Realizing Nanostructure-Enabled Applications through Dealloyed Materials

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Abstract

Nanoporous metals produced via dealloying have attracted significant interest due to the interesting physics surrounding their morphological evolution and how their topologically complex structure influences mechanical, optical, and electrochemical properties. Their impressive nanostructure-enabled properties – such as increased catalytic activity, surface-enhanced Raman signals, high strength and large surface-to-volume ratio – have led to catalysts, sensors, actuators, energy storage, and biomedical device coatings with superior properties and performance. However, translation of nanoporous metals into practical applications has revealed needs for new material systems and manufacturing approaches, and consequently better predictive models for application-specific operating conditions. The goal of this MRS Bulletin issue is to elaborate on the latest advances in emerging methods and technologies of dealloyed materials that enable new structures and form factors, machine learning-guided design and synthesis, material recovery and sustainability for scaled-up production, and stable performance in intended operational environments.

Introduction

The landscape of nanoporous metals has dramatically changed over the last 25 years. What began as a handful of researchers elucidating the fundamental mechanism of porosity evolution has now expanded across the globe, with numerous groups studying a range of phenomena related to the synthesis and properties of these materials. An abbreviated, non-exhaustive trajectory of nanoporous metals is captured in **Figure 1**, which is intended to highlight its evolution from application in metalworking to modern fields such as biomedicine, additive manufacturing and catalysis. However, there are also many more paths this discipline will take in the future – ranging from commercialization to emerging research topics. The most pressing challenges and opportunities in nanoporous metals are explored in this issue.

Research on nanoporous metals dates back to binary alloys in aqueous electrolytes under free corrosion conditions. Cu-Zn and Au-Ag were initially studied because the elements in these respective alloys have sufficiently large differences in their standard reduction potentials that facilitates selective dissolution[20, 62, 63]. The dealloying nomenclature originates from this work, where the "less noble" species (Zn and Ag in the examples above) dissolve into the electrolyte while the remaining "noble" species (Cu and Au in the examples above) diffuse along the alloy/electrolyte interface. As noted in a previous MRS Bulletin issue[64], dealloying was first seen as an undesirable corrosion phenomenon (de-zincification of brass received substantial attention as a failure mechanism during the Civil War era[65]), which then spurred investigations to understand how selective dissolution leads to brittle fracture in ductile metals[12, 18, 66-70].

Turning to the modern day, it is recognized that the competition between dissolution and surface diffusion during dealloying drives the self-organization of a bicontinuous porous network with a characteristic length scale on the order of 10 nanometers. The underlying physics of this process have been described in a previous MRS Bulletin issue[71] and can be largely attributed to the anomalously high surface diffusivity of metals in electrolytes[72], which had eluded researchers for several decades[73] until the seminal work by Erlebacher[26]. Nevertheless, dealloying had been used for centuries prior – in a metalworking process known as depletion gilding[73] – to enrich the gold content on the surface of objects made from gold alloys.

