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Grain boundary formation through particle detachment during coarsening of nanoporous metals

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Grain boundary formation during coarsening of nanoporous gold (NPG) is investigated wherein a nanocrystalline structure can form by particles detaching and reattaching to the structure. MicroLaue and electron backscatter diffraction measurements demonstrate that an in-grain orientation spread develops as NPG is coarsened. The volume fraction of the NPG sample is near the limit of bicontinuity, at which simulations predict that a bicontinuous structure begins to fragment into independent particles during coarsening. Phase-field simulations of coarsening using a computationally generated structure with a volume fraction near the limit of bicontinuity are used to model particle detachment rates. This model is tested by using the measured NPG structure as an initial condition in the phase-field simulations. We predict that up to \(\sim 5\%\) of the NPG structure detaches as a deylloyed \(\text{Ag}_{25}\text{Au}_{75}\) sample is annealed at \(300 \degree\text{C}\) for 420 min. The quantity of volume detached is found to be highly dependent on the volume fraction and volume fraction homogeneity of the nanostructure. As the void phase in the experiments cannot support independent particles, they must fall and reattach to the structure, a process that results in the formation of new grain boundaries. This particle reattachment process, along with other classic processes, leads to the formation of grain boundaries during coarsening in nanoporous metals. The formation of grain boundaries can impact a variety of applications, including mechanical strengthening; thus, the consideration and understanding of particle detachment phenomena are essential when studying nanoporous metals.

Nanoporous metals are prototypical bicontinuous structures with a network of pores and ligaments. They are created by a number of metallic deylloying processes (1–6) allowing nearly any bulk metal to be transformed into a bicontinuous two-phase mixture of metal and void phase (7). These metals have a large interfacial area per volume enabling exciting applications in oxygen reduction (8), electromagnetic devices (9), battery electrodes (10), actuators (11), and catalysts (12). Given the large surface area per volume, nanoporous structures frequently undergo coarsening when annealed at elevated temperatures. Nanoporous metals coarsen by surface diffusion (13–15), a process where the characteristic length, \(L\), increases in time, \(t\), according to the power law \(L \sim t^{1/4}\) (16). Coarsening decreases the total interfacial energy of the structure, which greatly affects its material properties. For instance, coarsening is used to select the length scale in the structure, which alters the sizes of pores and ligaments (7, 17–20), ultimately impacting optical, chemical, and mechanical properties (21, 22), such as the elastic modulus (23). Nanoporous gold (NPG) often serves as a prototype for studying nanoporous metals (7). This paper investigates grain boundary formation as NPG coarsens and shows that the formation of a significant number of these boundaries is from particle detachment and subsequent reattachment.

Metallic samples prior to deylloying have grain sizes on the order of 10 to 100 \(\mu\text{m}\) (24). Deylloying and annealing of bulk nanoporous metals are typically believed to preserve the grain orientation of the original metallic sample. This was demonstrated through electron backscatter diffraction (EBSD) measurements (1) and scanning electron microscopy (SEM) images (25) for NPG. However, these techniques provide information only about the external surfaces, not the bulk structure. The formation of an in-grain orientation spread would demonstrate that nanoporous metals can develop nanocrystallinity. Some recent work has observed a developed nanocrystalline structure in nanoporous metallic samples after deylloying and annealing. Sun et al. (26) observed grain boundary formation during annealing of NPG but assumed that the varying orientations formed due to the small grain size in the original alloy. High-resolution

### Significance

Nanoporous metals are prototypical bicontinuous structures that have a large surface area and many applications. We demonstrate that an in-grain orientation spread develops during coarsening in nanoporous metals, leading to the formation of a nanocrystalline–nanoporous structure. The process of particles detaching and reattaching as the structure coarsens is identified as a mechanism of grain boundary formation. Coarsening the structure results in significant particle detachment with detachment rates that vary drastically with changes in the volume fraction and volume fraction inhomogeneities in the nanostructure. These results demonstrate that particle detachment must be understood to have full control of the nanocrystalline–nanoporous structure and improve material properties.


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transmission electron microscopy (HRTEM) (27) and X-ray diffraction (28) were used to identify a nanocrystalline structure in NPG postdealloying. Nanocrystalline structures have also been identified in nanoporous platinum (29) and copper (30) postdealloying. Theories of how these grain boundaries form during dealloying and annealing have not been fully investigated. Dealloyed NPG samples have been shown to contain lattice dislocations (24). It is possible that there are driving forces for dislocations to form low-angle grain boundaries in the structure when coarsening at elevated temperatures.

Coarsening of nanoporous metals is often compared to simulations that coarsen computationally generated (CG) bicontinuous structures, e.g., those formed in simulations of spinodal decomposition (31). Evolution of these structures has been studied with phase-field (31–35) and kinetic Monte Carlo (KMC) (36–38) methods. In certain volume fraction ranges, particle detachment is observed during simulations of coarsening, altering the topology of the structure. This breaking of ligaments in the structure is due to a Rayleigh–Plateau instability (38), the same mechanism causing ligament pinch-off (a ligament breaking in one place) during coarsening of nanoporous metals (13, 39, 40). The topology of an object in three dimensions (3D) is quantified by the Betti numbers: \( \beta_0 \), the number of independent objects; \( \beta_1 \), the number of handles (genus); and \( \beta_2 \), the number of enclosed voids in the structure. Assuming no enclosed voids, the Euler characteristic of a 3D structure is given by \( \chi = \beta_0 - \beta_1 + \beta_2 \) (41). When a particle detaches from the microstructure, \( \beta_0 \) increases by 1. As particles detach from the end of ligaments, \( \beta_1 \) remains the same. If a ligament breaks in one place (a process that is referred to as a ligament pinch-off), \( \beta_1 \) decreases by 1 and \( \beta_0 \) remains the same. Here we define particle detachment as the process of creating small (in size when compared to the main bicontinuous structure) isolated bodies.

