Chapter 2
Formation and Microstructural Regulation of Nanoporous Metals

Abstract In the past 15 years, dealloying has been growing into the most important method to fabricate nanoporous metals. In this chapter, we will address the dealloying-driven formation of nanoporous metals, the methods to characterize the microstructures of nanoporous metals, as well as the strategies to regulate the microstructures of nanoporous metals. Dealloying is a common corrosion process, during which the less noble element(s) is selectively etched away and the more noble element(s) is retained to form a nanoporous structure. First, we briefly discuss the history of dealloying, including “depletion gilding” at the time of pre-Columbian Central America and the early Middle Ages in European and Near Eastern, Raney® metals dealloyed from Al-based precursors in 1920s, and dealloying to form functionalized nanoporous metals at the beginning of this century. Additionally, in the most time of last century, people were concerned with dealloying mainly from the viewpoint of corrosion/protection. To understand the dealloying mechanisms is crucial to the design/fabrication of nanoporous metals. We then outline the related mechanisms being operated in the dealloying process. Since the 1960s, in situ/ex situ experiments and computer simulations have been performed to unveil the formation mechanism of nanoporous metals during dealloying, considering the selective dissolution of the less noble element(s), the surface diffusion of the more noble element(s), the critical potential, and the parting limit. The influence of anions (like halide ions) and the phase constitution should also be taken into consideration. Nanoporous metals exhibit a three-dimensional bicontinuous ligament (metal)-channel (void) structure. Many techniques can be used to characterize the microstructures of nanoporous metals, including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM, scanning TEM, scanning tunneling microscopy (STM), energy dispersive X-ray analysis, small angle neutron scattering (SANS), and so forth. Three-dimensional tomographic reconstruction is also popular to reveal the interior microstructures of nanoporous metals. In addition, the methods to evaluate the characteristic length scale and the specific surface area of nanoporous metals are also reviewed. In the last section of this chapter, we discuss how to regulate the microstructures/compositions/morphologies of nanoporous metals. First, we talk about the design of precursors for dealloying, considering the composition (elements), phase constitution, crystallinity, and
microalloying. Second, the microstructural regulation of nanoporous metals can be achieved by controlling over the dealloying parameters, including chemical/electrochemical dealloying, the dealloying solution, temperature, the applied potential, the dealloying step (two-step or multistep), the effect of atmosphere, and dealloying in nonaqueous media. The post-dealloying treatment has also been briefly outlined. Third, we discuss the strategies which are often adopted to further modify nanoporous metals, based upon their potential applications.

**Keywords** Dealloying • Nanoporous metals • Formation mechanisms • Microstructural characterization • Microstructural regulation

### 2.1 The Dealloying Method and Its History

Dealloying is the most important method to fabricate nanoporous metals. Eventually, dealloying is a common corrosion process during which an alloy is “parted” by the selective dissolution of the most electrochemically active element(s) [1]. For a binary alloy to be dealloyed, one element should be more noble (or inert) and another element should be less noble. During dealloying, the less noble element is selectively etched away (into the dealloying solution or electrolyte) and the more noble element is retained. Figure 2.1 schematically illustrates the dealloying process of a binary alloy.

In fact, dealloying is an ancient process and has a long history. Indians of pre-Columbian Central America had invented a depletion gilding technique for the coloration of castings prepared from copper–gold alloys (also referred to as tumbaga or tumbago), Fig. 2.2 [2]. Depletion gilding is such a process by which the surface of a dilute gold alloy becomes gold-enriched by the selective removal of the less noble component. At that time, the depletion gilding process involved by either the removal of Cu from the Cu–Au alloy surface in a corrosive solution, or the dissolution of Cu oxides which were formed by heating the Cu–Au alloys in air. North Peruvian

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**Fig. 2.1** Schematic illustration of the dealloying process of a binary alloy
craftsmen also used similar processes to decorate objects made from silver-based alloys [2]. In addition, before the early Middle Ages, European and Near Eastern goldsmiths had used a very closely related process (known as cementation) for the coloration of silver–gold alloys [2]. They removed Ag from the Ag–Au alloy objects by forming soluble chlorides, making the surface of objects gold-rich. Of course, at that time, people had not known the formation of nanoporous structures on the surface of objects during the dealloying or depletion gilding process.