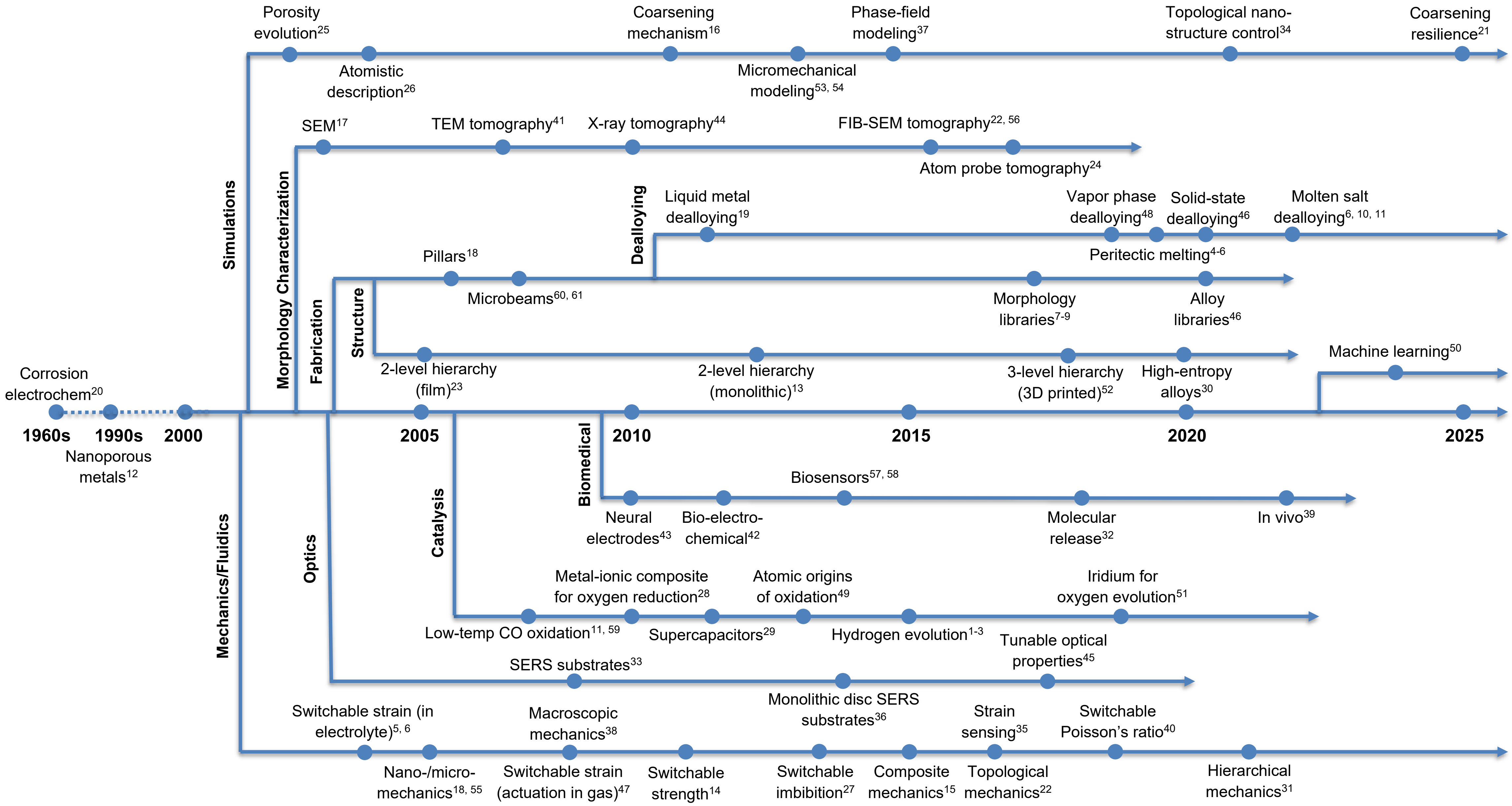

Figure 1. A non-exhaustive trajectory of nanoporous metals. The upper branches primarily illustrate the progression of nanoporous metals from fabrication methods to structural control, followed by advanced characterization and modeling of their structural evolution during and after dealloying. The lower branches highlight the exploration of their key material properties such as mechanical, fluidic, and optical properties without/with electrolytes and their potential applications, including catalysis and biomedical applications, along the trajectory.

Developing a Diverse Class of Porous Materials

The insights gained from Erlebacher et al. provided a blueprint for the materials community to build out an entire class of nanoporous metals[25]. Until now, more than 30 unary metals and metalloids have been fabricated into porous structures via dealloying techniques[74]. The number of dealloyed porous metals and metalloids has increased nearly tenfold over the past two decades, as shown in Figure 2a. This expansion beyond nanoporous gold was made possible by innovations in dealloying techniques (Figure 2b). Chemical or electrochemical dealloying was primarily relegated to fabricating noble-metal bicontinuous networks[75], which drove researchers to explore if selective dissolution in other solvent media could produce these structures in non-noble metals. The first major foray was liquid metal dealloying (reviewed in 2018 issue of the MRS Bulletin[76]), but even more techniques have emerged over the last few years, including vapor phase dealloying[48], reduction-induced decomposition[77], peritectic melting[4] and molten salt dealloying[10]. These new techniques and novel materials produced by each technique, along with their characteristics that enable novel properties and applications are reviewed in the article by Jin et al. of this issue.