Simulations have demonstrated that the topology of a structure has a strong dependence on the minority phase volume fraction, \( \phi \), and can vary drastically within a small range of \( \phi \) (34, 38). Using KMC, Li et al. (38) investigated coarsening via surface diffusion of structures initialized as leveled Gaussian random fields with \( \phi \) of 22, 25, and 37% and increments of 5% from 30 to 50%. By investigating the topology, they found that structures with a \( \phi \) lower than 30% are evolving toward a particle-dominated system, while structures with a \( \phi \) higher than 40% are evolving as a fully connected system (\( \beta_0 = 1 \)). As the topological changes are related to how particles detach, we establish two regimes of topological evolution. In the particle-dominated regime (low \( \phi \)), the structure evolves toward a state where the number of handles (\( \beta_1 \)) is either zero or low compared to the number of particles (\( \beta_0 \)). In the ligament-dominated regime (high \( \phi \)), the structure evolves toward a state where there is a low number of particles (\( \beta_0 \)) compared to the number of handles (\( \beta_1 \)). In between these regimes (intermediate \( \phi \)), the structure evolves to a state with an intermediate number of particles and handles, and any transition to the particle-dominated regime or the ligament-dominated regime occurs too slowly to be feasibly observed. We define this approximate boundary between regimes as the limit of bicontinuity, as the structure begins to break up while still maintaining a high degree of connectivity. Due to the approximate nature of this definition, a range of \( \phi \) (e.g., 30 to 35%) may be considered to be “at” the limit of bicontinuity. We are most likely to observe particle detachment in structures with a \( \phi \) at the limit of bicontinuity, where \( \beta_0 \) might be stable or increasing throughout coarsening (signifying particle detachment) while a majority of the solid volume is contained in the main bicontinuous structure. Simulations with a \( \phi \) in the range 30 to 35% have not yet been extensively studied despite the many coarsening experiments of nanoporous metals that are within this range.

Experiments commonly study NPG samples with a \( \phi \) between 25 and 36% postdealloying and report fully connected bicontinuous structures (17, 19, 20, 42–47). In this case, the minority phase volume fraction, \( \phi \), corresponds to the gold volume fraction. These \( \phi \) values are just below or at the limit of bicontinuity predicted by simulation. However, the stability of the structures during coarsening is not always investigated, especially at lower \( \phi \). Detachment of particles from the bicontinuous structure can be kinetically inhibited due to slow coarsening rates. However, experiments that coarsen NPG for sufficiently long times such that the mean ligament diameter increased by a factor of 16 have still reported fully connected bicontinuous structures (19, 20). The bicontinuity does not necessarily indicate that disconnections do not occur during the evolution; since the vapor phase cannot support independent particles, any particles that detach would presumably fall under their own weight and reattach elsewhere, leading to a fully connected bicontinuous structure and the formation of grain boundaries.

As the \( \phi \) of many NPG samples is at the limit of bicontinuity, we show that particles detach as NPG coarsens, and we hypothesize that the reattachment of particles leads to the formation of many of the grain boundaries that are observed in the microstructure. The results of microLaue and EBSD measurements of coarsened NPG samples with \( \phi \) at the limit of bicontinuity identify large grain orientation spreads that develop during coarsening. Phase-field simulations of coarsening of a CG bicontinuous structure with a \( \phi \) at the limit of bicontinuity are conducted to investigate how particle detachment occurs in this regime. Subsequently, the morphology of the CG and NPG structures is characterized to search for evidence of particle reattachment phenomena. A coarsened NPG structure is then used as an initial condition in a phase-field simulation to observe how particle detachment would occur if the sample had continued to coarsen. These calculations that begin with the experimentally measured structure have identified the critical role of volume fraction homogeneity in particle detachment phenomena.

**Results**

In this section, experimental NPG and CG structures are studied to understand grain boundary formation and particle detachment during coarsening. Four experimental NPG samples are studied. All of the samples start as a \( \text{Ag}_{57.5}\text{Au}_{42.5} \) alloy and are dealloyed by the same procedure, outlined in Methods. The coarsening process results in fully connected bicontinuous structures with a mean ligament diameter, \( D_{\text{lig}} \), of about 25 nm. One of the samples is not processed further and is referred to as the as-dealloyed NPG sample. Three of the samples are annealed for 420 min at 300 °C to coarsen the structure, resulting in fully connected bicontinuous structures with a \( D_{\text{lig}} \) of about 400 nm. These samples are referred to as the coarsened NPG samples. The \( \phi \) of the as-dealloyed NPG sample is \( \sim 30\% \) and the \( \phi \) of the coarsened NPG samples is \( \sim 33\% \). Thus, some volume shrinkage occurred during both dealloying and annealing and the implications of this process are analyzed in Discussion. The NPG samples have a gold phase and void phase.

The CG structure is obtained from a phase-field simulation. A phase-field simulation of coarsening by surface diffusion is initialized such that the order parameter takes a constant value of 0.32 plus random noise sampled within ±0.04. After phase separation, a bicontinuous structure with a \( \phi \) of 32% emerges with two phases based on the values of the order parameter. Phase \( \phi \) (order parameter = 1), the minority phase, corresponds to the gold phase and phase \( \beta \) (order parameter = 0) corresponds to the void phase in the experiments.

**In-Grain Orientation Spread in Coarsened NPG.** Prior to dealloying, the \( \text{Ag}_{57.5}\text{Au}_{42.5} \) samples contained multiple grains with a mean grain size of 50 μm. The original grains in the \( \text{Ag}_{57.5}\text{Au}_{42.5} \) alloy are referred to as parent grains. Grains that formed within
one of the parent grains during dealloying and coarsening are referred to as sibling grains. A set of sibling grains was identified in coarsened NPG through microLaue and EBSD measurements. The microLaue diffraction experiments, detailed in Methods, were completed at the European Synchrotron Radiation Facility (ESRF) on the as-dealloyed NPG sample and one of the coarsened NPG samples. The microLaue measurements of the as-dealloyed NPG sample were taken on a small piece of the bulk as-dealloyed NPG sample that was generated by taking advantage of the macroscopic brittleness of bulk NPG. The measurements from the microLaue experiment of the as-dealloyed sample were used to construct a (001) pole figure, shown in SI Appendix, Fig. S1A. One parent grain was identified for analysis, as described in SI Appendix. Uncorrelated misorientation angles, defined as the differences between orientations of all pairs of orientations, were calculated for the orientations of the sibling grains within the parent grain identified in the pole figure. A histogram of the uncorrelated misorientation angles in the identified parent grain for the as-dealloyed sample is shown in Fig. 1A, which indicates that any misorientations that form during the dealloying process are very small (on the order of $1^\circ$).

