How Can We Efficiently Fabricate Nanostructured Materials with Unprecedented Properties?

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Introduction

Decades of research have been devoted to studying the properties of nanostructured materials – e.g., single crystalline wires, porous materials, polycrystals and laminates – for applications ranging from heterogeneous catalysts to high-strength structures.[1] Interest in nanoscale materials is motivated by their new (and often enhanced) properties, which are attributed to large interfacial areas and high surface defect concentrations.[2] Nanoscale catalysts exhibit superior activities due to surface strains, increased population of dangling bonds, and unique surface electronic states established by surface/sub-surface atomic interactions.[3,4] For instance, bulk Au surfaces are relatively inert but Au nanoparticles exhibit excellent catalytic behavior.[1,3] In a similar fashion, nanocrystalline metals possess exceptionally high yield strengths due to an increased barrier for plasticity mechanisms to operate in confined volumes and in close proximity to interfaces.[1,2,5] Unfortunately, fabrication techniques for these materials are frequently resource-intensive, and cannot be translated into commercial-scale processing.

One of the grand challenges in materials science is pivoting from *observational science* to *control science* at relevant time, length, and energy scales.[6] In other words, addressing the question: how can we efficiently fabricate nanostructured materials with unprecedented properties? The authors are tackling this issue of scalable processing by researching low-cost and low-energy methods, such as self-organization *via* dealloying. We define self-organization as the spontaneous emergence of a three-dimensional structure with a characteristic length scale and morphology.

Dealloying, traditionally a corrosion phenomenon, is the selective dissolution of one or more element(s) from an alloy.[1,7] Although reports on this process date as far back as Leonardo Da Vinci,[8] only recently have researchers identified it as an effective method to engineer nanoscale features (called ligaments) into a material. This nanoscale engineering can be understood by considering linear stability analysis (Figure 1): selective dissolution serves to roughen and perturb the surface.[9] If the surface mobility of the remaining elements is sufficiently high, dealloying drives the emergence of a percolating, three-dimensional structure with a characteristic ligament diameter and morphology.[7,9]

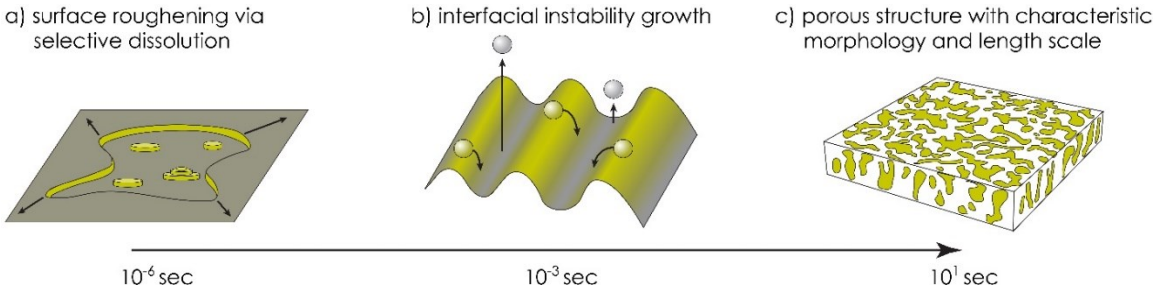

Figure 1. Graphic illustration of self-organization during dealloying of an AgAu-alloy into an aqueous electrolyte. a) Selective dissolution of Ag drives the formation of Au-rich islands on the surface. b) These island perturbations trigger an instability that corrugates the surface with a characteristic wavelength. c) This instability grows in amplitude, exposing subsurface Ag, and dealloying proceeds into the material, eventually forming a bicontinous Au-rich network.

What excites the authors about this approach is that it is spontaneous and requires minimal energy expenditure beyond the initial alloy fabrication.[1,7,10] However, Figure 1 only illustrates the most simplistic embodiment of dealloying, and there are numerous kinetic and thermodynamic factors that can be harnessed to engineer pattern formation at the nanoscale – some of which have been realized in the literature, but many more remain unexplored. This Viewpoint is intended to provide a perspective on the current state of self-organization *via* dealloying, and what knowledge gaps remain to make this grand challenge a reality. For clarity, we have broken these knowledge gaps into distinct thrusts, Figure 2, whose individual aspects will be addressed in the following sections.

