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Self-similarity in the structure of coarsened nanoporous gold

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ABSTRACT

Nanoporous gold (np-Au) samples of ligament sizes 68.6, 248.6, 462.9, and 710.9 nm are prepared by heat treatment, and representative volumes are reconstructed by focused ion beam (FIB) tomography. The increase in relative density by thermal coarsening is not pronounced. We analyze the distribution of ligament size, surface-to-volume ratio, and scaled connectivity density for coarsened np-Au, revealing that np-Au coarsens in a self-similar way. The measured activation energy for thermal coarsening supports that it is accomplished by surface diffusion of Au.

Nanoporous gold (np-Au), which is composed of a bi-continuous network of Au ligaments and pores, has attracted attention in applications such as catalysis, sensors, and actuators [1,2]. Dealloying, selective dissolution of a less-noble elemental component from a precursor alloy, is an effective way to fabricate np-Au [3–5]. By post-heat treatment, the size of ligaments and pores can be coarsened up to microscales [6,7], and this feature size is critical in determining the mechanical and chemical properties of np-Au. In particular, the mechanical properties of np-Au are found to depend strongly on ligament size [6,8–10]; in general, the strength of np-Au increases as ligament size decreases, as in the size-dependent mechanical properties of nanopillars [11,12]. The Gibson-Ashby model [13], correlating mechanical properties and relative density of cellular materials, has been applied to describe np-Au's ligament-size-dependent mechanical behavior; however, there have been deviations due to various issues as well as high relative density of np-Au around 30% [10,14–18]. Modified scaling equations [10,19] have been suggested in the form of a function of relative density and ligament size based on experimental results. Sun et al. [20] investigated a variety of scaling laws in ligament-size-dependent mechanical properties by using molecular dynamics (MD) simulations. Liu et al. [21] evaluated the network connectivity of np-Au using the concept of effective relative density by measuring elastic modulus. Understanding the irregular ligament structure in np-Au as well as its network connectivity is critical in mechanical behavior, and hence recently three-dimensional (3D) reconstruction experiments, tomography using transmission electron microscopy (TEM) [22,23], non-destructive X-ray tomography [24,25], and serial cross-sectioning by focused ion beam (FIB) and reconstruction [26,27], have been applied. To study whether the ligament-size-dependent mechanical behavior of coarsened np-Au should be attributed to size-dependent material properties and/or to the evolution of nanoporous structure in terms of morphology and topology, it is very important to discover whether np-Au coarsens in a self-similar way or not. Although extensive computational and experimental work has given insight into this topic [25,27–31], the interpretation of self-similarity as np-Au coarsens is still under debate and the evidence still seems inconclusive.

We investigate the evolution of critical parameters in ligament-size-dependent mechanical behavior such as ligament size distribution, surface-to-volume ratio, and connectivity of coarsened np-Au. We prepare four coarsened np-Au samples with average ligament size 68.6, 248.6, 462.9, and 710.6 nm by free corrosion dealloying and post-heat treatment, and obtain reconstruction volumes using serial FIB cross-sectioning and scanning electron microscopy (SEM) imaging. The edge lengths of reconstruction volumes are set as 20–30 times the average ligament size to ensure that reconstruction volume contains enough ligaments

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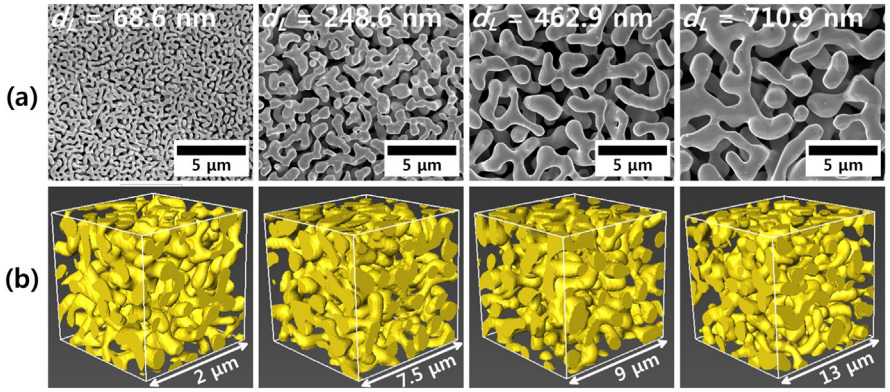

Fig. 1. (a) SEM images of coarsened np-Au samples and (b) volumes reconstructed by FIB-tomography.

to be representative, and >20 volumes are reconstructed for each sample for a statistical approach. Using experimental results, we discuss self-similarity of coarsened np-Au.