Another important thing for dealloying is the invention of Raney® metals which were named after their inventor Murray Raney. In 1925, Raney got a patent on the preparation of Raney® metals [3]. Typically, Raney® metals could be fabricated by dealloying Al-based alloys (such as Al–Cu, Al–Ni, Al–Co, Al–Fe, Al–Ag, etc.) in alkaline solutions. During these processes, the more active Al is selectively removed from the Al-based alloys and the non-active element(s) is retained to form Raney® metals with high specific surface areas. Until now, Raney® metals are still important industrial catalysts for hydrogenation reactions [4]. For example, Huber et al. [5] have reported that tin-promoted Raney nickel catalyst could promote the production of hydrogen (H_2) by aqueous phase reforming of biomass-derived oxygenated hydrocarbons at temperatures near 500 K. And the performance of this non-precious metal catalyst compares favorably with that of platinum-based catalysts for production of hydrogen from ethylene glycol, glycerol, and sorbitol. However, these high surface area metal catalysts are often practiced in an engineering manner, and the correlations among structures, morphologies, and properties are less appreciated and understood.

In the most of the twentieth century, dealloying received great attention in the context of corrosion, including stress corrosion cracking (SCC) and corrosion fatigue, such as dezincification of brass [6–13]. For example, it was found that binary Cu–Zn alloys cracked intergranularly in the ammoniacal solutions, whereas cracking was transgranular in the ternary Cu–Zn–Ni alloy. Dealloying was observed to be a common feature of both modes of cracking, and occurred only during crack propagation and not during the incubation period before crack propagation.
initiation [6]. People investigated the dealloying phenomena and mechanisms of alloys in different environments, but mainly thought about how to avoid the occurrence of dealloying and to protect the alloys.

At the beginning of the new century, dealloying has been receiving renewed attention due to the fact that some alloy systems undergo nanoporosity evolution upon dealloying to form functional nanostructured porous metals. Different from the role of dealloying in corrosion/protection of alloys, this time people consider how to use the powerful top-down strategy to fabricate nanoporous metals. As early as in 1963, Pickering and Swann [14] first used transmission electron microscopy (TEM) to investigate the dealloyed microstructures of copper–gold, copper–aluminum, copper–zinc, and magnesium–aluminum alloys. They have found that the pitting or tubular type of attack may be initiated at grain boundaries and antiphase boundary junctions in ordered copper–gold alloys, gold alloys, and the superficial chemical disturbance can be as small as a six-atom cluster. In 1979, Forty [2] for the first time presented TEM micrographs for a free-standing nanoporous gold (NPG) membrane material with a pore size of approximately 20 nm, which was made by etching an Ag–Au (50–50 wt%) alloy film in 50 % HNO₃ solution. Almost at the same time (in 1980), Keir and Pryor [15] revealed the porous and brittle nature of the Cu-50 % Mn alloy polarized at 0 V for 20 h in 0.5 M NaCl solution, using scanning electron microscopy (SEM). In 1991, an in situ scanning tunneling microscope (STM) was used to observe the morphological changes accompanying the selective dissolution of Ag from low Ag content Ag–Au alloys in dilute perchloric acid [16]. In 2001, Erlebacher et al. [1] further clarified the underlying physical mechanism of dealloying of Ag–Au alloys using experiments and computer simulation. Since then, dealloying-driven nanoporous metals have been receiving more and more attention, as a novel type of nanostructured porous metallic materials.

Figure 2.3 summarizes the history of dealloying and the dealloying-driven phenomena/materials.

Fig. 2.3 The history of dealloying
2.2 Formation Mechanisms of Nanoporous Metals by Dealloying

Since the 1960s, efforts have been dedicated to clarify the dealloying mechanisms. Theoretically, when one metal is preferentially dissolved one or more of the following three mechanisms may operate: (i) both metals ionize followed by redeposition of the more noble metal; (ii) only the less noble metal ionizes and enters the solution while the atoms of the more noble metal aggregate by surface diffusion; (iii) only the less noble metal ionizes and enters the solution and atoms of both metals move in the solid phase by volume diffusion. However, the experimental results indicate that interdiffusion of the constituent metals in the Cu–Au alloy occurs to a significant extent and dissolution of Au does not take place, and electrochemical measurements with a Cu–Zn alloy give no indication of occurrence of the ionization–redeposition mechanism [17]. Electron microscope observations of Cu$_3$Au exposed to a ferric chloride solution suggested that surface diffusion or ionization and redeposition of Au occur on the walls of corrosion tunnels, and no evidence was found to support the volume diffusion theory [18]. Later, Forty et al. [2, 19, 20] proposed a corrosion disordering/diffusion reordering model, Fig. 2.4. They have argued that the formation of the island channel structure can be explained by this model in which corrosion proceeds by selective dissolution of the less noble component, thereby creating a disordered surface layer which subsequently reorders by surface diffusion of gold adatoms during dealloying of Ag–Au alloys. Pryor and Fister [21] have shown that dealloying cannot propagate into the Cu-based alloys by diffusion of solute from the bulk to the surface. Instead, dealloying is maintained by solution intrusion under conditions where continuous solute paths exist in the alloy and where solute removal results in atomic rearrangement of the depleted alloy.