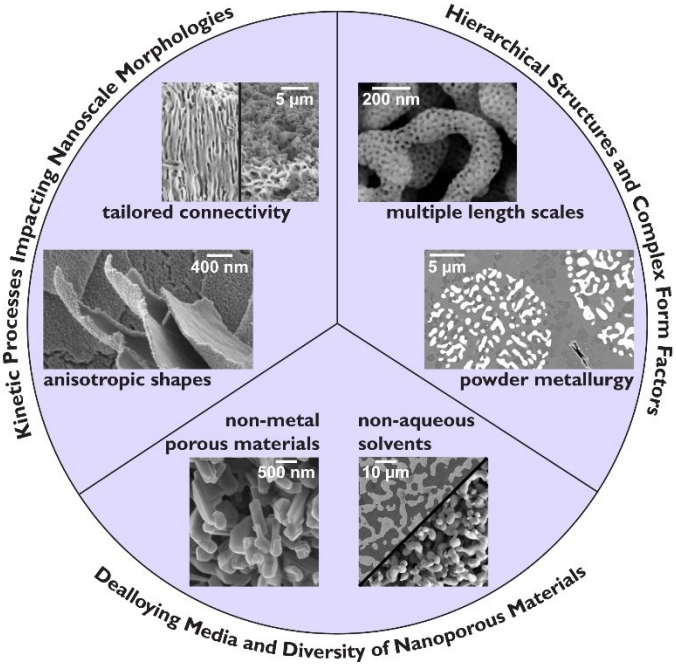

Figure 2. The three key research areas in order to realize control science via self-organization processes: (bottom) extension of these tools to any material class;[14,25] (left) manipulating kinetic and thermodynamic factors during self-organization to control the resulting nanoscale morphology;[15,26] and (right) sequential self-organization and post processing protocols to develop multi-scale nanocomposites.[23,24]

Dealloying Media and Diversity of Nanoporous Materials

To be a truly universal approach, dealloying needs to be applicable to any material system. The most well-known example of dealloying is the selective leaching of Ag from AgAu leaf in an acidic aqueous solvent to form nanoporous gold.[1,7] Insights into the formation mechanism of nanoporous gold led to the discovery of new systems (e.g., nanoporous Ni, Cu, Ag, Pt, Pd, Ir and Ru).[7] However, in order to survive acidic/basic environments, electrochemical dealloying is limited to fabricating *noble* nanoporous materials. This issue was overcome in a breakthrough by the authors (and others) that selective dissolution could be generalized to any liquid solvent.[11,12]

To-date, dealloying has been carried out in aqueous liquids, molten metals, and molten salts.[1,7,10,11,13] Beyond the apparent novelty, these new solvents relax the constraint of synthesizing only noble nanoporous metals. Consequently, dealloying has been extended to a number of more common alloy systems, including: refractories (V, Nb, Mo, Ta, W), steels, Ti-base alloys, Ni-base superalloys, and semiconductors such as Si.[7,14] Furthermore, gas-phase reactions, selective evaporation, and diffusion couples have recently extended dealloying to non-liquid solvents.[7,15–17] Although the dissolution media and environment have changed, the common thread between all of these examples is that a nanoscale pattern emerges from two competing processes: roughening by selective removal, and smoothing driven by interfacial diffusion.[9]

The authors predict insights garnered from pattern formation in these new solvents will enable dealloying to be extended to technical ceramics and oxides. Both material classes find use in structural (e.g., thermal barrier and wear-resistant coatings) and catalytic applications (e.g., catalytic converters and solid oxide fuel cells), but are notoriously difficult to process. Bringing a diversity of nanoscale morphologies will undoubtedly provide a new means to process these systems, and lead to a wealth of studies on microstructure-property relationships.

Kinetic Processes Impacting Nanoscale Morphologies

In addition to being applicable to a wide range of materials, there is emerging evidence that the kinetic knobs during dealloying can be varied to tailor the resulting morphology.[12] It has been previously established that the ligament diameters of dealloyed materials scale universally with homologous temperature; activation energies for diffusion vary linearly with an element's melting point, which enables the ligament diameter to be tuned by altering the reaction temperature.[7] However, recent work has demonstrated that their morphology can also be altered – from globular, to lamellar, and bicontinous – by changing the starting composition of the initial alloy.[12] Prior work in the field suggested that the bicontinuous structure of nanoporous gold was the sole morphology available to dealloyed materials, regardless of starting alloy composition. This wider palette of accessible morphologies has been observed in both liquid metal and vapor phase dealloying systems,[12,15] and was attributed to a much faster dissolution rate (1-2 orders of magnitude higher than electrochemical dealloying) in comparison to surface diffusion.

These new observations have sparked an interest in mapping out the "morphology design space" (to achieve further tailored material properties) as a function of alloy composition, surface mobility, and dissolution rate. Along this vein, the authors are currently examining the effect of surface impurities on the resulting ligament diameter and morphology.[18,19] Slow-diffusing surface impurities are commonly used to improve catalyst stability (i.e., increase their resistance to coarsening); for instance, adding 2-8 at.% Pt to AgAu refines the resulting ligament diameter of nanoporous gold from 25 to 2 nm.[20,21] What has yet to be

studied, however, is how slow (or fast) diffusing impurities affect the evolution of a nanoporous structure. The authors believe understanding the role of trace dopants during dealloying is critical to developing catalysts that are simultaneously highly active and resistant to coarsening.