For the microLaue measurements of the coarsened NPG sample, a rectangular micropillar (size $30 \times 13 \times 13$ µm$^3$) of the coarsened NPG sample was prepared by focused ion beam (FIB). The micropillar has dimensions that are smaller than the average parent grain size. The micropillar could potentially be taken across grain boundaries and thus may contain two or more parent grains; indeed the (001) pole figure shown in SI Appendix, Fig. S1B shows that there are two parent grains within the sample volume, but only one of the parent grains was selected for analysis. The FIB preparation does not induce noticeable orientation artifacts in the microstructure, as discussed in SI Appendix. The same analysis method was used on this sample as on the as-dealloyed sample, and uncorrelated misorientation angles were calculated for in-grain orientations in one parent grain identified in the (001) pole figure in SI Appendix, Fig. S1B. Fig. 1B shows the histogram of the uncorrelated misorientation angles in this parent grain. By comparing Fig. 1A and B, it is evident that annealing of the sample leads to a significant increase in misorientations as seen in the histograms; specifically, the average value of the misorientations increases from $0.3^\circ$ to $8.4^\circ$. The mechanism for the development of misorientations on the order of $5^\circ$ is partially attributed to existing dislocations in the structure that are driven to form low-angle sibling grain boundaries, as discussed in Discussion. In addition to the primary misorientation distribution that developed upon annealing, the sample also contained sibling grains with much larger misorientations (greater than $25^\circ$), as shown in Fig. 1B, Inset. There are even larger misorientations in the structure that cannot easily be assigned to the sibling grains identified in the (001) pole figure due to the limited spatial resolution owing to the beam size and the associated volume probed at each scan point. Thus, the micro-Laue measurements presented in Fig. 1B underestimate the orientation spread. Nevertheless, the histograms of uncorrelated misorientation angles obtained from microLaue measurements provide clear evidence that an in-grain orientation spread develops throughout the structure during annealing and that the grain orientation of the original metallic sample is not preserved under these coarsening conditions.

To obtain the orientation data at higher resolution, EBSD measurements were taken on the second of the three coarsened NPG samples, as described in Methods. A 3D reconstruction of 2D inverse pole figure maps from EBSD measurements is shown in Fig. 2A and the standard EBSD orientation color key is shown in Fig. 2B. The 3D reconstruction demonstrates that this NPG sample contains multiple sibling grains with different orientations within an original parent grain that had an approximate orientation noted by a star on the color key (Fig. 2B), as determined by the average color of the ligaments (not including the green grain, which has a significantly different orientation). Fig. 2A shows that the sample has low- and high-angle sibling grain boundaries. Fig. 2A contains a green sibling grain that is a significantly different color, and thus a different orientation, from its surroundings. This sibling grain is entirely enclosed in the displayed $3.13 \times 3.13 \times 0.75$-µm$^3$ region of the microstructure. As shown in Fig. 2C–E, the sibling grain is connected to other ligaments toward the bottom of the region and the top of the object is not connected to other ligaments in the microstructure. The green sibling grain is oriented $35^\circ$ differently from the surrounding ligaments; such grains were not detectable in the microLaue measurements due to the resolution of the method that is limited by the beam size.

**Particle Detachment in the CG Microstructure.** Phase-field simulations of a CG structure with a $\alpha$ of 32% coarsened by surface diffusion are studied to understand how particle detachment occurs at the limit of bicontinuity. Further details of the simulations are in Methods. A unit of simulation length was scaled to a length representing a nanoporous gold system. To ensure that the product of the average mean curvature and interfacial thickness is much less than one, one simulation length in
computation coordinates is set to 3.1 nm. A structure coarsening by surface diffusion evolves as \( L \sim t^{1/4} \). In this case, \( S_V^{-1} \), the domain volume divided by interfacial area, is used as the characteristic length. Data were analyzed after an initial period to allow for phase separation and the formation of a bicontinuous microstructure. Thus, the structure was characterized as \( S_V^{-1} \) changed from 62.6 to 148.7 nm, a 237% change in characteristic length. The scaled morphology and topology vary slowly throughout the simulation, and thus the evolution is not strictly self-similar. A thorough investigation of the self-similarity of the structure is found in ref. 49, chap. 5.

As the structure coarsens, particle detachment is observed, and 65 independent particles are present when \( S_V^{-1} = 62.6 \) nm. In these simulations, a particle can be reincorporated into the main bicontinuous structure (the largest region of phase \( \alpha \)) if evolution brings their interfaces into contact or close proximity. Thus, particles are created and destroyed during the simulation and the number of independent particles fluctuates between 59 and 71. The detached particles continue to coarsen and are primarily spherical in shape, but they cannot disappear due to diffusion since there is no bulk diffusion. This is in contrast to the situation in NPG, where, if particles detach during coarsening, they fall and are immediately incorporated into the structure. As the reattachment mechanisms are different, we investigate the particles that are created as \( S_V^{-1} \) changes from 62.6 to 148.7 nm. In this regime, 98 new particles detach from the main region of phase \( \alpha \). Details regarding the detection of newly detached particles can be found in SI Appendix. The cumulative volume of newly detached particles as a fraction of the total volume of phase \( \alpha \), \( \phi^d_\alpha \), is plotted vs. \( S_V^{-1} \) in Fig. 3. The volume fraction of detached particles increases proportionally to the increase in \( S_V^{-1} \) for much of the simulation.