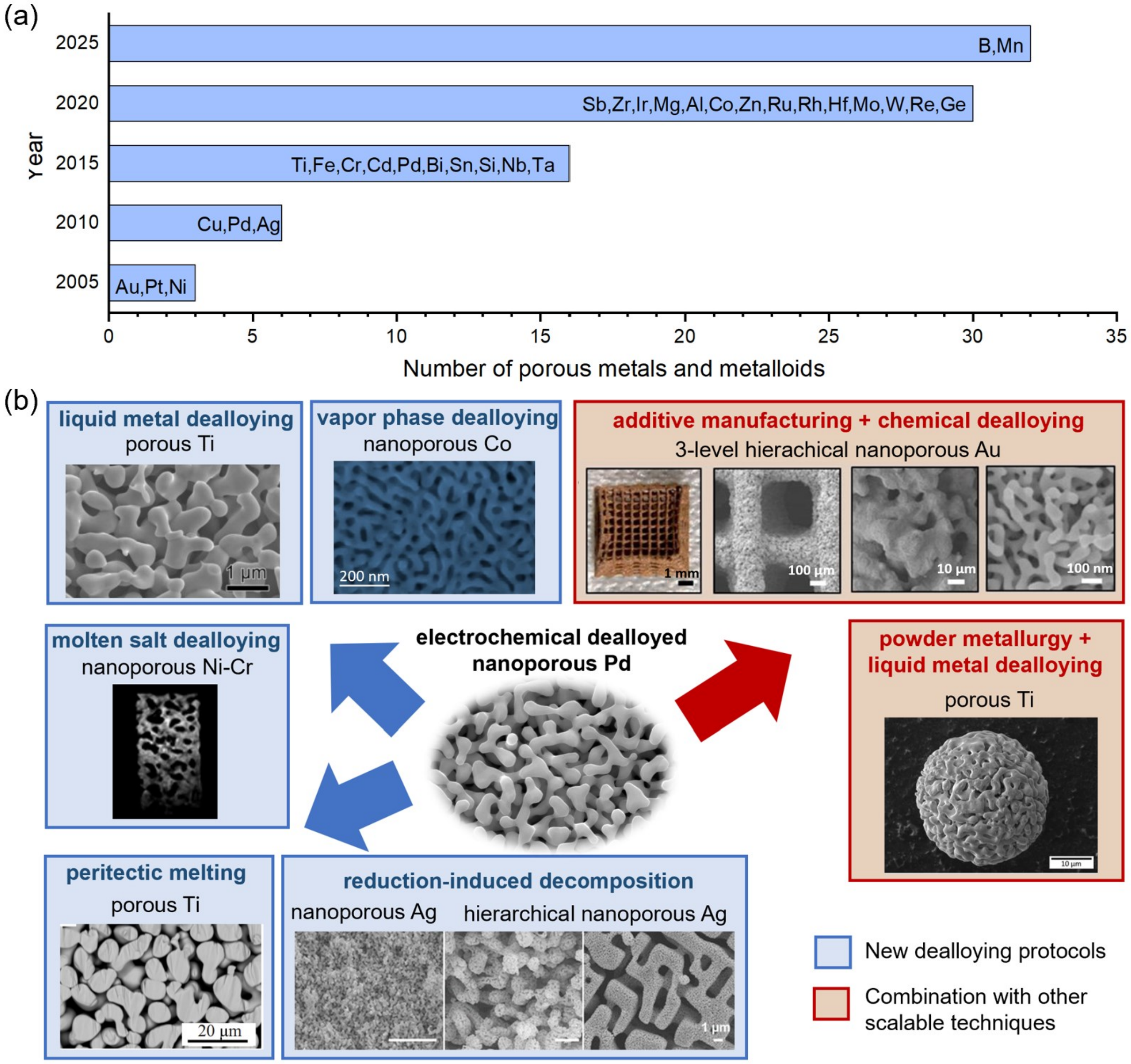

Figure 2. Evolution of dealloying techniques and dealloyed porous metals (a) Expansion of dealloyed porous metals and metalloids over the last two decades. (b) Examples of (nano-)porous and hierarchical nanoporous metals produced by various new dealloying techniques (left), such as liquid metal dealloying[19], vapor phase dealloying[48], reduction-induced decomposition[77], peritectic melting[4] and molten salt dealloying[10], beyond electrochemical dealloying[78] (center) and their combination with other scalable techniques (right), such as additive manufacturing[52] and powder metallurgy[79]. Reproduced with permission from Wada et al.[19] and Shi et al.[78] Copyright (2011) by Elsevier; Copyright (2018) by Springer Nature; Copyright (2018) by American Chemical Society; Copyright (2019) by American Physical Society; Copyright (2021) by Springer Nature; Copyright (2018) by Elsevier; Copyright (2018) by The American Association for the Advancement of Science; Copyright (2022) by Elsevier.

