Monolayer oxide enhanced flow stress in nanoporous gold: the size dependence

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ABSTRACT
Compression of nanoporous gold in situ under electrochemical control reveals that its flow stress can be enhanced by surface coverage of monolayer oxide. Here we present a study on the monolayer oxide induced changes in flow stress of an nanoporous gold, while the ligament size is varied by more than 2 orders of magnitude. The increase percentage of flow stress (of nanoporous gold and nano-ligaments) induced by surface monolayer oxide is negligible when the ligament size (L) exceeds ~2 µm, increases with decreasing L for ~200 nm < L < ~2 µm, and then saturates at ~27% for L < ~200 nm. These results indicate a transition from bulk-like to surface-mediated deformation behavior of nano-ligaments as L decreases from ~2 µm to ~200 nm. Our observation at L < ~200 nm support the notion that the deformation is dominated by the surface-dislocation-nucleation at this scale.

IMPACT STATEMENT
This study shows that the surface-modification induced hardening in nanoporous Au doesn’t increase monotonically with decreasing structure size as usually thought, providing new clues to the understandings of nano-crystal plasticity.

Introduction
Small-scale (μm-scale to nanoscale) solids often exhibit exceptional high strengths compared with their bulk counterparts [1–4]. The effects of size and pre-existing defects (e.g. dislocations) on their deformation behavior have been extensively studied [5–7]. But the impact of surface characteristics (e.g. roughness, facet [8], adsorption [9], and other constrains such as surface coating [10]), which are equally important in understanding small-scale deformation, was rarely explored experimentally owing to the difficulties in controlling surface characteristics during mechanical testing. This obstacle may be overcome by studying nanoporous (np) metals [11] instead of individual small-scale objects. The np metals fabricated by dealloying [12–15] are macroscopic samples consisting of a large number of nano-ligaments [11]. Their macroscopic strength and elastic modulus are proportional to that (the mean values) of the ligaments at microscopic scale [16–24]. All pores in the np sample are interconnected and open to the surrounding environment, so that all ligaments’ surface can be modified chemically or electrochemically. Thus the surface-induced changes in the mechanical response of nanoscale ligaments can be detected by examining the np metals at macroscopic scale. Jin and Weissmuller [25] demonstrated that the strength and flow stress of the np Au can be recoverably tuned electrochemically due to OH adsorption (monolayer oxide coverage) or surface changing [25,26]. Similarly, the hardness [27–29], creep rate [30], elastic modulus [31], fracture behavior [32] and even plastic Poisson’s ratio [33] of np Au were also found surface-sensitive. These findings testify that the surface characteristics have important impact on the mechanical response of a crystal if it’s sufficiently small. Further
understanding of the underlying mechanism requires to clarify how these ‘surface effects’ vary with the size, or alternatively, with specific surface area. Here we present a study on the effect of monolayer oxide on the flow stress of np Au while its ligament size was varied by more than 2 orders of magnitude. It turned out that such surface-effect doesn’t increase monotonically with decreasing size, which sheds new light on the understanding of plasticity at nanoscale.

**Experimental**

The np Au and Au(Pt) samples were obtained by electrochemical dealloying of Au$_{25}$Ag$_{75}$ and (Au$_{0.95}$Pt$_{0.05}$)$_{25}$Ag$_{75}$ precursor alloys respectively. The purpose of adding a small amount of Pt, which is remained after dealloying, is to slow down the surface diffusion thus refine the obtained nanoporous structure and suppress its coarsening. The precursor alloys were fabricated by repetitive arc-melting of Au, Ag and Pt wires (with purity > 99.99%). The ingots were homogenized in Ar atmosphere at 850°C for 100 h, then compressed and cut into cuboids (1.2 x 1.2 x 2 mm$^3$ and 3 x 3 x 4.5 mm$^3$). These samples were then annealed at 600°C for 4 h for recovery. The dealloying were performed in a 1M HClO$_4$ aqueous solution under potentiostatic control (AUTOLAB PGSTAT 302N). The reference electrode was a pseudo Ag/AgCl electrode, whose potential is 0.53 V more positive than the standard hydrogen electrode (SHE). All potentials mentioned in this paper have been converted to the SHE scale. All samples were dealloyed at 1.28 V, ensuring that the obtained np samples were free of native cracks [21,34]. When the dealloying was complete, the potential was enhanced to and held at 1.53 V for ~ 3 h to decrease residual Ag content (< 5 at.%).

