

## Introduction

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### Introduction

Porous metals consist of a solid metal/alloy matrix with empty or fluid-filled voids or pores. If the voids are connected, porous metals are said to be open-celled; otherwise they are referred to as close-celled. Liquid metallurgy and powder-metallurgy are the most common manufacturing techniques for porous metals, whose microstructure is thus determined by their foaming, solidification and sintering history, as well as any subsequent thermo-mechanical treatments. Additive manufacturing of porous metallic structures is also a rapidly growing area of research, and both routes (melting/solidification and sintering of powders) are used<sup>1–3</sup>. Most technical metals and their alloys have been created with porous structures, including iron, aluminum, nickel, copper, magnesium, titanium, zinc, lead, silver, gold, platinum, tantalum and tungsten. Capabilities for producing complex shapes and three-dimensional sandwich structures employing porous metals are available. Interests in porous metals with varying length scales of pores (macro-, micro-, nanoporous metals) as well as hierarchical and multiscale porous metals, as highlighted in the cover image of this Focus Issue (from data presented in Ref. <sup>4</sup>), continue to create new opportunities in novel research as well as advanced functional and structural applications.

### Thirty Years of Research in Porous Metals

A wave of research and development on porous, foamed and cellular metals, which started in the 1990s, has produced a growing number of publications documenting new scientific findings, both fundamentals and applied, and many new industrial applications. Probably the most known textbooks covering the field are *Cellular Solids* by Gibson and Ashby (1997), the *Design Guide* by Ashby et al. (2000), the *Handbook* by

Degischer and Kriszt (2002), and Dukhan's *Metal Foams, Fundamentals and Applications* (2013). Many extensive reviews, including those by Banhart and coworkers<sup>5–9</sup> and Zhao et al.<sup>10</sup>, are comprehensive literature sources on metal foams as well. Other reviews focus on particular metals and alloys, e.g., aluminum<sup>11,12</sup>, steels<sup>13</sup> and titanium<sup>14–17</sup>. In particular, a recent review by Wan et al.<sup>18</sup> concerning fabrication, properties, and applications of open-cell aluminum foams, has just appeared. These works summarize a great deal of insight, from fundamental physical phenomena (such as liquid foam stability, solid sintering kinetics, or rapid solidification), to more applied engineering performance, applications, and design. They contain virtually all the then-current state-of-the-art of porous metals and alloys, in terms of production methods, properties, microstructure characterization and applications. In addition to these valuable resources, two biannual conferences are partially or totally focused on metal foams: CellMat and MetFoam. The last MetFoam conference took place in 2019 in Dearborn, MI (USA), while the upcoming edition will be held in 2021 in Dresden (Germany), where Cellmat 2022 will also take place. International symposia on nanoporous metals by alloy corrosion also occur biennially, with the mostly recent one in 2019 in Philadelphia, PA (USA).

### Porous Metals and Alloys – Non-structural Applications

Historically, porous metals have focused on structural applications where specific stiffness and strength were optimized, using conventional casting, sintering, cutting, machining and joining techniques to create ductile and strong porous metallic structure. For such load-bearing applications, porous metals are studied and used in many sectors, e.g., transportation, architecture, and medicine (for bone-replacement implants).

*This special issue of the Journal of Materials Research contains articles that were accepted in response to an invitation for manuscripts.*

Non-structural applications are being increasingly studied in porous metals, because of their many favorable properties as compared to porous ceramic and polymers. For example, porous metals have high thermal and electrical conductivities, useful for heat-exchanger applications and electromagnetic shielding, respectively. Other attributes include chemical, corrosion and oxidization resistance, high-temperature stability, recyclability, and high acoustic and vibration damping. Open-cell porous metals are permeable and can show a wide range of surface area density useful for catalyst substrates and heat-exchangers, for example.