To predict the number of particles that detach at the limit of bicontinuity, a model for particle detachment is created and validated against the simulation results of the CG structure. The volume of phase \( \alpha \) detached is \( V^d_\alpha = \phi^d_\alpha V_\alpha \), where \( V_\alpha \) is the volume of the phase \( \alpha \) (32% of the volume of the computational domain). Based on the trend observed in Fig. 3, we assume that

![Fig. 2](image_url) (A-E) A 3D reconstruction of 2D (001) inverse pole figure maps from EBSD measurements (A); standard EBSD orientation color key (48), in which a star denotes the approximate orientation of the original parent grain (B); and 2D slices of A at (C) \( z = 0.20 \mu m \), (D) \( z = 0.48 \mu m \), and (E) \( z = 0.75 \mu m \) each of size \( 3.13 \times 3.13 \mu m^2 \).

![Fig. 3](image_url) The fraction of the volume of phase \( \alpha \) that has detached as independent particles since \( S_V^{-1} = 62.6 \) nm is plotted against \( S_V^{-1} \).
for $dV^2$ and $(V_p)$, $dN = R_0 dS_y^{-1}\frac{1}{CS_y^{-3}}$ and the number of particles detached as $S_y^{-1}$ changes from $S_y^{-1}\text{, initial}$ to $S_y^{-1}\text{, final}$ is

$$N = \int \frac{R_0 dS_y^{-1}}{CS_y^{-3}} = \frac{R_0}{C} \left[ \frac{1}{25y^{-2}} \right]_{S_y^{-1}\text{, initial}}^{S_y^{-1}\text{, final}}.$$  \[1\]

Eq. 1 predicts that 98 particles detach as $S_y^{-1}$ changes from 62.6 to 148.7 nm, in agreement with the number of particles detached in the simulation. However, the standard deviation in $C$ is large: $C = 2.6 \pm 1.8$, where the latter value indicates the standard deviation. Utilizing the upper (4.4) and lower (0.8) bounds on $C$ predicts that between 57 and 324 particles detach.

**Particle Detachment in NPG.** To investigate the possibility of particle detachment in NPG, the morphology of the remaining coarsened NPG sample is compared to that of the CG structure and examined for signs of particle detachment. Then, the experimentally measured NPG structure is used as an initial condition in a phase-field simulation to observe particle detachment and to estimate the volume and number of particles detached in the experimental study based on the model developed in the prior section (Eq. 1). The fabrication and some microstructural characterization of the NPG sample in this section were previously reported in refs. 19, 20, and 50. A 3D reconstruction of this coarsened NPG sample was acquired as described in Methods. The coarsened NPG sample is fully connected with $(D)_{\text{CE}} = 421$ nm, while $(D)_{\text{CE}} = 27$ nm in the as-dealloyed state. The 3D reconstruction of the coarsened sample was divided into four representative regions (identified and labeled by ref. 19), each of size $(6 \mu m)^3$, with a gold phase and a void phase. The average $\phi$ of the four representative regions is 33.2%, at the limit of bicontinuity. As discussed in ref. 20, due to slight changes in morphology during coarsening, self-similar evolution of the NPG structure cannot be strictly confirmed. However, in some applications these changes may be minimal enough for the evolution to be seen as “sufficiently” self-similar.

**Microstructure morphology.** As the $\phi$ of the NPG sample is at the limit of bicontinuity, it is expected that particles have detached during coarsening. However, the NPG structure is fully connected and we assume that any detached particles have most likely reattached to the structure at a different orientation, creating a sibling grain boundary. The morphologies of the coarsened NPG and CG (last recorded time step) structures are compared via the mean curvature ($H$) and the spatial distribution of $H$ via its autocorrelation to identify differences due to particle detachment phenomena. The methodology of the characterization techniques is presented in Methods. To remove the dependence on length scale, we nondimensionalize all results by a function of $S_y^{-1}$. For the NPG structure $S_y^{-1} = 350.8$ nm and for the CG structure $S_y^{-1} = 148.7$ nm (last recorded time step).

The interfacial mean curvature is an important measure of the morphology of the structure, as it determines the chemical potential that drives mass flow during coarsening. The mean curvature is given by $H = (\kappa_1 + \kappa_2)/2$, where $\kappa_1$ and $\kappa_2$ are the principal curvatures. As a complement, we specify that a convex shape made up of gold phase (e.g., a spherical particle) will have positive mean curvature. The average scaled mean curvatures, $(H/S_y)$, are 0.66 and 0.67 with standard deviations in scaled mean curvature, $\sigma_{H/S_y}$, of 0.78 and 0.48 for the NPG and CG structures, respectively. Although $(H/S_y)$ is very similar between the two structures, they have very different mean curvature distributions. Fig. 4 shows $(8S_y^{-1})^3$ regions of the interface colored by the scaled mean curvature for one of the representative regions of the NPG structure (Fig. 4A) and the CG structure (Fig. 4B). The $(8S_y^{-1})^3$ region represents 10% of one of the representative regions of the NPG structure and 6% of the computational domain of the CG structure. Due to its larger $\sigma_{H/S_y}$, the distribution of mean curvatures is wider for NPG, as shown by the larger variation in color across the structure. The mean curvature of the CG structure varies gradually along the interface. The NPG structure has many regions with sharp changes from high negative mean curvature to high positive mean curvature located very close to each other, as shown by the black circled region in Fig. 4A. These disk-like bands of highly negative mean curvature are very prevalent in the experimentally measured NPG structure. It is possible that some of these bands represent a grain boundary formed from a detached particle falling and reattaching at a different orientation.