Hierarchical Structures and Complex Form Factors

While structural engineering materials make use of macroscopic shape (tubes, I-beams, etc.) to maximize performance for a given boundary condition, they lack the internal structural hierarchy that natural materials possess.[22] This deficiency is largely a manufacturing challenge. It is not easy to form or machine thin-walled shapes, which often need additional support to suppress local buckling. While there has been success in fabricating low-density nano-truss structures, their synthesis is not scalable and offers limited microstructural control. In contrast, the synthesis of hierarchical nanoporous metals – with distinct length scales that span five orders of magnitude – are the closest example of a bulk synthetic material with an internal complexity that rivals those found in bone and wood.[23]

This complexity is achieved via multi-step dealloying protocols, whereby three distinct length scales exist: the macroscopic material (~1 mm^3), consisting of large nanoscale struts (~200 nm), which themselves are nanoporous (~10 nm).[23] Although there are only a few published examples of hierarchical nanoporous materials, they serve as blueprints for more complex structures. The holy grail of man-made structures is to exploit unique microstructural elements (comprised of distinct phases) at the smallest possible length scale.[22] We believe that bulk composite strategies (fiber embedding, laminates of dissimilar materials, etc.) can be achieved with nanoscale precision by developing multi-step dealloying protocols in different media – such as combining electrochemical and liquid metal dealloying.

Opportunities on the Horizon

Throughout this Viewpoint, we have discussed emerging research areas in self-organization via dealloying: new classes of materials, compositionally tailored surfaces, and nanoscale designer composites. In addition, one of the most attractive aspects of dealloying that we left out of this discussion is its ability to be used in conjunction with virtually any fabrication technique, including top-down (powder metallurgy, thin film deposition, etc.) and/or bottom-up (co-precipitation, sol-gel, etc.) strategies. While dealloying exists on its own as a scalable processing tool, its barrier for wide-spread adoption can be substantially reduced if it is merged with existing industry processes.

For structural materials, one particularly high-impact fabrication area is powder metallurgy (e.g., hot isostatic pressing, thermal spray, or additive manufacturing).[24] These processes are all near net-shape fabrication, which has challenges in achieving the traditional degree of microstructural control offered by forging. Liquid metal dealloying can address this shortcoming by providing a means to tailor the

microstructure at the nanoscale with seamless integration.[25] For instance, both the solvent and parent alloy could be dispersed as powders throughout a component, which would lead to simultaneous dealloying of individual particles when heated. More complex variations, involving different classes of materials, are easily imagined by locally varying the powder composition and constituent elements. These new materials could enable simultaneous improvements across multiple properties, and provide a rich area to study the governing role of interfaces between dissimilar materials and their resulting performance.

For industrially relevant nanocatalyst materials, self-organization can overcome costly batch processing that plagues scalability. This impact is exemplified by electrocatalysts for fuel cells and electrolyzers, where performance is directly tied to dangling bond density on the catalyst surface.[26] Optimization of the catalyst surface is currently challenging, where high temperature and/or chemically-induced reduction during batch processing result in compositional and morphological variability. In contrast, dealloying affords nanometer-scale control through simple modification of its reaction kinetics. Additionally, dealloying enables new catalyst architectures, such as hierarchical porosity and compositional gradients, which can overcome hurdles in heterogeneous catalysis and processes limited by species transport.[26] Moving forward, directed morphology control through self-organization has the potential to discover new (or evolve old) designs for high aspect ratio catalysts that do not require supports, and are more resistant to operational degradation through active area loss.

Biographies

Ian McCue is an Assistant Professor at Northwestern University in the Department of Materials Science and Engineering. He received his PhD degree in Materials Science and Engineering from Johns Hopkins University in 2015, and then held a postdoctoral appointment at Texas A&M University. Prior to joining Northwestern University, he was a Senior Scientist at Johns Hopkins University Applied Physics Laboratory. His research interests focus on advanced manufacturing, phase transformations, pattern formation during diffusional processes, and the mechanical behavior of nanostructured metals.

Josh Snyder is an Associate Professor at Drexel University in the Department of Chemical and Biological Engineering. He received his PhD in Chemical and Biomolecular Engineering from Johns Hopkins University in 2012. He was a Director's Postdoctoral Fellow in the Materials Science Division at Argonne National lab from 2012-2014. His research interests include fundamental electrocatalyis in well-defined systems, nanocatalyst development, and renewable fuel generation.

Notes

The authors declare no competing financial interest.

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