**Results and discussion**

The np Au sample was mounted in an electrochemical cell for in situ compression test while a minimum load was applied to hold the sample in position. Then the applied potential was cyclically swept between 0.00 and 1.80 V until a repeatable cyclic voltammogram (CV) curve was obtained. Subsequently, the sample was polarized at 1.13 V that renders a ‘clean’ surface state (cs) according to its cyclic voltammogram (CV) curve (see Figure 2(a)). The potential was held at 1.13 V and the surface state was maintained at cs state during initial stage of compression test. While the sample was compressed to a strain between 0.10 and 0.15, the potential was immediately switched to 1.53 V, which turns the surface state from cs to an oxygen-adsorbed or monolayer oxidized surface (os). The change of flow stress in response to potential was documented, as shown in Figure 2.

At the strain (0.10 ~ 0.15) of potential jumping, the compression has readily entered the steady plastic flow region. At this point, the ‘surface effect on flow stress’ is

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**Figure 1.** (a) Schematic illustration of in situ compression of nanoporous gold in electrochemical environment. WE: working electrode. RE: reference electrode. CE: counter electrode. (b) Photograph and (c) typical SEM image of np Au.
also weakly dependent on the plastic strain, in contrast to the large variation of ‘surface effect’ with strain at larger strains as reported in Ref. [25].

Figure 2 shows that for all np samples with various ligament sizes, the flow stress increases immediately when the applied potential changes from 1.13 to 1.53 V, which is consistent with Ref. [25]. The net increase of flow stress \( \Delta \sigma_{np}(= \sigma_{os_{np}} - \sigma_{cs_{np}}) \) increases monotonically with decreasing ligament diameter \( L \). Here \( \sigma_{os_{np}} \) and \( \sigma_{cs_{np}} \) represent the flow stresses of np sample with os and cs surface states respectively, at the point of potential-jumping. The \( \Delta \sigma_{np} \) value is negligibly small (\( \sim 0.1 \) MPa) at \( L = 1.4 \) μm, and increases to \( \sim 9.0 \) MPa at \( L = 9 \) nm.

The relative changes of flow stress induced by monolayer oxide (\( \sigma_{os_{np}}/\sigma_{cs_{np}} \) and \( \Delta \sigma_{np}/\sigma_{cs_{np}} \)) are summarized in Figure 3 and plotted as function of \( L \). To our surprise, this variation is not monotonic. The \( \sigma_{os_{np}}/\sigma_{cs_{np}} \) approaches \( \sim 1 \) when \( L \) is enhanced to \( \sim 2 \) μm, indicating that the flow stress of Au ligaments is insensitive to the surface state at and above \( 2 \) μm. When \( L \) decreases from \( 2 \) μm to \( \sim 200 \) nm, \( \sigma_{os_{np}}/\sigma_{cs_{np}} \) increases gradually from \( \sim 1 \) to \( \sim 1.27 \), and \( \Delta \sigma_{np}/\sigma_{cs_{np}} \) increases from nearly zero to \( \sim 27 \%). The \( \sigma_{os_{np}}/\sigma_{cs_{np}} \) then levels off at around \( L \sim 200 \) nm.