To quantify the prevalence of sharp changes in mean curvature, the spatial distribution of the mean curvature is investigated over the entire domain of the NPG and CG structures. Specifically, we follow refs. 51–53 in determining the two-point Pearson autocorrelation of the interfacial mean curvature, the $H$ autocorrelation, which calculates how correlated the mean curvature is in space. The $H$ autocorrelation ranges from $-1$ to $1$, where $-1$ is perfect anticorrelation, 0 is no correlation, and 1 is perfect...
correlation. The results are radially averaged as the structures are isotropic, which collapses the 3D dataset into a one-dimensional representation. The radius, \( r \), of the averaging sphere (or, equivalently, the distance between two patches of interface) is scaled by the length \( L_p = 4S_{V}^{-1}(\phi - \phi^{2}) \). This length scale incorporates an effect of volume fraction that is intrinsic to the Pearson autocorrelation while retaining an explicit relationship to \( S_{V}^{-1} \) (35, 54).

Fig. 5 shows the \( H \) autocorrelation of the NPG and CG structures. The \( H \) autocorrelation for NPG is an average of the curves for the four representative regions. For each structure, after a distance of about \( r = 2.8L_p \), the mean curvatures in the structure are not strongly correlated as the amplitude of the \( H \) autocorrelation is small. A large region of anticorrelation begins at \( r = 2L_p \) and extends to about \( r = 3.6L_p \) for both structures. At larger values of \( r/L_p \ (>2) \), the \( H \) autocorrelation of the structures is quite similar, having the same length of the anticorrelation band and a similar shape, with slightly higher correlation around \( r > 2.5L_p \) in the NPG structure. However, at small values of \( r/L_p \ (<2) \) the \( H \) autocorrelation of the NPG structure is very different from that of the CG structure. The mean curvatures of the NPG structure are significantly less correlated than the mean curvatures of the CG structure, which is seen by the \( H \) autocorrelation for the NPG structure having significantly lower correlation at the same value of \( r/L_p \). This is explained by examining the structures colored by the mean curvature values, shown in Fig. 4. Fig. 4B shows that in the CG structure the mean curvature varies slowly with position across the structure; thus, it is very likely that the mean curvatures would be similar at small separation distances. This is not the case for the NPG structure, shown in Fig. 4A, since the curvature changes drastically even at short distances. This difference in morphology explains why the \( H \) autocorrelation for the NPG structure has a significantly lower value at small values of \( r/L_p \) compared to the CG case. The \( H \) autocorrelations themselves demonstrate that the difference in morphology (i.e., bands of highly negative mean curvature in the NPG case but not the CG case) exists throughout the microstructure, not just in the portion shown in Fig. 4A.

**Phase-field simulations and estimating particle detachment.** The morphological analysis of the NPG microstructure provides evidence of particle detachment and reattachment averaged over the entire structure. To address the particle detachment process in depth, the experimentally measured NPG microstructure coarsened for 420 min was used as the initial condition in a phase-field simulation of coarsening by surface diffusion. While this technique does not allow us to detect particles that previously detached, it does give insight into the particles that would detach if it was possible to observe the particle detachment process experimentally. The microstructure was evolved until \( \langle D \rangle_{lig} \) changed by 10% (from 421 to 463 nm). A simulation was completed for each of the four representative regions and particle detachment was observed. Further details of the simulations are in Methods and details regarding particle identification are in SI Appendix. Table 1 reports the number of detached particles and the gold volume detached as a fraction of the total gold volume \( \phi_{g} \) in the simulations of each representative region (RR) and the \( \phi \) for each region is indicated. On average, \( N = 3 \pm 2 \) and \( \phi_{g} = (0.3 \pm 0.2) \%. \) This clearly establishes that particles can detach from NPG during the experiment.

Due to the reduced sizes of the microstructures of these sub-volumes RR1 to 4, these simulations could be conducted only for a limited time before the boundary effects and reduced statistics would become an issue. Therefore, their simulation time was set to examine the process of particle detachment, rather than to observe global detachment trends or to directly calculate the total number of particles detached over the entire coarsening process in the NPG sample. In the phase-field simulations that coarsened the CG microstructure, the characteristic length increased by 237%, a change larger than the 10% increase in characteristic length in the simulations of the experimentally measured NPG structure. Thus, the simulations of the CG structure allowed us to create a model for how particle detachment occurs in structures with a \( \phi \) at the limit of bicontinuity. From the simulation results using the experimentally measured NPG structure, we predict the volume of gold and the number of particles that detach in the annealing experiment of NPG as \( \langle D \rangle_{lig} \) changes from 27 to 421 nm. The mean ligament diameter, \( \langle D \rangle_{lig} \), is approximately related to \( S_{V}^{-1} \) by a constant \( a \); i.e., \( \langle D \rangle_{lig} \approx aS_{V}^{-1} \) for the NPG microstructure (50), where \( a = 1.2 \).

The application of the developed model to the NPG experiment relies on the assumptions that 1) the gold volume detached in the experiment is proportional to changes in \( S_{V}^{-1} \) and 2) the mean particle size is \( \langle V_{p} \rangle = CS_{V}^{-3} \), where \( C = 2.6 \pm 1.8 \), which was determined from the mean volume of particles detached in the simulation of the CG structure as described earlier. The volume detachment constant is defined as \( R_g = dV_g/dS_{V}^{-1} \), where \( dV_g \) is the volume of gold detached and \( dS_{V}^{-1} \) is the change in \( S_{V}^{-1} \). The volume of gold detached \( V_d = \phi_k V_{g0} \), where \( V_{g0} \) is the total volume of gold. We assume that \( R_g \) is constant and thus the volume detachment constants observed in the simulations using experimentally measured NPG data are equivalent to the volume detachment constants in the experiment. The volume detachment constant \( R_g \) is thus calculated utilizing the volume information (found in Table 1) and \( S_{V}^{-1} \) change from the simulations using the experimentally measured NPG structure and reported in Table 2. The volume detachment constant ranges from \( R_g = (2.9 \pm 10.2) \cdot 10^{9} \) nm\(^2\) and is on the same order of magnitude as the volume detachment constant in the simulations of the CG structure (\( R_g = (2.4 \pm 10^{9}) \) nm\(^2\)). Due to the short simulation time, \( R_g \) was estimated from the detachment of one to five particles, depending on the RR. However, even with these sparse statistics, we choose to estimate the number of detached particles utilizing the \( R_g \) for each RR (instead of \( R_{\text{det}} \)) to capture effects of volume fraction inhomogeneities in the nanostructure, as discussed below.