Beyond the types of materials that can be fabricated, the morphology of nanoporous metals has changed dramatically since the theoretical description of porosity evolution[25]. As noted by others[34, 37], the connectivity of the resulting nanoporous network is highly sensitive to the initial alloy composition, dissolution rate during dealloying, and thermodynamic interactions between the elements in the alloy and the solvent media. By leveraging these insights, the characteristic bicontinuous structure of nanoporous gold is no longer fixed[80, 81] and the morphology of nanoporous metals can now be finely tuned to meet the needs of a given application. Researchers have been able to fabricate globular and lamellar structures, as well as connected networks with distinct curvature distributions. However, the effect of morphology on physical properties has yet to be rigorously quantified and remains a ripe area for research.

Finally, the dealloying protocols themselves have evolved as researchers became more experienced with nanoporous metal synthesis. Nanoporous metals were initially fabricated via free corrosion, where the starting alloy was immersed in an acidic solution. This process often led to samples with macroscale cracks and large volume shrinkage[61, 82], which has been since solved by using potentiostats and aqueous chemistry to dealloy in specific regions of the Pourbaix diagram at controlled dissolution rates[83-88] and by other approaches, including imposing compressive plastic strains prior to dealloying[89]. Further advancements have included multi-step treatments to create hierarchical networks, and infiltration techniques to create composites of nanoporous metals with polymers, glasses and dissimilar metals[90, 91]. Looking forward, researchers have begun to explore combinations of dealloying techniques with standard synthesis strategies such as powder metallurgy and additive manufacturing[52, 79, 92, 93]. These combined approaches offer the ability to control microstructural hierarchies in a scalable manner, which could lead to components with complexities that rival biological materials[94].

History and Progress on Material Properties

As illustrated in Figure 1, the properties of these materials are examined and employed across very different fields. Initial work focused on catalytic features[49, 95-100], mechanical behavior[18, 61, 82, 101], and optical properties[33, 36, 102] due to an interest in “nano-enabled” properties (e.g., increased catalytic activity and inhibition of dislocation motion due to confined volumes and free surfaces). These investigations were carried out on nanoporous gold due to its ease of fabrication. However, new nanoporous systems were developed to better suit the application under study (e.g., moving from nanoporous gold to nanoporous platinum for hydrogen fuel cell catalysis[28, 103, 104]). While these specific disciplines have continued to advance with substantial research activity, it is expected that new applications will drive the exploration of new properties in nanoporous metals; a few are mentioned below.

In the context of mechanical properties, nanoporous gold has served as a model system to study mechanics of nanoscale network materials. The effect of various parameters – including solid fraction, ligament size and topological connectivity on network strength and stiffness – has been extensively explored by both experiments and modelling, and reviewed in 2009 and 2018 issues of the MRS Bulletin[71, 105]. Work in this area identified the role of surface stress on dislocation activity, and that a high-density of surfaces leads to unusual behavior, such as yield stresses approaching the theoretical strength of the material[55, 106]. In addition, researchers are now reporting on the deformation behavior of more traditional structural materials (Fe, Mg, Nb, Ni, Ti, etc.) in both nanoporous[107] and nanocomposite form factors (i.e., infiltration of or coating nanoporous metals with polymers, ceramics and other materials)[15, 108].