For \( L < 200 \) nm, \( \sigma_{os_{np}}/\sigma_{cs_{np}} \) appears to decrease slightly with decreasing \( L \). The mean value of \( \sigma_{os_{np}}/\sigma_{cs_{np}} \) varies from maximum (\( \sim 1.28 \)) at \( L \sim 100 \) nm to minimum (\( \sim 0.23 \)) at \( L \sim 30 \) nm. But the variation (\( \sim 0.05 \)) is no much larger than the sampling error. A statistical analysis of \( \sigma_{os_{np}}/\sigma_{cs_{np}} \) data between 50 and 150 nm shows a standard deviation of 0.04. After all, all \( \sigma_{os_{np}}/\sigma_{cs_{np}} \) data locates in a rather narrow range between 1.20 and 1.33 (with mean value of 1.27 \( \pm 0.07 \)) when \( L \) decreases by more than one order of magnitude, from 200 to 9 nm. The variation of \( \sigma_{os_{np}}/\sigma_{cs_{np}} \) in this region is also much smaller.
than that between 200 nm and 2 μm. Therefore, below 200 nm, the $\sigma_{np}^{os}/\sigma_{np}^{cs}$ is weakly size-dependent, or even size-independent.

It should be noted that the data for $L \sim 9$ nm were obtained from np Au(Pt). The in situ compression of np Au(Pt) were performed with potential jumping from 0.60 to 1.53 V, and from 1.13 to 1.53 V, respectively: the former involves oxidation/reduction of both Au and Pt, while the latter only involves oxidation/reduction of Au. Figure 3 shows that in two cases, the obtained data differ only slightly, indicating our major conclusion was not influenced by the minor alloying of Pt.

Most experiments in this study were conducted on cuboid samples with dimensions of $1.2 \times 1.2 \times 2$ mm$^3$. For samples with very low yield strength and flow stresses, the in situ compression experiments were also conducted (repeated) using larger samples ($3 \times 3 \times 4.5$ mm$^3$). Figure 3 shows that the data from large and small samples are consistent.

It is assumed that the yield strength or flow stress of np samples ($\sigma_{np}$) can be correlated to that of the nanoligaments ($\sigma_{lig}$) and the relative density ($\varphi$) via a Gibson-Asby scaling equation [16]

$$\sigma_{np} = 0.3\sigma_{lig}^{3/2}$$  \hspace{1cm} (1)

Although many studies [11,21,35] have revealed that the yield strength of macroscopic np samples, particularly those with $\varphi < 0.30$ [11], are significantly lower than that predicted using this equation, the proportional relationship between $\sigma_{np}$ and $\sigma_{lig}$ still holds for np samples. Several modified scaling equations have been proposed for np metals [20,22,23,36–43]. In all these equations the $\sigma_{np}/\sigma_{lig}$ is expressed as a function of $\varphi$ and other geometrical structure parameters. In our case, the np structure does not change at the moment of potential-jumping, when the surface state was switched from os to cs. At this point, the $\sigma_{np}/\sigma_{lig}$ remains unchanged during surface modification, i.e. $\sigma_{np}^{cs}/\sigma_{lig}^{cs} = \sigma_{np}^{os}/\sigma_{lig}^{os}$. Therefore,

$$\frac{\sigma_{np}^{os}}{\sigma_{np}^{cs}} = \frac{\sigma_{lig}^{os}}{\sigma_{lig}^{cs}}$$ \hspace{1cm} (2)

and

$$\frac{\Delta\sigma_{np}}{\sigma_{np}^{cs}} = \frac{\Delta\sigma_{lig}}{\sigma_{lig}^{cs}}$$ \hspace{1cm} (3)

From this point of view, Figure 3 shows the increase in mean strength of Au ligaments induced by the surface monolayer oxide coverage, while the ligament diameter changes by three orders of magnitude. The two ‘turning points’ in this plot, at the critical sizes of $\sim 2 \mu$m and $\sim 200$ nm respectively, illustrate the transition of deformation mechanisms with $L$.

When $L$ approaches $\sim 2 \mu$m, the strength or flow stress of Au ligament (or np Au) are weakly dependent or independent on the surface monolayer oxide coverage. It indicates that at (and above) this length scale, the deformation is ‘bulk-like’, i.e. the plastic deformation proceeds via dislocation multiplication (double cross-slip and similar processes) in the interior; the surface-dislocation interactions, if there are any, do not make major contribution to the overall strength of ligaments. This notion is consistent with previous reports on deformation of small-scale solids [5,6,44]. And indeed, the length scale for dislocation multiplication for Au is on the order of $\sim 1 \mu$m [45], which agrees fairly well with the critical size identified in Figure 3.

