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Review

The enabling role of dealloying in the creation of specific hierarchical porous metal structures—A review

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ABSTRACT

Hierarchical porous materials exist widely in nature as a result of the survival rules of nature. Inspired by the unique properties of these native hierarchical porous materials, researchers have long endeavoured to develop hierarchical porous metal materials for specific industrial needs. This review discusses the developments to date in hierarchical porous metallic materials by focusing on dealloying-enabled hierarchical porous structures, with or without the combination of other manufacturing processes, and their distinctive properties and industrial applications. It is shown that the dealloying method opens up new avenues in the creation of functional hierarchical porous metals for a wide variety of promising applications.

1. Introduction

Hierarchy is a general organisational or ordering rule of nature, and natural hierarchy can be found everywhere in nature, with or without our cognizance [1,2]. For example, hierarchical tissue organisation acts as a general mechanism to limit the accumulation of somatic mutations [3]. Natural porous materials are no exception. Common examples include butterfly wing, macaw feather, plant leaf and stem, wood, cotton, bone, diatom, kelp and coral, which all contain hierarchical porosity ranging from nanoscale to microscale or even to milliscale [4,5]. This multiscaled hierarchical porosity is critical to ensure both their survival and functions in nature, e.g., the transport of necessary electrolyte, ions and nutrients at required flow rates and profiles to cells in different parts of the plant, in addition to the provision of the basic structural stability (see Fig. 1a) [4]. The exceptional hierarchical porous structure that makes up the wings of a green hairstreak is even more revealing [6]; it offers structural colouration (optical property) for survival, communication and other functions. In these and many other examples in nature, porous material structures derived their distinctive properties through the natural hierarchy of their internal structural units.

Inspired by nature, researchers on porous materials have long focused on developing hierarchical porous materials for specific industrial needs [7–9]. For example, in catalysis, hierarchical porous substrates can markedly enhance the interactions between host and guest molecules, where fine pore channels offer a high specific surface with numerous catalysing sites, whilst coarse pore channels facilitate timely and consistent transport of guest molecules to catalysing sites [10]. Another notable example is about bone implants. Bone-mimetic metal implants with hierarchical porosity can outperform both dense and monoporous implants due to improved biocompatibility and functionality [11,12]. Recently, an innovative use of the interplay between light and hierarchical porosity has enabled the development of hierarchical porous material sensors for unique applications [13]. Owing to their increasingly widespread impact, the last two decades have witnessed extensive in-depth studies on hierarchical porous materials, including hierarchical porous metals, oxides, carbon, polymers and composites [14–17]. A detailed literature survey (Supplementary Tables 1 and 2) has found that a comprehensive review of hierarchical porous metallic materials is missing, despite the substantial developments made over the last decade.

Dealloying, which is a selective corrosion process, has proved to be a potent approach for the fabrication of both monoporous (i.e., nanoporous or microporous) and hierarchical (i.e., micro-nano) porous metal structures (see Fig. 1b) with novel properties. Although several reviews have been published on dealloying since 2007 (Supplementary Table 2) [19–22], none has focused on the development of hierarchical porous metal structures enabled by dealloying (with or without the combined use of other manufacturing processes). On the other hand, as shown in Supplementary Fig. 1(a,b), research on hierarchical porous metal structures based on dealloying has attracted substantial interest in recent years due to the simplicity, affordability and high effectiveness of dealloying. In addition, new exciting developments have begun to take shape in the field. For example, the combination of additive manufacturing (AM) or 3D printing with dealloying is now capable of

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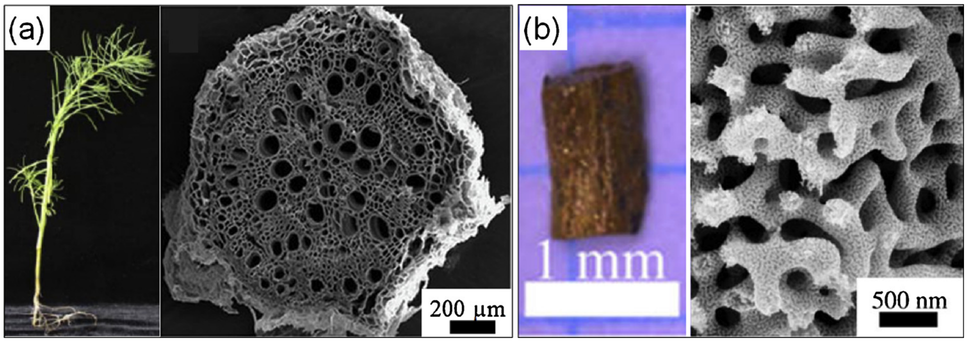

Fig. 1. (a) Hierarchical porous structures in the stem of Suaeda glauca consisting of channels and pores across multiple length scales [4]. (b) Hierarchical porous gold structures achieved by dealloying [18].

producing unprecedented hierarchical porous metal structures. This review discusses the developments to date in hierarchical porous metal materials, including their distinctive properties and important industrial applications. In particular, we will focus on the enabling role of dealloying in realising sophisticated hierarchical porous metal structures, with or without the combination of other manufacturing processes, from both research and application perspectives.