Moreover, the mechanical properties of nanoporous metals in electrolytes can be reversibly tuned via controlling the metal/electrolyte interface. The ability to modulate their strain, stiffness, strength and Poisson’s ratio has led to a new class of hybrid nanomaterials with interface-controlled functionalities[5, 14, 40, 109-114]. For instance, work by Weissmüller et al. demonstrated the first nanoporous metal actuator and active strain sensor based on the connection between capillary force (surface stress) and electric potential change or charge displacement[5, 35]. Recent advances have gone beyond interfacial control. By electrochemically controlling the concentration of hydrogen atoms in nanoporous palladium, Shi et al. observed an actuation amplitude as large as 4% for >1500 cycles and ~ 40% switchable compliance change[114, 115]. These results were in excellent agreement with the strain-concentration coupling coefficient in metal hydrides and Larché-Cahn open-system elasticity theory[114]. The ability to reversibly and significantly change the mechanical properties of a material by controlling the surface state or concentration of interstitial atoms is remarkable and effectively unique to nanoporous metals. What remains to be explored is the extent to which strategies of combining chemical-mechanical coupling and nanoscale geometry to achieve switchable mechanical properties (achieved in model materials such as nanoporous gold and palladium) can be extended to other, more sustainable materials, and ultimately integrated into devices.

As catalysts, nanoporous metals display enhanced performance (e.g., low temperature CO oxidation) due to undercoordinated atoms (on high-curvature ligament surfaces) coupled with large surface area to volume ratios[59, 95]. In addition, the dealloying process can be controlled to create core-shell structures, where the surface is enriched in a single element (e.g., Pt) while the bulk of the ligament maintains a composition similar to the initial alloy (e.g., P_3Ni). This "skin effect" has been examined extensively in thin film and nanoparticle form factors, and some of the most active catalysts rely on this concentration grading[116-118]. However, one aspect that helps set nanoporous metals apart from commercial nanoparticle catalysts is their ability to be unsupported; removing the need for a carbon support can increase stability during operation. Furthermore, performance records for the oxygen-reduction reaction have been achieved by infiltrating the porous metal network with an ionic liquid that has a higher affinity for oxygen than water[119] – an architecture not possible using nanoparticles or other traditional catalyst geometries.

Finally, other intriguing features of nanoporous metals – such as enhanced surface plasmon resonance and ease in functionalizing surfaces with biomolecular receptors against target molecules (e.g., environmental pollutants, disease markers) – gave rise to numerous sensor applications, which was covered in a previous MRS Bulletin issue[120]. The high electrical conductivity and biocompatibility of nanoporous gold elevated some of these early applications to biomedical tools[39, 58, 121-125]. The possibility of using nanoporous metals came about just as conventional blanket coatings (on silicon wafers, slides, and coupons) became insufficient for these newer applications. Several groups demonstrated techniques to integrate nanoporous metals in the microfabrication/lithography processes to pattern them to advance studies of structure-mechanical property relationships[60, 61], control optical properties[33, 36, 45], and electrochemical biosensor arrays[9]. Emergence of nanoporous metals composed of various elements create additional application opportunities, some of which are described in the "Sustaining Functionality in Extreme Conditions" section. While some of the newer materials in their nanoporous form (listed in Figure 2a) have obvious potential applications (e.g., titanium and tantalum for biomedical implants, germanium for photovoltaics, manganese for energy storage, hafnium for hydrogen storage and sensing), it is likely that we will witness non-obvious applications enabled by the novel nanoporous materials.

Optimizing Material Properties through Structural Hierarchy

The above properties (catalysis, sensing, and switchable mechanical behavior) of nanoporous metals all share similar physical processes: reaction at the nanoporous metal surface/interface and transport of reaction constituents (i.e., precursors and/or products). Small features are desirable to increase the surface area, and thus performance, but these processes become transport limited due to the sluggish rates of moving material through tiny pore channels. Thus, deliberate incorporation of structural hierarchy is at the forefront of efforts to optimize these materials. This need spurred innovations in dealloying across multiple length scales, where micron-scale channels surrounded by nanoporous ligaments alleviate transport limitations to the metal surfaces[23, 52, 126].