In the human health field, a particularly timely example for the functional (non-structural) use of open-porosity metals is covered in a July 2020 article describing an air disinfection system fabricated from commercial nickel foams.<sup>19</sup> When heated to 200 °C, these nickel-foam filters show a 99.8% reduction of aerosolized SARS-CoV-2 viruses and 99.9% reduction of Anthrax spores (*Bacillus anthracis*) between pre- and post-device levels. This low-cost approach to catching and killing aerosolized SARS-CoV-2 may become a useful and rapidly-deployable tool for controlling the spread of this virus in enclosed spaces where air is recirculated. The commercial nickel foam used is 95% porous, and despite pore sizes (between 50 and 500 μm) and strut diameters (~ 65 μm) much larger than the virus, its large surface area very effectively catches most of the virus-containing aerosol droplets suspended in the air passing through the filter. The high electrical conductivity of pure nickel (a non-structural property) permits simple, direct resistive heating of the foam, while the high ductility of pure nickel (a mechanical property) allows for multiple folding of the foam, increasing its effective thickness.

## Pore size effects

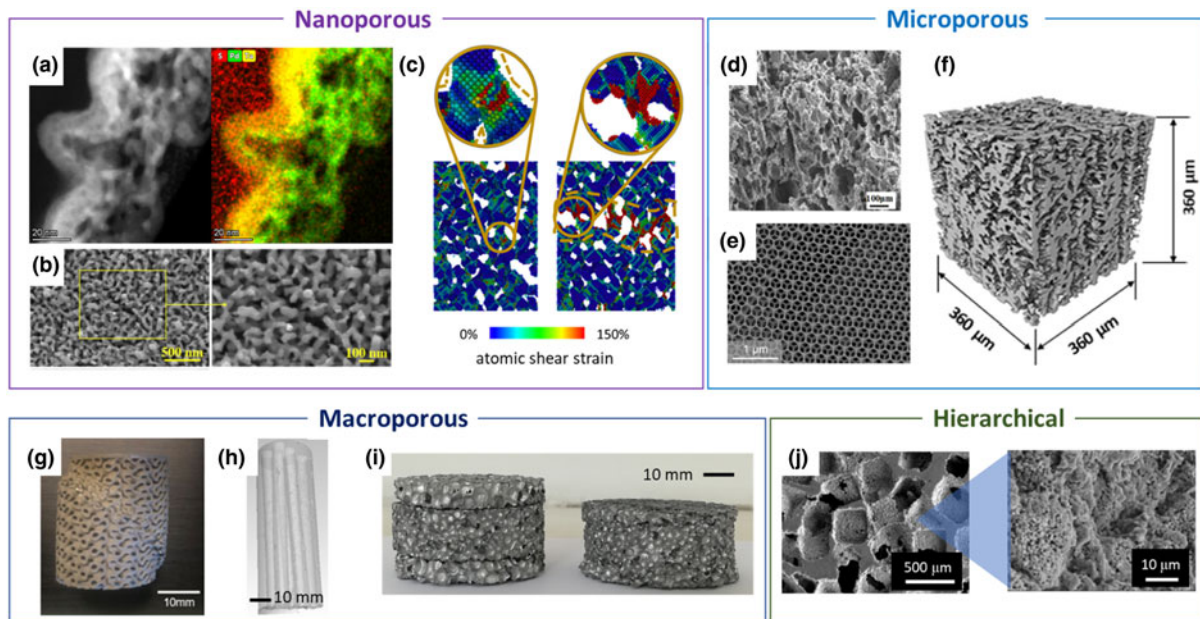
The two main *architectural* parameters affecting properties of porous metals are (i) pore volume fraction and (ii) pore size; other pore parameters include pore shape, tortuosity, connectivity and orientation, as well as distribution of these attributes. *Microstructural* parameters pertain to the alloy itself (e.g. composition, grain size, dislocation density, second phases) and are only weakly connected to the above *architectural* pore parameters.