Kaesche [22] has argued that dealloying requires the nucleation of terrace site vacancy clusters, since easily dissolvable kink sites of screw dislocations are blocked by noble metal atoms. Based upon the percolation theory, Sieradzki et al. [23] have
developed a new model to account for all the known features of dealloying, including a porous morphology of the dealloyed residue, coarsening of this porosity, sharp dealloying thresholds or parting limits, and the development of intermediate compositions. Their Monte Carlo simulations give a support to the mechanism involving the selective dissolution of the reactive element and surface diffusion of the more noble element during dealloying. In situ scanning tunneling microscopy (STM) results show that there exist three different regimes during dealloying of Cu$_3$Au [24]. At low overpotentials, two-dimensional clustering of gold atoms occurs near sites of copper dissolution due to the highly mobile nature of the surface species. At higher potentials, the electrode is largely passivated by the enrichment of gold. However, there exist small localized regions of three-dimensional roughness which may be correlated to extended dealloying catalyzed by bulk solid-state defects. When the potential is increased above the critical potential ($E_c$), global surface roughening occurs by nucleation and growth. At the same time, in situ STM was also used to observe the morphological changes accompanying the selective dissolution of Ag from low Ag content Ag–Au alloys in dilute perchloric acid [16].

The authors have argued that the selective dissolution can be interpreted within the framework of the kink-ledge-terrace model and percolation theory. The corrosion process leads to roughening of the surface by dissolution of Ag atoms from terrace sites at high overpotentials. Sieradzki [25] further proposed that dissolution of the less noble constituent can proceed only by injection of regions of negative curvature into the solid surface, and the critical potential for macroscopic selective dissolution is associated with a kinetic roughening transition which results from a competition between curvature-dependent dissolution and surface diffusion. Smith et al. [26] believed that the overall mechanism of formation/rearrangement of the Raney® copper structure was found to be mainly dissolution/redeposition of copper atoms, with surface or volume diffusion, or possibly both, playing a minor role.

At the very beginning of this century, a continuum model was proposed by Erlebacher et al. [1] to rationalize experiments and theoretical simulations of dealloying. They have demonstrated that nanoporosity in metals is due to an intrinsic dynamical pattern formation process involving the formation of nanopores because the more noble atoms are chemically driven to aggregate into two-dimensional clusters by a phase separation process (spinodal decomposition) at the solid/electrolyte interface. Figure 2.5 clearly shows the simulated nanoporosity evolution during dealloying of Ag–Au alloy at a fixed potential. Erlebacher [27] further described the microscopic details of porosity formation during dealloying using a kinetic Monte Carlo model incorporating site coordination-dependent dissolution of the less noble atoms and site coordination-dependent surface diffusion of all alloy components. His simulation model reproduces the entire range of phenomena associated with dealloying, including composition and geometric restrictions on dealloying (parting limit), a composition-dependent critical potential, a passivation regime, a regime of steady-state dissolution flux, and porosity formation. Moreover, the formation and undercutting of the more noble islands as well as the bifurcation of pores play an important role in the nanoporosity evolution during dealloying.
Conventionally, the critical potential represents the potential marking the onset of bulk dealloying, Fig. 2.6. The current density below the critical potential is only weakly dependent on potential, and the physical processes responsible for this passive-like behavior are poorly understood. Wagner et al. [28] used in situ STM to study the nature of the surface morphology which develops at potentials less than the critical potential. They found that at fixed potential, the time-dependent evolution of the surface morphology was correlated with the observed current decay. Two general regimes of power-law behavior in the current decay exist,

![Fig. 2.5 Simulated evolution of an artificial pit in Au10–Ag90 % (at.%), \( \phi = 1.8 \) eV. Cross sections along the (11-1) plane defined by the yellow line in (a) are shown below each plan view.](image)