Multistep dealloying and additive manufacturing-assisted dealloying methods appeared as efficient approaches to create metals with multiscale hierarchical porosities[13, 23, 52, 127]. For instance, two-level hierarchical nanoporous gold monolithic samples with ligaments at each hierarchy level have demonstrated enhanced electrochemical performance, improved mechanical properties, and reduced density[13, 31]. Three-level hierarchical nanoporous gold monolithic samples have been fabricated by combing dealloying and direct ink writing techniques, demonstrating further reduced density and improved catalytic performance through increasing the number of structural hierarchies[52]. The combination of bottom-up dealloying and top-down additive manufacturing facilitates highly customizable shapes at the coarsest hierarchy, a broad range of densities and intricate geometries. However, achieving adequate mechanical robustness in these materials remains a major challenge. This limitation arises from substantial volume shrinkage during dealloying, loss of structural connectivity during coarsening, and non-uniform porosity formed during sintering (in the case of additive manufacturing). Developing scalable manufacturing techniques that ensure tailored structure and good mechanical robustness, coupled with a thorough understanding of the interplay between material synthesis, structure, and properties in hierarchical nanoscale network materials, is crucial for advancing the use of nanoporous metals in catalysis, energy storage, sensing, and lightweight structural applications.

Sustaining Functionality in Extreme Conditions

The discussion above demonstrates the painstaking efforts researchers have gone through to finely tune the structure of nanoporous metals to achieve a desirable set of properties. Unfortunately, as is often the case with nanoscale features, nanoporous materials are metastable, and their structures will change over time if given sufficient energy. These changes typically involve coarsening of the nanostructure, which in turn leads to diminished properties and performance. The article by Snyder et al. in this issue explores the degradation (and design considerations for stability) of nanoporous metals in emerging applications: extreme environments. While degradation via temperature has been extensively studied and strategies have been developed to mitigate thermal coarsening[108], the role of other thermodynamic variables (such as mechanical force, electrochemical potential, and radiation) has received limited attention. The applications discussed in their article represent emerging disciplines, which require both new materials and fundamental studies on morphological evolution in these environments. Some promising materials and strategies are highlighted in **Figure 3**.

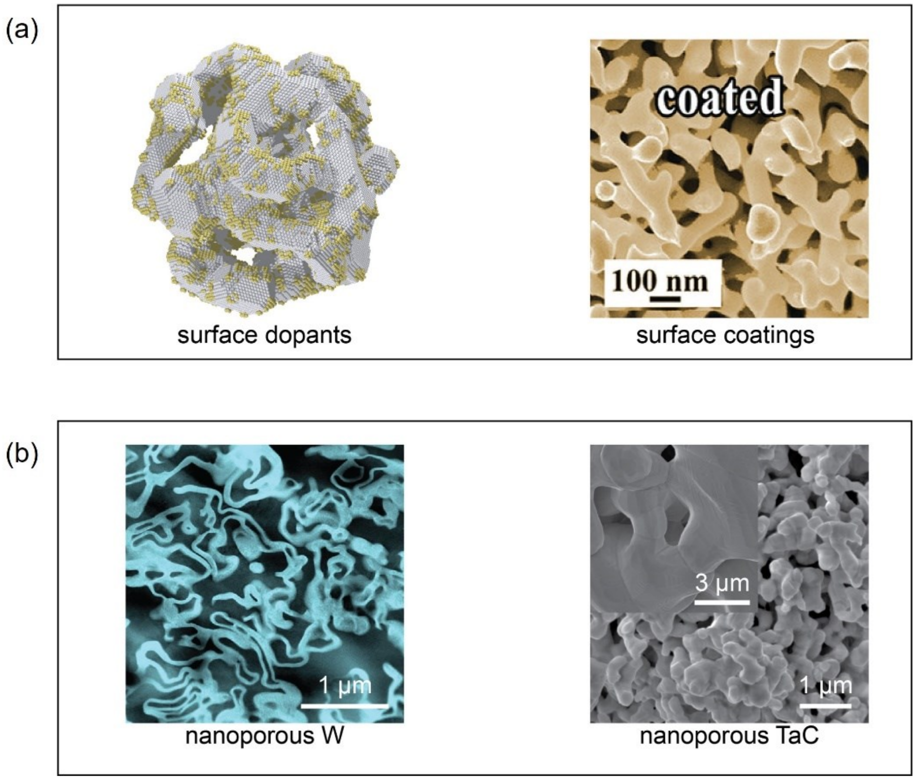

Figure 3. Material and microstructural solutions for nanoporous metals under extremes. (a) Promising strategies to modify the surface of nanoporous metals to prevent degradation: (left) surface dopants to reduce coarsening and impart additional catalytic functionality[21]; (right) ALD-coatings to improve densification via thermal coarsening and mechanical deformation[108]. (b) Emerging refractory materials to enable operation at high temperatures and radiation environments: (left) nanoporous W formed via liquid metal dealloying of a Ti_xW_{1-x} alloy in molten copper[128]; (right) nanoporous TaC formed via low-temperature gas carburization of de-hydrided Ta power[129]. Reprinted with permission from Biener et al.*[108]*. Copyright (2011) American Chemical Society.