The volume fraction of pores affects strongly the property of porous metals, similar to the effect of volume fraction of reinforcement in metal matrix composites, or of second phases in precipitation- or dispersion-strengthened alloys. Recently, high and ultra-high porosities (>96% and >99.5%) have been achieved in metals *via* various manufacturing methods (e.g., combustion synthesis<sup>31</sup>, microstereolithography<sup>32</sup>, electrodeposition on a removable substrate<sup>33</sup>), making these very light metal structures attractive in industrial applications where very high surface area is desirable. The typical range of pore

volume fraction reported in porous metals is, roughly, 50 to 99.95%; when expressed as relative density, it is 50 to 0.05%, or three orders of magnitude.

Pore size, the second main architectural parameter for porous metals, varies over a much wider range, as demonstrated by the articles in this Focus Issue and as illustrated in Fig. 1: from nanometers (e.g., for dealloyed metals), to micrometers (e.g., for freeze-cast or replicated foams), to sub-millimeters (e.g., for additively manufactured lattices), to centimeters (e.g., for open-channel metals), with some porous metals displaying hierarchical macro/micro/nano pores. At the low end of this scale, with nanometer-sized pores and ligaments, are nanoporous alloys fabricated by dealloying<sup>34–36</sup>, which may be combined with methods such as additive manufacturing<sup>37–39</sup>, powder metallurgy<sup>4,40</sup> or other strategies to create hierarchical structures.<sup>41</sup> These display promising applications in areas such as catalysis<sup>42</sup>, sensing<sup>43</sup> and energy storage.<sup>44</sup> The complex mechanisms underlying nanoporosity formation and coarsening<sup>47–49</sup> has also attracted great interest in fundamental mechanism studies and continuing innovation on dealloying methods such as liquid metal dealloying<sup>50–52</sup>, solid-state interfacial dealloying<sup>53,54</sup>, vapor phase dealloying<sup>55, 56</sup>, and reduction/thermal decomposition<sup>57, 58</sup>. At the high end of the scale (as illustrated in Fig. 2), meter-size struts, defining meter-to-decameter voids, are present in built metal lattice structures such as the 324m high *Eiffel Tower* in Paris (built in 1889 from wrought-iron elements) or the 17m high *Hive* in London's Kew Gardens, a 44-ton aluminum honeycomb sculpture celebrating the beauty of bees (designed and built in 2015 by architect Wolfgang Buttress). This 10-order of magnitude range in pore size (from nanometers to decameters) translates into a 30-order of magnitude in pore volume range (from cubic nanometers to thousands of cubic meters). Nevertheless, many of the same fundamental concepts and mechanisms are present in these porous metals over this huge dimensional scale, at least until the nano-scale is approached.

As the size of micro- and nanopores becomes close to the size of microstructural features (grain size, precipitate spacing, dislocation spacing, phonon and electron mean free path), the properties of porous metals may become pore-size dependent. For example, nanoporous gold exhibits ligaments which, because they are dislocation-free, are brittle, unlike bulk or micro-porous gold<sup>62</sup>. In another example, as the oxide layer forming on most metals (e.g., sub-micron is thickness) displays a thickness comparable to that of submicron metallic struts, the oxide must be taken into account into prediction of the properties of the porous metal<sup>63</sup> (e.g., its higher stiffness will stiffen it, its high strength will strengthen it). In a third example, if struts or walls of the porous metals are smaller than the grain size, they become mono- or oligocrystalline, thus showing anisotropic mechanical and thermal properties<sup>64</sup>. Only