The volume detachment constant, along with the change in \( S_{V}^{-1} \) from the as-dealloyed to coarsened state (22.5 to 350.8 nm), is then used to predict the volume fraction detached in the experiment in each RR. By replacing \( R_g \) in Eq. 1 with \( R_{\text{det}} \) along with the values of \( S_{V}^{-1,1} \) and \( S_{V}^{-1,3} \) for the entire duration of the experiment, it is possible to estimate the number of particles detached in the experiment in each RR. A lower and upper bound on the

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Fig. 5. \( H \) autocorrelation for NPG (blue) and CG (orange) structures.
Table 1. Number of detached particles (N) and volume fraction of gold detached (\(\phi_g\)) in the simulation for each RR, reported with \(\phi\).  

<table>
<thead>
<tr>
<th>RR ((\phi), %)</th>
<th>(N)</th>
<th>(\phi_g), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (33.6)</td>
<td>1</td>
<td>0.14</td>
</tr>
<tr>
<td>2 (33.1)</td>
<td>3</td>
<td>0.19</td>
</tr>
<tr>
<td>3 (32.9)</td>
<td>5</td>
<td>0.50</td>
</tr>
<tr>
<td>4 (33.3)</td>
<td>4</td>
<td>0.46</td>
</tr>
<tr>
<td>Average ((\pm)(\sigma))</td>
<td>3 ± 2</td>
<td>(0.3 ± 0.2)</td>
</tr>
</tbody>
</table>

The average is reported with the standard deviation, \(\sigma\).

number of particles detached during the experiment, \(N_1\) and \(N_\infty\), respectively, is calculated based on the standard deviation in \(C\). Table 2 reports the predicted \(R_\infty, \phi_g^\infty, N_1\), and \(N_\infty\) for each representative region, shown with the \(\phi\) of each RR. Using the lowest and highest values as bounds, we estimate between 1.3 and 4.7% by volume of the microstructure detached, resulting in the formation of \(\approx\) 650 to 13,500 particles in a (6-\(\mu\)m\(^3\)) region of a NPG structure when coarsened from its dealloyed state for 420 min at 300 °C.

The \(\phi\) of the representative regions, reported in Tables 1 and 2, is the \(\phi\) of the entire (6-\(\mu\)m\(^3\)) domain. The \(\phi\) for domain sizes of (6 \(\mu\)m\(^3\)) or larger was shown to converge to the same value (19). However, the \(\phi\) is not homogeneous throughout the domain, but rather it contains subvolumes within which the \(\phi\) can vary significantly from the average value. Ref. 19 calculates the \(\phi\) in the representative regions as a function of cube size. The authors find regional variations in \(\phi\) of 1.4, 5.1, 7.9, and 6.7% for regions 1 to 4, respectively, when compared to the \(\phi\) of the entire (6-\(\mu\)m\(^3\)) domain. Our phase-field calculations find that in region 1, the \(\phi\) has the smallest variation leading to the lowest \(R_\infty\) while region 3 has the highest \(R_\infty\) and largest variation in \(\phi\), reaching a \(\phi\) as low as 25% in a (1.5-\(\mu\)m\(^3\)) portion of the domain. Three of the detached particles in the simulations using region 3 as the initial condition were contained in this region of low \(\phi\), shown in SI Appendix, Fig. S2. It is expected that the volume detachment constant decreases as the \(\phi\) increases. This is confirmed when observing the RR with the lowest and highest \(\phi\), regions 3 and 1, respectively. However, the volume detachment constant and \(\phi\) are higher in region 4 (\(\phi = 33.3\)% when compared to region 2 (\(\phi = 33.1\)%). This is because there is a larger regional variation in \(\phi\) (6.7 and 5.1% for regions 4 and 2, respectively).

Discussion

Phase-field simulations of NPG and a CG structure established that particles detach during coarsening of nanoporous metals, and microLaue and EBSD results demonstrate that in-grain orientations develop during coarsening. The existence of sharp changes in mean curvature throughout the NPG structure confirmed by the \(H\) autocorrelations presented in Microstructure morphology provides additional evidence of particle reattachment. While we find that a significant number of particles can detach during the simulations using the experimental NPG structure as the initial condition, the volume detachment constant during experimental annealing of NPG is approximated using a model developed for particle detachment during simulated coarsening of a CG structure with a volume fraction at the limit of bicontinuity. We find that the volume detachment constants between the NPG and CG structures are on the same order of magnitude, which indicates some level of similarity between the detachment processes in the different microstructures: The volume detachment constant is \(R_\infty = 2.4 \cdot 10^9\ \text{nm}^2\) for the CG structure and ranges from \(R_\infty = (2.9 - 10.2) \cdot 10^9\ \text{nm}^2\) for simulated evolution of the NPG structure. Since the \(\phi\) is 32% in the CG structure and ranges between 32.9 and 33.6% for the representative regions of the NPG structure, it might be expected that the volume detachment constant would be higher for the CG structure, as 32% is closer to the lower end of the range assumed for the limit of bicontinuity. However, this prediction does not account for inhomogeneities in \(\phi\) across the NPG structure. While the CG structure has a \(\phi\) that does not significantly vary in small volumes and the full domain, this is not the case in the NPG structure where the \(\phi\) in subvolumes was shown to significantly vary from the \(\phi\) of the full (6-\(\mu\)m\(^3\)) domain. We find that the volume detachment constant increases with increased variation in regional \(\phi\). The simulations of region 3 have the largest volume detachment constant and we observed a 7.9% variation in regional \(\phi\) when compared to the \(\phi\) of the entire (6-\(\mu\)m\(^3\)) domain.