The operating environments for electrochemical devices drive substantial degradation – possibly counterintuitive considering nanoporous metals are often fabricated via electrochemistry. Separate work by Fujita[130], Li[131] and Erlebacher[132] revealed that oxidation/reduction processes during electrochemical cycling introduces additional mass transport mechanisms for species on the surface of a metal. The diffusion length of these new mechanisms is often larger than what is possible via surface diffusion, driving extremely rapid coarsening rates and requiring new mitigation strategies. Minor additions of surface dopants have been proposed to reduce this new transport mechanism, but selection needs to be centered around electrochemical stability rather than surface mobility. As a result, the appropriate dopant is not always apparent.

Exposure to radiation, either in a fission or fusion environment, offers a potentially disruptive opportunity to employ nanoporous metals. A seminal study by Bringa et al. demonstrated that nanoporous metals could behave as perfect sinks for radiation-induced defects provided the defects migrate to the free surface of ligaments over timescales shorter than collision cascades[133]. However, these environments are also at temperatures where thermal coarsening will be operative. It is possible that displaced atoms within the ligaments could have a large effect on surface atoms, potentially driving surface currents that are several factors larger than pure capillary smoothing. However, detailed and systematic studies are needed to understand morphological evolution in this complex environment. In addition, the demands of this environment require the design of radiation-relevant materials such as nanoporous W and SiC.

It is also important to note that it is not only the nanoporous metal that needs to sustain functionality in extreme conditions, but also the substrate supporting the nanoporous metal coating. Various substrates have been used that range from temperature/corrosion-resistant yet rigid materials (e.g., silicon, glass) to less resistant yet mechanically-compliant materials (e.g., silicone elastomers, polyimide). Ultimately, the nanoporous metal coating and its substrate should be considered together for its resilience in intended application.

Integrating Modern Techniques with Nanoporous Metal Fabrication

The dealloying community has established several processing-structure-application relationships. For example, rapid dissolution of the less noble constituent of an alloy thin film, results in microcracks in the resulting nanoporous film, which can be utilized to enhance molecular transport and improve biosensor performance[57]. Similarly, tuning the porosity hierarchy controls mechanical behavior[31] and catalysis performance[52]. Nevertheless, following the topics in this article, one can appreciate that the parameter space (e.g., elements, solvent media, synthesis protocols) now available for creating nanoporous metals is expansive compared to two decades ago. Various – often competing – application-specific needs (e.g., high effective surface area vs. unhindered mass transport) increase the complexity of the design space. To evaluate these properties, multi-modal characterization methods are often needed. However, selecting the type of characterization, details of the approach, and subsequently analyzing this output to inform the iterative design of nanoporous metals is a daunting task. Systematic variation of dealloying parameters (and protocols) in order to reach a multi-dimensional optimum for a specific application is simply not practical.

Fortunately, the surge of machine learning (ML) research has been timely for addressing the ever-increasing complexity of the nanoporous metal synthesis-characterization-application space[134, 135]. To that end, Karen Chen-Weigart et al.'s article in this issue discusses recent (ML)-augmented computational methodologies for predicting precursor alloy composition and final nanoporous structures. In addition, ML approaches are enabling autonomous experimentation for material design and assessment, further accelerating nanoporous metal discovery. While representative use of these techniques currently focuses on mechanical properties, it is expected that the ML approaches can be expanded to other properties (e.g., mass transport, catalytic activity, surface plasmons) that enable a wide range of applications. The article also describes how more advanced characterization techniques, such as real-time synchrotron X-ray tomography, can be used for guiding ML-approaches in a closed-loop manner.