- **a** The initial condition is a surface fully passivated with gold except within a circular region (the “artificial pit”).
- **b** After 1 s, the pit has penetrated a few monolayers into the bulk. We note how there are fewer gold clusters near the side wall than at the center of the pit.
- **c** After 10 s, a gold cluster has nucleated in the center of the pit.
- **d** At 100 s, the pit has split into multiple pits; each will continue to propagate into the bulk to form a porous structure. (Reproduced from Ref. [1]. Copyright 2001, Nature Publishing Group)
corresponding to exhaustion of an activation-controlled dissolution process ($t^{-1}$) and the operation of one of three mechanisms of surface mass transport control ($t^{-5/8}$, $t^{-1/2}$, and $t^{-1/4}$). Erlebacher [27] has found that an intrinsic critical potential exists as a well-defined threshold potential separating surface passivation and porosity formation behaviors, but this intrinsic critical potential typically sits at values well below the experimental measurements of the empirical critical potential. Dursun et al. [29] developed a steady-state method to accurately determine the dealloying critical potential, and found that the more traditional approach of extrapolation from anodic polarization data could overestimate the critical potential of Ag–Au alloys by $\sim 100 \text{ mV}$. Furthermore, morphological investigations confirm the presence of porosity for a potential hold only 10 mV above the critical potential.

The conventional view of morphology evolution in the region below the critical potential is that the alloy surface maintains a stable planar interface while enriching in the more noble constituent. Renner et al. [30] performed atomic scale observations of the initial stages of corrosion of a Cu$_3$Au (111) single crystal alloy within a sulphuric acid solution by in situ X-ray diffraction (XRD) with picometrescale resolution. They observed the formation of a gold-enriched single crystal layer with thickness of two to three monolayers and an unexpected inverted (CBA-) stacking sequence, below the critical potential. At higher potentials, the protective passivation layer dewets and pure gold islands are formed. STM images further indicate an interlayer exchange of topmost surface atoms during initial dealloying of Cu$_3$Au (111) single crystal alloy, while scanning Auger electron microscopy (SAEM) data clearly reveal that the surface is fully covered by a continuous Au-rich layer at an early stage. Initiating below this first layer a transformation from stacking reversed toward substrate-oriented Au surface structures is observed close to the critical potential [31]. Below the critical potential, no distinct diffraction signal is evidenced by in situ XRD but atomic force microscopy (AFM) reveals the existence of islands on the surfaces of Cu$_3$Pd single crystal [32].

Kamundi et al. [33] have found that the dealloying critical potential of (111) oriented alloys is systematically more positive than the one for polycrystalline alloys with identical composition. Thin alloy films (thickness of 20–100 nm) exhibit almost
identical $E_c$ to the bulk samples, whereas spherical particles (diameters $\sim 100$ nm) feature consistently lower $E_c$ (by about 0.050–0.100 V). A trend toward even lower $E_c$ (0.300–0.450 V) is illustrated by the dealloying of Au$_x$Ag$_{(1-x)}$ nanoparticles (NPs, diameter 10–15 nm). Moreover, no dealloying threshold applies to Au$_x$Ag$_{(1-x)}$ NPs. Oezaslan et al. [34] reported the particle size dependence of dealloyed morphology for Pt–Co and Pt–Cu alloy nanoparticles with diameters of several to 100 nm (the morphology of “single core–shell nanoparticles,” “multiple cores–shell nanoparticles,” and “surface pits/nanoscale pores” takes place with increasing particle size). Through Kinetic Monte Carlo simulations, Callejas-Tovar et al. [35] have found that two critical potentials define regions where Pt-based alloy nanoparticles may exist as core–shell, porous, and hollow structures after dealloying. Chen and Sieradzki [36] have recently demonstrated that dealloying of Li from Li–Sn alloys depends on alloy composition, particle size and dealloying rate, and all known dealloyed morphologies evolve including bicontinuous nanoporous structures and hollow core–shell particles. Cui et al. [37] have found that the PtNi octahedra nanoparticles preferentially leach in their facet centers and evolve into “concave octahedra.” Li et al. [38] have demonstrated that above the potential corresponding to Ag$^+/Ag$ equilibrium only core–shell structures evolve in the 2–6 nm diameter particles, and dealloying of the 20–55 nm particles results in the formation of porous structures analogous to the behavior observed for the corresponding bulk alloy. Similar results have also been reported for PtNi$_3$ nanoparticles by Rudi et al. [39]. Most recently, Han et al. [40] have found that smaller size, less-oxidative acid treatment and annealing significantly reduced Ni leaching and nanoporosity formation in PtNi$_3$ nanoparticles while encouraged surface passivation.