In addition, the impact of volume contraction during dealloying and coarsening needs to be considered. Prior to dealloying, the alloy composition of the sample was \(\text{Ag}_{75}\text{Au}_{25}\). After dealloying, the average \(\phi\) of the NPG sample was 29.6%, reported in ref. 19. This indicates that the sample volume contracted during dealloying. Ref. 55 demonstrates that volume shrinkage during dealloying is due to bulk transport via plastic flow, a process that requires the nucleation of dislocations. This was previously suggested by the computational work of ref. 40. The average \(\phi\) of the NPG sample annealed for 420 min was 33.2%, indicating that the sample volume contracted during coarsening. As the sample coarsens, it is likely that the motion of dislocations leads to the formation of low-angle grain boundaries in the structure, as seen in Fig. 1B. The continuing volume contraction during coarsening may be caused by the formation of low-angle boundaries and continued plastic deformation (40). Since the as-dealloyed value of \(\phi = 29.6\)% is at the low end of the range assumed for the limit of bicontinuity, the volume detachment constant might be higher than predicted at early times, and the number of particles detached given in Table 2 may be an underestimate. Nevertheless, these results show that significant particle detachment is likely occurring as NPG samples with a \(\phi\) at the limit of bicontinuity coarsen via isothermal annealing. The extent of the initial volume contraction, and thus the resulting \(\phi\) of the as-dealloyed sample, is dependent on the dealloying conditions (24). Since two samples with the same initial AgAu composition might have a different \(\phi\) if they are dealloyed with different methods, particle detachment rates may be dependent on how a sample is dealloyed.

Evidence of reattached particles is present in prior work on the same NPG samples (19, 20) if one assumes that variations in \(\phi\) between regions can be both a cause and a product of increased particle detachment. The NPG sample utilized in the phase-field simulation is part of a larger experimental study in which four different as-dealloyed samples, prepared in the same way, were annealed for 2, 30, 240, and 420 min at 300 °C. On average, the regional variation in \(\phi\) within a given NPG structure was found to increase with increased annealing time (50). In the as-dealloyed sample the regional \(\phi\) ranges from 28 to 34%. The variation in regional \(\phi\) increases during annealing, and in the sample annealed for 420 min the regional \(\phi\) ranges from 25 to 42%. The implications of this particle detachment process are that it would be self-catalyzing. When a particle detaches, it

Table 2. Predicted volume detachment constant \((R_\infty)\), volume fraction of gold detached \((\phi_g^\infty)\), and a lower \(N_1\) and upper \(N_\infty\) bound on the number of particles detached in the experiment for each RR, reported with \(\phi\).  

<table>
<thead>
<tr>
<th>RR ((\phi), %)</th>
<th>(R_\infty(10^9\ \text{nm}^2))</th>
<th>(\phi_g^\infty), %</th>
<th>(N_1)</th>
<th>(N_\infty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (33.6)</td>
<td>2.9</td>
<td>1.3</td>
<td>653</td>
<td>3,741</td>
</tr>
<tr>
<td>2 (33.1)</td>
<td>3.9</td>
<td>1.8</td>
<td>884</td>
<td>5,065</td>
</tr>
<tr>
<td>3 (32.9)</td>
<td>10.2</td>
<td>4.7</td>
<td>2,360</td>
<td>13,516</td>
</tr>
<tr>
<td>4 (33.3)</td>
<td>9.3</td>
<td>4.3</td>
<td>1,507</td>
<td>8,630</td>
</tr>
</tbody>
</table>
creates a region of low $\phi$, and when it reattaches, it creates a region with a higher $\phi$, which could accelerate the particle detachment process. Thus, a slight inhomogeneity in $\phi$ in a dealloyed sample, with a $\phi$ at the limit of bicontinuity, has the potential to create an even larger variation in regional $\phi$ as the structure is annealed.

Particle reattachment can create both low- and high-angle sibling grain boundaries, depending upon how a particle falls and rolls post-detachment. The microLaue results demonstrate that a large in-grain orientation spread develops during annealing. The 3D EBSD reconstruction also shows low- and high-angle sibling grain boundaries in the NPG sample. The green sibling grain in Fig. 2 appears to be a prime example of a particle that has reattached at a significantly different orientation from its surroundings. Since it is clear that a significant number of sibling boundaries can be created during coarsening and there is strong evidence that sibling boundaries exist, it is necessary to consider whether sibling grain boundaries created at some early time via particle detachment will remain in the structure at a later time during coarsening. Unlike classic grain growth in bulk crystals, in this case the grain boundaries will contact the gold surface and develop grain boundary grooves. These grooves can stabilize the grain structure by slowing grain growth (56). For example, if a grain boundary stretches from one side of a ligament to the other, it can form a bamboo-like structure with very flat grains that are extremely stable with respect to coarsening. There are multiple examples of such grain boundaries, e.g., the green and purple grains in Fig. 2. It is possible that reattached particles may rotate to reduce grain boundary energy (57–60). In some cases, low-angle grain boundaries may disappear by these rotations (61). Thus, the grain boundaries present in the microstructure at any given time that are caused by particle detachment consist of all such boundaries that have not disappeared through particle rotation. While it is clear that stable high-angle sibling grain boundaries form from particle reattachment, the micro-Laue and EBSD results show that there are significant amounts of low-angle sibling grain boundaries in the structure. In addition to recently reattached particles forming low-angle sibling boundaries, it is possible that dislocations in the dealloyed structure are driven to form low-angle sibling grain boundaries as the structure coarsens at elevated temperatures. The sibling grains that are observed experimentally are thus those that form due to the particle reattachment process and, perhaps, low-angle sibling grain boundaries that may form through other means, such dislocation motion.