We envision that a material design pipeline, as depicted in **Figure 4**, might become a routine workflow in the future for rationally designing application-specific nanoporous metals. In this scheme, combinatorial material libraries (e.g., thin-film alloys of varying elemental compositions[136]) are generated and subsequently dealloyed to produce a corresponding library of nanoporous metals. ML-based techniques aid in the selection of elements, their composition ranges, and most suitable dealloying parameters[50]. The resulting nanoporous metal libraries can then be further modified, that is, their morphology can be tuned via annealing techniques[7, 8, 137], electrochemical cycling[9, 138, 139], conformal deposition of ceramics[108], or attaching functional molecules onto surfaces[9, 124, 140, 141]. These materials are interrogated at each stage of the process to assess their properties, which are fed into ML algorithms to enhance predictions of structure-property relationships. Successful “hits” from the later-stage material libraries are incorporated as functional coatings in devices or systems for specific applications (e.g., biomedical implant coating, fuel cell electrodes, supported catalysts) for validating their within-application performance and further fine-tuning ML-based prediction algorithms.

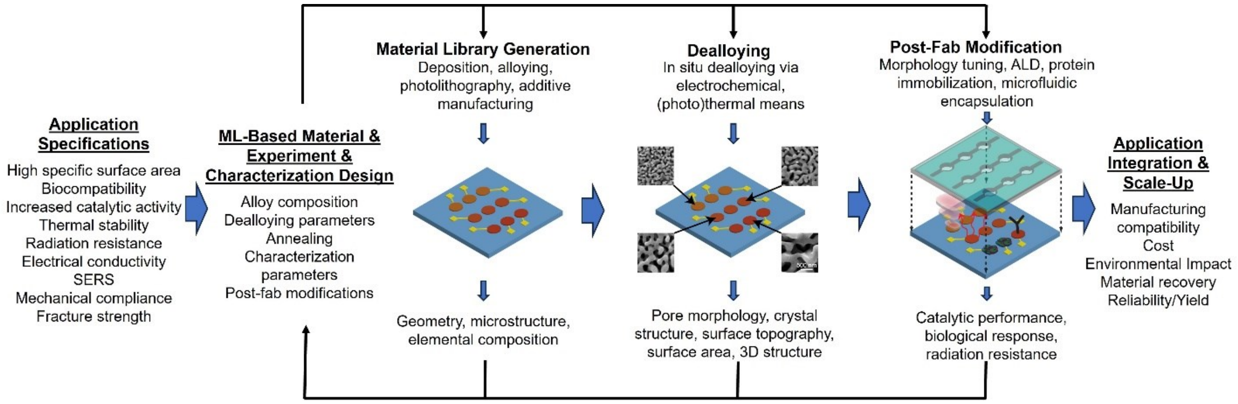

Figure 4. Envisioned functional nanoporous metal design workflow. Application-specific requirements, informed by ML algorithms, guide the generation of a material library that displays many alloy combinations. The dealloying stage converts the precursor library to nanoporous metals, which are subsequently further modified. Ultimately, selected material combinations from the later libraries are integrated into application-relevant form factors for further validation. Each stage has numerous processing and characterization options and parameters, which tune the ML algorithms to improve predictive power.

A natural progression of material innovations is the eventual integration of select material systems into commercial or industrial products, which come up with its own set of considerations, including cost, environmental impact, and compatibility with existing manufacturing processes. The article by Detsi et al. describes a recent technique that leverages the Kirkendall effect (motion of interface between two metals due differences in their atomic diffusivities) as a method to recover sacrificial materials generated during the typical dealloying process, where a less noble metal is electrochemically dissolved[142]. Since the electrochemical dissolution is relatively easy to scale up to large form factors methods, the described method has the potential to aid in sustainable manufacturing of nanoporous metals.

Concluding Remarks

Taken together, translation of the fundamental knowledge to practical applications highlights the need for new material systems and manufacturing approaches, and consequently better predictive models for application-specific materials. The goal of this special issue is to elaborate on the latest advances of these newer methods and technologies that allow scale-up, machine learning-guided design and synthesis, and stable and predictable operation in intended environments. We expect that the advancements described in the included articles will inspire the next level of innovations in engineering nanoporous metals for impactful applications.

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Conflicts of Interest

The authors declare no conflicts of interest.

Author Contributions

All authors contributed equally to the conceptualization, visualization, and writing/editing the manuscript.

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