When $L$ is decreased to below $2 \mu$m, the surface oxide induced increase in flow stress of Au ligaments becomes apparent and increases with decreasing size. It indicates that below $\sim 2 \mu$m, as $L$ decreases, the dislocations interact more frequently with ligament surface during plastic deformation. The increase of $\sigma_{np}/\sigma_{lig}$ suggests that the dislocation activity in Au- ligaments gradually changes from a bulk-like behavior toward a surface-mediated behavior in a broad range between $\sim 200$ nm $< L < 2 \mu$m. These details were not clearly shown in previous ‘strength vs. size’ plots of small scale solids, although some (but not all) studies showed a crossover of power-law slope at submicron scale [23,44].

For $L < \sim 200$ nm, the $\sigma_{lig}^{os}/\sigma_{lig}^{cs}$ ratio saturates at around 1.27. The preliminary data from Ref. [25] are consistent with this study. Another recent study by Mameka et al. [26] also found that at this length scale ($L = 20, 40, 150$ nm), in the double-layer capacitive charging region, the surface charge induced flow stress changes (normalized by the actual flow stress) in np Au is also weakly dependent on $L$. All these observations confirm that below 200 nm, the surface modification induced relative changes in strength (or flow stress) of Au nano-ligaments is weakly dependent on or even insensitive to the ligament size. Below 200 nm, in plastic deformation of Au nano-ligaments, the bulk-like dislocation activities may have ceased so that almost all dislocations operate via surface-mediated processes.

Our observation of a weak or even vanishing size-dependence of $\sigma_{lig}^{os}/\sigma_{lig}^{cs}$ at $L < \sim 200$ nm provides a new clue to understanding deformation mechanism of the nanoscale crystals. Empirically, the strength of a nano-crystal $\sigma$ is expressed by a Hall-Petch-like relation, $\sigma = \sigma_0 + kL^{-\beta}$, where $\sigma_0$, $k$ and $\beta$ are constants and $L$ is the characteristic size. For $L < 200$ nm, $\sigma_0$ is negligibly small compared with $kL^{-\beta}$, thus

$$\sigma \approx kL^{-\beta}$$  \hspace{1cm} (4)
Many experimental studies indeed revealed a power-law relation between $\sigma$ and $L$ in submicron scale crystals. According to this relation, the size-insensitive $\sigma_{\text{lig}}^{\text{os}}/\sigma_{\text{lig}}^{\text{cs}}$ observed in this study implies that in a log-log graph, the switch of surface state from $\text{cs}$ to $\text{os}$ gives rise to a parallel shift of $\sigma_{\text{lig}}-L$ plot to a higher stress level. In other words, the monolayer surface oxide does not change the slope of $\sigma_{\text{lig}}-L$ plot, i.e. the power-law exponent $\beta$, but increases the pre-factor $k$ by a factor of 27%, for Au with $L < 200 \text{ nm}$.

There are several models that may account for the physics of power-law relationship between $\sigma \sim L$ for small-scale solids. Using discrete dislocation dynamics (DDD) simulations, El-Awady [7] developed a model that successfully predict the strength of microcrystals larger than 200 nm. In this model, the power-law exponent is influenced by the dislocation density. It also predicts that when the size is small and the dislocation density is low (as in this study), the strength $\sigma$ scales reversely with $L^{1/2}$, where $\rho$ is the dislocation density. But the model does not include criterion to surface dislocation nucleation, which may limit its application to crystals smaller than 200 nm as in this study. Nevertheless, surface adsorption does not change $\rho$ in our case thus does not change the power-law exponent according to this model—it is consistent with our observation.