**Figure 1:** “Porous metals – from nano to macro”: figures reproduced from articles in this Focus Issue illustrate the range of pore size in porous metals. (a) scanning transmission electron micrograph of a nanoporous palladium - polymer composite membranes for separations and catalysis; the nanoporous Pd was prepared by the dealloying method<sup>20</sup>, (b) scanning electron microscope (SEM) micrograph of nanoporous copper prepared by dealloying<sup>21</sup>, (c) molecular dynamics simulations of crystalline copper nanoporous structures during tensile loading<sup>22</sup> – scale is provided by individual atoms visible in enlarged view in circles, (d) SEM micrograph of tensile section of a carbon nanotubes reinforced aluminum foam prepared by powder metallurgy<sup>23</sup> (e) three-dimensionally ordered porous tungsten (inverse opals structure), prepared by a templating method<sup>24</sup> (f) tomographic view of porous iron created by freeze casting, ice template removal and sintering<sup>25</sup> (g) a 3D printed Ti-6Al-4V gyroid-structured scaffold showing diagonal shear bands from compression tests<sup>26</sup> (h) X-ray tomographic reconstruction of open-channel aluminum fabricated by casting and subsequent extraction of lubricated metallic wires<sup>27, 28</sup> (i) photographs of closed-cell aluminum foams with graded density before and after a compression test<sup>29</sup> (j) SEM micrographs of hierarchically-porous titanium with macro-/micro-/nanopores, prepared using NaCl spacer and dealloying methods<sup>30</sup>.

properties which are affected solely by atoms and their nearest neighbors are unaffected by pore size, for example: stiffness, thermal expansion, melting point, and mass density (except for the so-far unreachable case of porous metals consisting of walls or ligaments only a few atoms in thickness).

## Conclusion

As we enter the 2020’s, we are witnessing the rapid development of new areas in the field of porous metals, including additive manufacturing, freeze-casting, electro-deposition, liquid- and gas-phase deposition, triply-minimal-surface foams, porous metallic metamaterials, and nanoporous metals. This Focus Issue of the *Journal of Materials Research* (“Porous Metals: From Nano to Macro”) provides a representative snapshot of some of the cutting-edge research activities in the field, illustrating new developments, applications, and analyses of these versatile materials by a growing community of scientists, engineers, designers, and architects, working on a continuum of experiments to modeling. The guest editors sincerely hope that this Focus Issue will serve as a timely resource for those interested in porous, foamed, and cellular metals and alloys, with pores and features at all length scales.

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### ON THE COVER:

The image displays a series of volume rendering from X-ray nano-tomography reconstruction, showing the 3D morphological evolution of an Al-Fe-Cu alloy during dealloying process, generating bimodal pores from micro-to-nano scales. The significance includes both the ability to design and create multiscale porous metals, as well as the advanced synchrotron nano-tomography characterization method used to visualize this process directly.

While it was demonstrated in this particular alloy, the image represents several key aspects in the field: 1) the ability to design and fabricate porous metals with hierarchical structure, and 2) the ability to analyze and understand the process *in situ*.

The character and the nature/reason of the change it demonstrates is a process to form multiscale porosity in ternary



**Figure 2:** (a) Upward view of the Eiffel Tower in Paris, showing hierarchical structure of 18,000 iron parts (mostly struts) connected with 250 million rivets.<sup>59</sup> (b) *The Hive*, installed in London's Kew Gardens in 2016, simulates a living beehive. Its lattice, 17 m in height, comprises 170,000 aluminum struts and connectors.<sup>60</sup> (c) A view inside the Bao'an airport at Shenzhen, with a 450,000 steel member structure allowing for high earthquake loads, with cross bracings providing high stiffness<sup>61</sup> (photo courtesy: Prof. J. Huang, Northwestern University, IL, USA).

alloys, with the micro-pores formed from chemical etching, and the nanopores formed from a dealloying process.

The work was conducted by Lijie Zou, Mingyuan Ge, Chonghang Zhao, Qingkun Meng, Hao Wang, Xiaoyang Liu, Cheng-Hung Lin, Xianghui Xiao, Wah-Keat Lee, Qiang Shen, Fei Chen, Yu-chen Karen Chen-Wiegart, see *ACS Appl. Mater. Interfaces*. 12(2), 2793 (2020). The X-ray nano-tomography was conducted at the Full Field X-ray Imaging of National Synchrotron Light Source II, Brookhaven National Laboratory. Images were created by Chonghang Zhao and Lijie Zou.

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