2. Primary methods for the fabrication of hierarchical porous metallic materials

A variety of methods has been developed to fabricate hierarchical porous metallic materials. The four primary methods are sintering, additive manufacturing, templating and dealloying. Their key features are briefly discussed below.

2.1. Sintering

Sintering has long been used to fabricate porous metallic materials [23]. For example, self-lubricating sintered aluminium bearings having 18–20% porosity were developed and used in the early 1960s [23], where the production process included cold pressing of aluminium powder at 70–140 MPa and sintering at 600 °C for 10–30 min, followed by impregnating and sizing. The sintering technique applies to most metal powders and can be used for mass production of net-shaped porous metal products.

A more commonly used approach is by sintering of a mixture of metal powders and space holders, followed by the removal of the latter [24–27]. This approach is, however, limited to the production of porous materials with isolated pores. In addition, the porosity or relative density is limited. Space holder materials in different sizes and shapes can be introduced simultaneously to enable the design and fabrication of hierarchical porous structures (Fig. 2a). A wide variety of materials can be used as space holders, including ceramic particles, hollow ceramic spheres, polymer grains, hollow polymer spheres, salts, metal particles or hollow metal spheres. Experimental evidence has shown that papers consisting of cellulosic fibres < 50 μm can also serve as space holder materials [28]. Their removal is facile and can be achieved by thermal treatment, leaching, or use of an aqueous solvent [24]. Besides, bimodal porous metal structures can be fabricated as well by sintering of fine metal powders dispersed with coarse space holders. Fig. 2(b and c) shows such a bimodal porous Ti structure where the large pores (525 μm–1500 μm) are obtained from the removal of Mg space holders while the smaller pores (30 μm–220 μm) result from the sintering of Ti powders [29]. The residual space-holders, if removed incompletely, can be a concern for specific applications. Another limitation is that it is challenging to produce sub-micron pores due to the difficulties to disperse ultrafine space-holder particles in metal powder. The hierarchical porous structures produced by this approach are thus restricted to microscaled pores, which are insufficient for specific industrial applications.

Apart from sintering of metal powders, sintering of metal fibres (e.g., stainless steel [30,31], Cu [32]) can also produce hierarchical porous structures, referred to as metal fibre felts as shown in Fig. 2(d and e) [30–32]. In this process, different diameters of metal fibres are randomly packed and pressed into a felt, and sintered subsequently at a high temperature in vacuum or a protective atmosphere. The resultant hierarchical porous structure is dependent on the metal fibre mixtures and sintering parameters used.

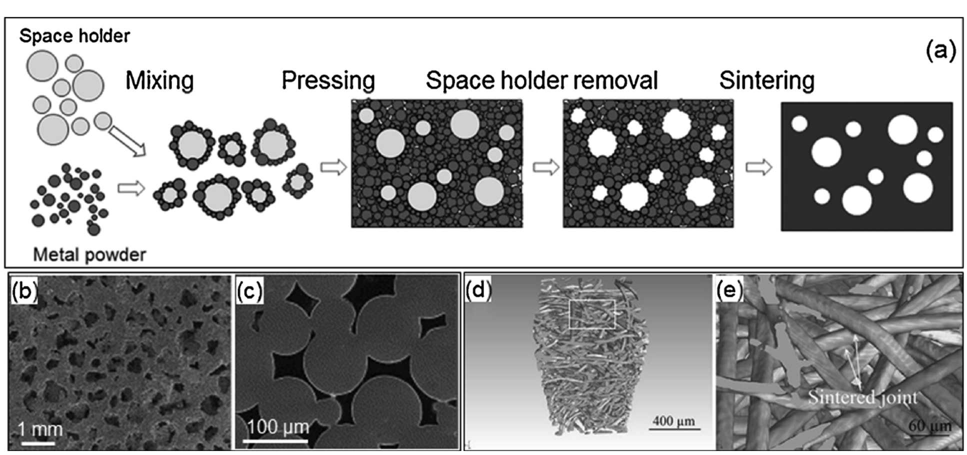

Fig. 2. (a) Schematic of the space-holders approach for the fabrication of hierarchical porous metals. (b and c) Bimodal porous Ti [29]: large pores from the removal of Mg space holders and smaller pores from sintering of Ti powders. (d and e) As-sintered stainless steel fibre felts (hierachical) [30].