Pure Ag (99.99%) and Au (99.99%) pellets were melted to prepare Ag—Au precursor alloys (28 at.% Au-72 at.% Ag) at 1100 °C for 30 min, and homogenization was performed at 800 °C for 72 h under N_2 environment. Precursor alloys were cut into slices, one side of which was polished with 1 μm diamond suspension, and samples were annealed at 800 °C for 24 h. Dealloying by free corrosion was carried out in 35% nitric acid solution at 80 °C for 72 h. We obtained coarsened np-Au samples by heat treatment at 300 °C, 400 °C, 500 °C and 600 °C for 2 h. We measured neck diameters in connecting ligaments, possibly the thinnest part in connecting ligaments, using SEM (FE-SEM, FEI Nanolab 230); this is here called 'average ligament size d_L'. Amounts of residual Ag in at.% were measured by X-ray spectroscopy (EDX). Before 3D reconstruction, epoxy [KEM 90, ATM GmbH] was infiltrated into np-Au under high vacuum so that all pores were filled with solid epoxy, making it possible to obtain cleaner cross sections by FIB milling and to define clearly boundaries between ligaments and pores in two-dimensional (2D) images. 3D reconstructions were carried out using dual-beams system (FEI, Helios Nanolab 650). Cross-sectioning and taking SEM imaging were repeated automatically by an 'auto slice and view' program. The 200 cross-sectional SEM images were reconstructed in 3D by Avizo software software [Avizo fire 8.1, FEI Visualization Sciences Group]. 3D reconstruction was accomplished by image filtering, segmentation, and mesh generation. Edge length of reconstructed volumes were set as 20–30 times of average ligament size. >20 volumes for each sample were reconstructed to alleviate stochastic uncertainty. The relative density of np-Au and surface-to-volume ratio were calculated using Avizo software. Connectivity and ligament size distribution were calculated using a BoneJ plug-in that is source of ImageJ [32].

Fig. 1 shows typical SEM and reconstructed 3D images of np-Au samples. Average ligament size d_L was measured as 68.6(±5.8) nm, 248.6(±24.9) nm, 462.9(±42.0) nm, and 710.6(±94.7) nm for np-Au heat-treated at 300 °C, 400 °C, 500 °C, and 600 °C, respectively. Fig. 2a shows the relation among the average ligament size d_L, the inverse ratio of ligament surface area to volume $1/S_V$, and the mean thickness $\langle D \rangle$. These parameters have been used to describe the characteristic ligament size of np-Au. The average ligament size d_L is the average diameter of necks in connecting ligaments, possibly the thinnest part measured by 2D SEM images. Although various measurement rules are possible, the average ligament size d_L can be intuitively understood in SEM images. $1/S_V$ and $\langle D \rangle$ can be calculated from parameters obtained during 3D reconstruction. S_V is the surface area per unit volume of the constituent solid, and $1/S_V$ has been suggested as a characteristic length scale of np-Au [26]. $\langle D \rangle$ is the average local thickness at any point that is the diameter of the largest sphere that contains this point and is inside the structure [33]. As shown in Fig. 2a, $1/S_V$ and $\langle D \rangle$ have very similar values for four samples, and these are also approximately proportional to d_L. Fig. 2b shows the relative density of np-Au calculated by reconstructed np-Au structures. Relative density increases gradually with increasing ligament size. However, the difference in relative density between $d_L =$ 68.6 nm and $d_L =$ 710.6 nm is only 1.8%, implying that any increase in relative density by sample shrinkage during thermal coarsening is not noticeable for these samples. Fig. 3a shows the distribution of local thickness normalized by the mean thickness $\langle D \rangle$. We obtained a probability density with integrated area 1 by fitting a Gaussian curve to histograms. Probability density curves for four samples almost overlap. This implies that even though ligaments in np-Au are randomly distributed for coarsened np-Au samples, distribution of ligament size normalized by mean thickness $\langle D \rangle$ is self-similar. Fig. 3b shows scaled S_V, S_V $\langle D \rangle$ as a function of average ligament size d_L. Surface-to-volume ratio S_V, also called as

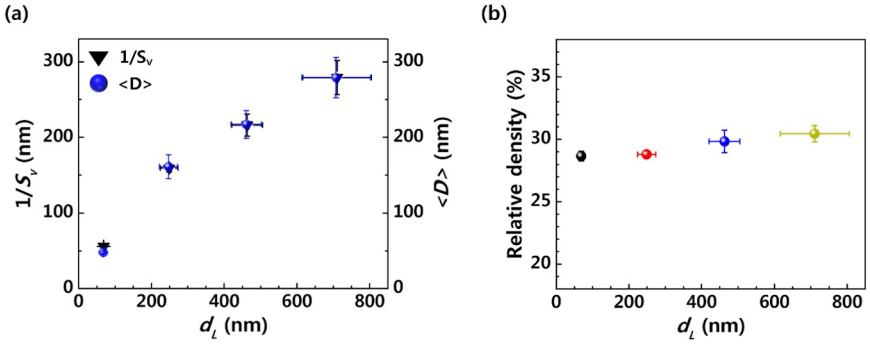

Fig. 2. (a) Comparisons of characteristic lengths of ligament size; average ligament size measured by SEM d_L, inverse of surface area-to-volume ratio $1/S_V$, and mean ligament thickness $\langle D \rangle$. (b) Relative density as a function of average ligament size.