentation with a Berkovich indenter $1 \leq C_H < 3$. The low bound is realized in low density foams when the plastic Poisson ratio is ~ 0 [61], while the high bound corresponds to fully dense solid. Experiments on large scale foams suggest that the geometrical parameter is $C_G = 0.3$ [42] for a range of random structures. The experimental data points in Fig. 10 (a) are shown for the case where $C = 2 \times (0.3) = 0.6$, while the error bars show a 50% uncertainty that reflects the uncertainty in C . For Fig. 10(b) the experimental data points are shown for the case where $C = 2 \times (0.65) = 1.3$.

We emphasize that the deformation mode of NP Pt is more likely a mix of bending and compression and the inserts of Fig 1(a) and (b) should be considered as upper and lower bound estimates of the strut strength. The estimates of strut strength inferred from the experimental data are reasonably close to the corresponding MD results under assumption of strut compression (panel b). This is not surprising given the relatively large relative density. More importantly, the experimental data points generally show the same trend as MD simulations, namely that the strut strength decreases with decreasing thickness in the range of values considered here. As described in Section 3.3, MD simulations suggest that as the polycrystalline strut thickness decreases, the deformation becomes increasingly localized within grain boundaries, as opposed to deformation in the main lattice, which likely is the reason for the observed decrease in the strength with t . The error bars on the experimental data points in Fig. 10 reflect only uncertainties in the proportionality constant C and do not reflect the uncertainty concerning the value of n or the

overall applicability of Eq. (1). A tighter estimate of the strength of individual struts would require developing and verifying a more accurate relation between relative density and porous metal strength for the structures with morphology resembling NP metals and with relative densities $\bar{\rho} \sim 0.5$. The uncertainty in C_H could be reduced by employing alternative experimental techniques for measuring strength.

While MD simulations demonstrate that the nanocrystalline struts are considerably weaker than single-crystal ones with the same thickness, the overall strength of nanocrystalline struts remains reasonably high. It is also worth emphasizing that MD simulations only considered deformations of individual struts and correspondingly did not account for mesoscale effects that may become important in a macroscopic system of size L with large grains, so that $L \gg D \gg t$.

4. Summary

In this paper we presented results of a combined experimental and numerical investigation of properties of nanocrystalline nanoporous Pt (NP Pt). The main results are as follows:

1) NP Pt obtained by electrochemical dealloying of amorphous platinum silicide alloys under residual stress is nanocrystalline with randomly oriented grains. A typical grain size D is approximately equal to strut thickness t . We propose that the amorphous state of the initial alloy promotes the nucleation of the nanocrystalline grains within the struts. By varying the dealloying potential, the characteristic geometrical length scales of the structure, such as the strut size and junction size can be controllably varied.

2) The hardness of NP Pt assessed via nanoindentation is 0.2-1.3 GPa for strut thickness in the $t=2-10$ nm range. The hardness decreases with decreasing average thickness of the struts.

3) Atomistic simulations of isolated idealized struts with thickness 2-25 nm, and aspect ratio and crystalline structure resembling TEM observations ($t/D \sim 1$) show that the strength weakly decreases with diameter for nanocrystalline Pt struts under compression, but remains in the range (2-4) GPa. While small struts deform almost entirely through grain boundary sliding, dislocation plasticity plays a significant role in struts of larger thickness.

4) The MD simulations demonstrate that nanocrystalline struts have a tension compression asymmetry that increases with decreasing t . It remains to be quantified what the effect of the tension compression asymmetry in the struts is on the overall foam behavior.

5) The strength of nanocrystalline Pt struts inferred from the hardness measurements is comparable to the MD simulations of struts under compression. Both simulations and the experimental data suggest that the strength of nanocrystalline struts with $t/D \sim 1$ reduces rather gradually with decreasing thickness.

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Figure captions

Figure 1. Plan SEM view of the various NP Pt morphologies synthesized from: co-sputtered amorphous $\text{Pt}_{0.1}\text{Si}_{0.9}$ films at (a) 0.6 V and (b) 0.7 V and NP Pt from co-evaporated amorphous $\text{Pt}_{0.2}\text{Si}_{0.8}$ at (c) 0.7 V.

Figure 2. (a) Bright field TEM cross-section view of multiple struts of co-evaporated NP Pt. (b) Selected area diffraction pattern of a region 470 nm^2 in size showing multiple nanocrystalline grains.

Figure 3. (a) HRTEM of a strut with diameter of 5 nm and length of 10 nm surrounded by glue. The insert shows the power spectrum of a section of the nearly horizontal strut. The average interatomic spacing is 0.24 nm . (b) HRTEM image of a multi-grain strut. The strut outlines are marked in black and approximate grain boundaries are shown by the red, blue and green outlines. To enhance contrast, images have been processed with a band-pass filter.

Figure 4. NP Pt hardness as a function of strut thickness, t . The error bars in t correspond to a 20% deviation from the average.

Figure 5. Nanocrystalline struts deformed under uniaxial tension (shown at 10% strain) in MD simulations with strut thickness (a),(b) 5 nm and (c),(d) 15 nm . For all cases $D/t \sim 1$ and aspect ratio of $t/l = 1/3$. Atoms are colored according to their (a),(c) potential energy and (b),(d) shear strain.

Figure 6. Nanocrystalline struts deformed under uniaxial compression (shown at 10% strain) in MD simulations with strut thickness t (a),(b) 5 nm and (c),(d) 15 nm . For all cases $D/t \sim 1$ and

aspect ratio of $t/l=1/3$. Atoms are colored according to their (a),(c) potential energy and (b),(d) shear strain.

Figure 7. Strength calculated in MD simulations of nanocrystalline and single crystal struts tested under tension and compression. For all cases $D/t \sim 1$ and aspect ratio of $t/l=1/3$. The peak stress is shown for the single crystalline struts. The flow stress is shown for the nanocrystalline struts.

Figure 8. Tension-compression asymmetry, $q = \sigma_y^T / \sigma_y^C$ as a function of strut size from MD simulations of nanocrystalline and single crystal struts.

Figure 9. Fraction of (a) uniaxial and (b) volumetric strain accommodated by lattice atoms (shown as FCC), grain boundary atoms (GB), and dislocations as a function of strut diameter, for both tension and compression.

Figure 10. Inferred low bound on the strut strength of nanocrystalline NP Pt in comparison to the results of MD simulations. Prediction under assumption of strut deformation by (a) bending and (b) compression. For all cases, blue squares represent the experimental data, black circles are the MD simulations of nanocrystalline struts, green and red diamonds are the single crystal struts with $\langle 111 \rangle$ and $\langle 100 \rangle$ orientations respectively. The dashed horizontal line represents extrapolation of results in Ref.[39] to the thickness below 10 nm. Power law fits to the experimental data are shown.

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; F5D_κ=75@56GF57H

Nanoporous Platinum

Nanocrystalline struts