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A principle curvatures analysis of the isothermal evolution of nanoporous gold: Quantifying the characteristic length-scales

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ABSTRACT

A study of the isothermal evolution of a nanoporous gold (npg) microstructure after dealloying has been performed. In order to adequately characterize its complex three-dimensional bicontinuous ligament-ring structure, an analysis of the scaled principle curvatures κ_1 and κ_2 based on representative volumes of meshed 3D reconstructions was applied. Five npg samples, as obtained from an electrolytical dealloying process, with different mean ligament diameters ranging from ca. 25 nm (as-dealloyed) to ca. 420 nm (from annealing at 300° C) were analyzed. The results indicate that ligament surface flattening effects lead to small but distinct morphological changes during the investigated early and mid-stages of coarsening, visible in the scaled κ_1- and κ_2- marginal distributions. Thus, strictly speaking, self-similar evolution of npg cannot be confirmed, but dependent on the specific application, the evolution might be seen as "sufficiently" self-similar. Moreover, it is shown that the inverse mean principle curvatures from the marginal distributions can be used to identify the mean sizes of the two salient structural features, namely the ligaments and the rings. Both inverse mean principle curvatures scale linearly with the mean ligament diameter. Thus, for the material used in this study, one parameter is sufficient to characterize its microstructure. Finally, it is shown that rings resembling the ones from the real samples can be generated computationally by applying modified torus parameterizations. Surprisingly, a calculation of the curvature distribution of only one "average" ring is sufficient to approximate the scaled kappa distributions accumulated from the ring distributions of the real samples.

1. Introduction

Apart from purely academic interest, microstructure evolution has provided attraction for materials science research ever since it was recognized that technologically interesting properties can be tailored via growth or coarsening of salient microstructural features such as grains in polycrystals. Mathematically, the link between some specific property and the structural sizes is often given as a scaling law. One prominent example is the Hall-Petch law that relates the yield stress of a coarse-grained material to the inverse square root of the mean grain size, see e.g. Ref. [1]. Implicitly, the validity of such a scaling law is founded by the self-similarity of an underlying phenomenon, grain growth in the given example. Loosely speaking, self-similarity implies "an object looks roughly the same on any scale" (from Wolfram Mathworld, http://mathworld.wolfram.com/Self-Similarity.html). Translated into a mathematical language and illustrated e.g. by growth and coarsening processes like normal grain growth or Ostwald ripening it means that the size distributions resulting from an isothermal evolution process are time-invariant upon scaling by the respective mean structural sizes [2,3].

While the examples given above describe systems which are typically characterized by one size measure, e.g. the mean grain size or mean particle size, there are microstructures exhibiting a much stronger three-dimensional morphological and topological complexity. The structural sizes of such systems might not be characterized sufficiently by only one metric. Nanoporous gold (npg), a material that gained considerable interest in the past decade, is one example of such a material. Its microstructure is usually described as a 3D bicontinuous, interconnected pore-ligament network with a typical initial mean ligament diameter of about 5–50 nm, depending on the dealloying conditions [4]. However, it appears to be more appropriate to call it a ligament-ring structure, since essentially two distinct morphologies can be

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discriminated (Fig. 1): the ligaments themselves and the irregular shaped, torus-like rings formed by the interconnected ligaments. Thus, the ligament and the ring diameters might be seen as the two fundamental metrics of npg. It should be noted that both of these structural features can have a distinctly different impact on the mechanical properties of npg. It is still unclear, if there is a correlation between these two mean sizes that might or might not be maintained during coarsening.

Structural coarsening of npg can be easily achieved via thermal annealing after dealloying, thereby increasing the ligament sizes as well as the ring sizes. This requires a reduction of the number of rings per unit volume over time while keeping the solid volume fraction constant. This means that in order to make self-similar coarsening of both ligaments and rings possible, rings must be opened. So-called pinch-off events have been proposed [5], which are necessary for a self-similar evolution of the topology of such a bicontinuous network structure [6]. Dead-end ligaments resulting from these events can be found in the microstructure throughout the coarsening process (see Fig. 1c and d). This is of great importance for mechanical applications, since dead-end ligament parts do not contribute to the load bearing parts of the npg network [7].