Most likely, below 200 nm, the deformation has entered the ‘dislocation starvation’ region [2] where dislocation nucleation becomes dominant. The occurrence of surface dislocation nucleation is a probabilistic event depending on intrinsic thermal fluctuations [46,47] and extrinsic surface defects [48], evidenced by large scatter of strength data of small-scale crystals. Using weakest link statistics, Sieradzki et al. [49] suggested that for small-scale deformation, the power-law exponent scales reversely with $m$, the Weibull modulus of strength data, which is sensitive to the type and distribution of the surface defects. From this point of view, our study indicates that the surface modification changes the threshold stress for surface dislocation nucleation, but not the probability distribution of its occurrence.

It is thus derived from our observation that the stress required to nucleate a dislocation from Au surface is $\sim 27\%$ higher when it is covered with monolayer oxide. But how such surface modifications influence the surface dislocation nucleation, particularly the roles of surface stress [50], surface tension [26], surface roughness and surface elasticity [31], require further study. Current study suggests that such investigations should be conducted on samples with characteristic size below 200 nm (at least for FCC metals).

Another issue that deserves more attention is the increase of $\sigma_{\text{lig}}^{\text{os}}/\sigma_{\text{lig}}^{\text{cs}}$ with increasing compression strain (for np Au with $L = 20$ and 45 nm), as reported in Ref. [25]. It was thought as an evidence to support the surface pinning of dislocations that may account for the strengthening of np Au due to surface monolayer oxide coverage—it is proposed that at large strains the dislocation may be pinned in the interior with other ends traveling on the surface, therefore the dislocation arm becomes shorter than the ligament diameter and may amplify the ‘surface effect’, leading to increase of $\sigma_{\text{lig}}^{\text{os}}/\sigma_{\text{lig}}^{\text{cs}}$ with increasing strain [25]. However, current study clearly shows that $\sigma_{\text{lig}}^{\text{os}}/\sigma_{\text{lig}}^{\text{cs}}$ does not increase with decreasing $L$ in this region. Thus above hypothesis may no longer be valid. The roles of the surface dislocation pinning and the mechanism that leads to the enhanced $\sigma_{\text{lig}}^{\text{os}}/\sigma_{\text{lig}}^{\text{cs}}$ at higher plastic strains need to be reconsidered. The surface effect on strength of nano-crystals may influenced by dislocation density, which requires experimental verification.

Current study also raises a question as to whether and how the strength of a polycrystalline material changes with varying interfacial properties (of grain boundaries and phase boundaries), and how the interfacial properties enters the Hall-Petch relationship that has been observed in almost all crystalline materials (see a recent review [51]). It might be interesting to clarify whether there is a critical grain size, below which the interface-effect becomes evident as well as the surface effect observed in np Au in this study.

**Conclusions**

The effect of surface monolayer oxide on the flow stress of np Au was investigated by compressing np samples *in situ* under the electrochemical control, while the ligament size, $L$, varied from a few µm to a few nm. The amplitude of flow stress increase induced by surface oxide, $\Delta\sigma_{\text{np}}/\sigma_{\text{np}}^{\text{cs}}$ (or $\Delta\sigma_{\text{lig}}/\sigma_{\text{lig}}^{\text{cs}}$), is negligible when $L > \sim 2 \mu m$, then increases gradually with decreasing $L$ and saturates when $L < \sim 200 \text{ nm}$. It suggests a transition in deformation behavior of nano-ligaments from a *bulk-like* to *surface-mediated* deformation behavior when $L$ decreases from $\sim 2 \mu m$ to $\sim 200 \text{ nm}$. Our study suggests that the deformation of Au nano-ligaments with $L < 200 \text{ nm}$ is dominated by the surface dislocation nucleation, and the mean stress required to nucleate a (full or partial) dislocation from Au surface increases by $\sim 27\%$ due to the presence of monolayer oxide. Current study may be improved in future by experimentally verifying the transition of deformation mechanism identified in this study, particularly the deformation mechanism of small-scale crystals with characteristic size below 200 nm.
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Disclosure statement

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