Conclusion

Annealed nanoporous metals are commonly thought to have the same grain orientation that the original metallic sample had prior to dealloying. By contrast, we find the following:

- In-grain orientation spreads that develop during coarsening of nanoporous gold appear as low- and high-angle sibling grain boundaries in the structure.
- Particle detachment and reattachment are identified as a mechanism that leads to the development of a polycrystalline structure. We find that up to 5% of the structure detaches as a nanoporous gold sample dealloyed from a $\mathrm{Ag}_{87.5}\mathrm{Au}_{12.5}$ alloy that coarsens for 420 min at 300 °C.
- The particle detachment process depends strongly on the volume fraction of gold. As the gold volume fraction is reduced, a larger quantity of the structure will detach, increasing structural effects caused by particle detachment phenomena.
- The volume detachment constant is highly dependent on the homogeneity of the nanostructure. When a particle detaches, it creates a region of lower gold volume fraction and when it reattaches, a region of higher volume fraction is created. Thus, any slight structural inhomogeneity present in a dealloyed sample will amplify as the sample coarsens, raising particle detachment rates.

Overall, this study identifies particle detachment and reattachment as a mechanism for grain boundary formation and demonstrates the important role the gold volume fraction has in controlling particle detachment phenomena and grain boundary formation during the coarsening of nanoporous metals.

Methods

Experimental Methods. Four NPG samples were made by applying electrochemical dealloying to a millimeter-sized polycrystalline $\mathrm{Ag}_{75}\mathrm{Au}_{25}$ alloy with a mean grain size of 50 µm. Each of the four samples has approximate dimensions of $1 \times 1 \times 1$ mm$^3$. The as-dealloyed NPG samples were fabricated by the authors of ref. 62, who use the sample preparation technique described in detail in the supplementary material of ref. 63 with a potential of 750 mV versus $\mathrm{Ag}/\mathrm{AgCl}$ reference electrode, to produce a bicontinuous structure with an initial mean ligament diameter of approximately 25 nm. Three of the dealloyed samples were isothermally annealed at 300 °C for 420 min in argon gas to coarsen the structure, resulting in a bicontinuous structure with a mean ligament diameter of approximately 400 nm. The experimental coarsening procedure is described in refs. 19 and 20.

Micro-Laue measurements were carried out on the as-dealloyed sample and one of the coarsened samples. To this end, sections of the samples were fractured into pieces of around $100 \times 100 \times 100$ µm$^3$ by taking advantage of the macroscopic brittleness of NPG. A SEM image of the ligament structure within the piece achieved in the as-dealloyed sample is shown in SI Appendix, Fig. S3A. Using FIB milling, a 30 µm × 13 × 13-µm$^3$ rectangular micropillar was fabricated from the piece achieved in the coarsened sample, which was used for micro-Laue measurements. The pillar was fabricated tens of micrometers away from the piece edge to ensure that the bulk structure was considered. A SEM image of the micropillar is shown in SI Appendix, Fig. S3 B and C, showing no evidence of ligament collapse, such as that seen in refs. 17 and 26. The micro-Laue data were taken at the Collaborating Research Group - InterFace (CRG-IF) BM32 beamline at the ESRF using a polychromatic X-ray beam (84), with an approach closely following that of ref. 65. Details of the experimental parameters and analysis are provided in SI Appendix.

The other two coarsened samples (of the three that were annealed) were infiltrated with epoxy, as detailed in ref. 2. To create the sample, basic metallographic tools were used, such as wire-saw cutting, grinding, and polishing. Care has been taken to remove the unavoidable deformation from the mechanical preparation steps by removing such layers with FIB. SI Appendix, Fig. S3D highlights the cleanliness of this approach. Further details of this process can be found in ref. 50. One of the epoxy-infilitrated coarsened samples was used for EBSD measurements. The EBSD measurements were performed using the same experimental setup and techniques outlined in ref. 66 with a scan step size of 50 nm.

A 3D reconstruction of the other epoxy-infilitrated NPG sample was obtained using a Nanolab 200 dual-beam SEM and FIB microscope. This sample is studied in Particle Detachment in NPG. The 3D reconstruction is completed through a serial sectioning procedure using FIB-SEM tomography. As part of this process, the FIB is used to remove a slice of the material and the material is subsequently imaged with SEM. A SEM image of a FIB milled cross-section of a region of the coarsened epoxy-infilitrated NPG microstructure is shown in SI Appendix, Fig. S3D. The data acquisition and reconstruction procedure is described in refs. 19 and 20, with extensive details given in ref. 50, chap. 3. The procedure resulted in four 3D datasets consisting of 6 in the void (epoxy) phase and 15 in the gold phase. The volume of each dataset is (6 µm$^3$), which has been shown to be a representative volume that is sufficiently large to represent the “overall, global microstructure” (19). One cube edge of the reconstructed volume of the NPG sample annealed for 420 min is ~14 times the mean ligament diameter.

Phase-Field Simulations. Phase-field simulations of coarsening via surface diffusion were conducted using the model proposed by Rätz et al. (67). In this model, an order parameter is evolved in time according to a governing equation based on mass conservation and flux driven by the chemical potential. Mass transport is limited to the interface due to the formulation of the chemical potential and the use of a chemical mobility that is dependent on the order parameter. The order parameter can be thought of as a scaled concentration that ranges from 0 to 1, which indicates the phase (e.g., solid) occupying the point in space. The order parameter = 1 phase represents the gold phase in the simulations using the experimentally measured NPG data.
as an initial condition and order parameter $= 1$ represents the $\alpha$ phase in the simulations of the CG structure. Full details of the model, simulation parameters, and preparation of the experimentally measured NPD data are given in SI Appendix.

Characterization Methods. The interfacial mean curvature was calculated using a level-set-based method (68). The H autocorrelations were calculated using the equation for the discretized two-point Pearson correlation defined in ref. 51. The interfacial normal distribution (IND) (69) was calculated to check for anisotropy in the structure and the results were found to be highly isotropic. Thus, a radial average of the autocorrelations was calculated as a function of the radius scaled by $L$.

Data Availability. Simulation results and some analysis data have been deposited in Materials Commons (10.13011/m3-3591-7648) (70).

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