Experimentally, Chen-Wiegart et al. concluded that npg does not coarsen in a self-similar manner [8], based on their results of the isothermal temporal evolution of the inverse specific surface area, and of the evolution of the surface principle curvatures κ_1 and κ_2, represented as so-called 2D scaled interface shape distributions (ISD). ISD's have already been used to characterize systems with complex microstructures, see e.g. Refs. [9,10], because direct access to 3D size distributions of the structural constituents was not possible. The scaled ISD's shown in Chen-Wiegart's work are clearly not time-invariant, and the explanation they give relates to a seemingly increasing anisotropy of the npg microstructure. However, it appears that the X-ray nanotomography approach taken to reconstruct the 3D structure negates volumes which can be considered as representative during the later annealing stages. We have already demonstrated the importance of using representative volumes in analyzing the npg microstructure [7]. It was shown that the side length of the representative cube volumes scaled with the mean ligament diameters by a factor of about 14–16 for the electrolytically dealloyed bulk npg samples used. On the other hand, it is unclear to what extent the various sample preparation steps, i.e. preparation of the AgAu alloy and dealloying, influence the resultant, as-dealloyed structure. The self-similar regime might be attained only in later coarsening stages, where Chen-Wiegart et al. are critically limited in the volumes analyzed. It has to be mentioned that Chen-Wiegart applied a free corrosion process to produce the npg samples which might yield different as-dealloyed structures than the ones from an electrolytical dissolution process.

Computationally, it was shown that bicontinuous structures, qualitatively resembling npg structures, can be generated by employing phase field spinodal decomposition [9]. Investigation of the structural evolution showed that self-similarity well describes late-stage coarsening via conserved dynamics of samples with a solid volume fraction of 36% [6].

We propose analyzing representative volumes and extending the surface curvature analysis by making use of not just only the 2D ISD representations but of the marginal κ_1- and κ_2-distributions as well. This approach is based on the assumption that the two basic npg microstructure constituents, rings and ligaments, are each representable by one of the two principle curvatures κ_1 and κ_2 respectively. This is identically the case for a regular torus surface, see Fig. 2, recognizing that for a regular torus κ_2 (due to our choice) exclusively reflects the inverse ligament radius, because $\kappa_1<\kappa_2$ always, due to $\mathrm{Max}(\kappa_1)=1/(R+r)<1/r$. Since the torus is a closed ring, the mean of the second principle curvature value $\langle\kappa_1\rangle$ is negative, and reflects the ring size in some way. If we consider the real npg microstructure to be built up by interconnected tori, each on average contributing by only half of its volume, the splitting of the two principle curvatures is even clearer, because κ_1 is mostly negative, reflecting the ring characteristics. Consequently, if the single principle curvatures are believed to reflect different structural features, then the 2D distributions can be split into the marginal κ_1- and κ_2-distributions, such that the ring and ligament characteristics are independently given. Though it is questionable in how far these two distributions reflect the "true" 3D ligament and ring diameter distributions, information about the mean ligament and ring sizes might be extracted from the inverse mean principle curvatures $\langle\kappa_1\rangle^{-1}$ and $\langle\kappa_2\rangle^{-1}$. Of course, the influence of the irregularities of the real rings, e.g. aspect ratios of the two main ring axes, have to be taken into account, which can be done by

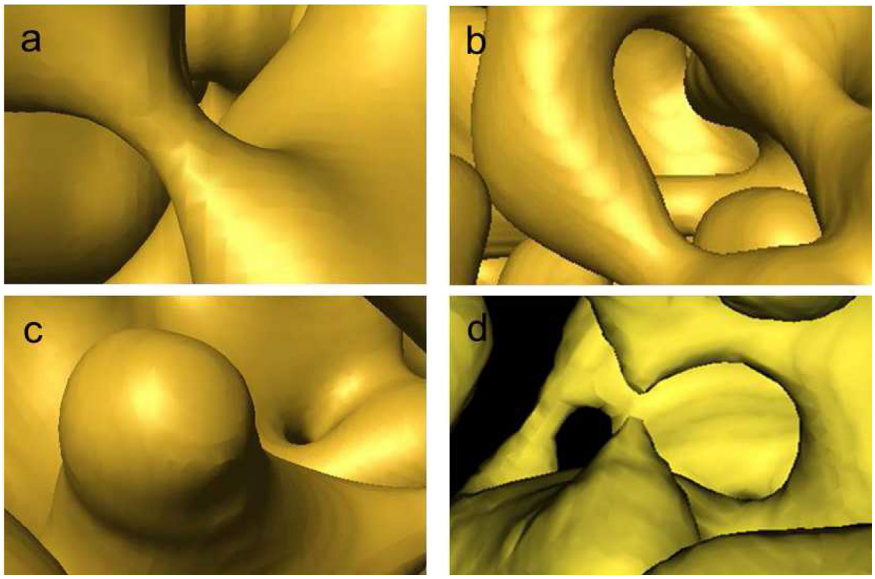

Fig. 1. Snapshots from a 3D FIB tomography reconstruction of a npg sample with mean ligament diameter of about 420 nm. The images reflect the typical structural features visible in all samples: (a) single ligaments that are connected to (b) irregular tori, which are sometimes opened exhibiting dead-end parts (c) and (d).