Petegem et al. [41] studied the evolution of the grain structure, internal strain, and the lattice mis-orientations of NPG during dealloying of bulk (3D) Ag–Au alloy samples by various in situ and ex situ XRD techniques including powder and Laue diffraction. Their experiments revealed that the dealloying process preserves the original crystallographic structure but leads to a small spread in orientations within individual grains. Initially, most grains develop in-plane tensile stresses, which are partly released during further dealloying. Simultaneously, the feature size of the developing nanoporous structure increases with increasing dealloying time.

The formation of NPG by open-circuit dealloying of 100 nm Ag–Au foils in nitric acid was investigated in situ and in real time by combining synchrotron small angle X-ray scattering (SAXS) and XRD. Several characteristic dealloying stages are observed, Fig. 2.7. First, there is a fast initial dissolution stage with an increase in surface area due to pore and mound formation, which leads to capillary pressure induced strain in NPG. After dissolution is complete, there is rapid coarsening of the quasiperiodic, pore–ligament morphology, together with strong strain anisotropies. Then a slow coarsening stage occurs where the SAXS patterns and the quasiperiodic morphology are self-similar in time. There is a strong correlation between the morphology evolution and strain development, which can be explained by capillary forces [42]. Galinski et al. [43] probed the dominating physical mechanisms of nanoporosity formation during the dealloying process of Pt–Al films, using focused ion beam (FIB) nanotomography and Rutherford backscattering spectroscopy (RBS). The RBS and FIB results show that the porosity evolution has to be regarded
as superposition of two independent processes, a linearly propagating diffusion front with a uniform speed and a slower dissolution process in regions which have already been passed by the diffusion front. The experimentally observed front evolution is captured by the Fisher–Kolmogorov–Petrovskii–Piskounov (FKPP) and the slower dissolution is represented by a zero-order rate law which causes a gradual porosity in the thin film. Recently, Ye et al. [44] have found that the dealloying of Au–Ag and Au(Pt)–Ag alloys occurs by two processes: a primary dealloying process that selectively dissolves Ag from the parent alloy and creates a nanoporous (np) structure, and a secondary dealloying process that occurs behind the corrosion front and further dissolves the residual Ag from the nanoligaments. The secondary dealloying can occur during coarsening, and/or when a more anodic potential is applied. With suppressed np structure coarsening in Pt-containing samples, the intrinsic np structure created by the primary dealloying contains small ligament diameter (3–7 nm) and high concentration of residual Ag (~50 at.%), irrespective of the dealloying potentials.

Chen-Wiegart et al. [45] have reported that the dealloying process can be directly imaged by using transmission X-ray microscopy (TXM) for the case of an Ag–30 at.% Au wire dealloyed under free corrosion in nitric acid. The propagation of a sharp dealloying front separating the alloy from nanoporous Au was observed by two-dimensional real time in situ imaging at 30 nm resolution, Fig. 2.8. They have found that the rate of the dealloying front propagation is independent of the dealloying time up to a 3 μm depth, indicating that the dealloying process to this depth is dominated by interfacial effects (i.e., gold surface diffusion and/or silver dissolution) rather than long-range transport effects (i.e., diffusion of acid and corrosion product in and out of the porous layer). Moreover, the dealloying front velocity depends exponentially on the alloy Ag/Au atomic ratio and the acid molar concentration [46]. Upon dealloying via successive voltammetric sweeps between −0.05 and 1.15 V versus standard hydrogen electrode, compressive stress develops in the dealloyed Pt layer at the surface of thin-film PtCu electrodes [47].
It should be noted that the minor dissolution of the more noble element is also possible during dealloying, especially when the electrolyte contains Cl\(^-\) or other halide ions. During electrochemical dealloying of brass in aqueous sodium chloride solution, Cu dissolves into the solution to form Cu(I) and Cu(II) complex ions [48]. At appropriately high dealloying potentials, relatively steady chloride compound or chloride complexes can form between chloride ion and the more noble metals included, such as soluble AuCl\(_3\)^-\, PdCl\(_2\), AgCl\(_2\)^-\, CuCl\(_2\)^- and insoluble AgCl and CuCl during the electrochemical dealloying of Al-based alloys [49]. Moreover, inductively coupled plasma (ICP) measurements also verify the existence of minor Ag ions in the electrolyte after chemical dealloying of Mg–Ag–Pd alloys [50]. In addition, Starr and Buttry [51] have reported that dealloying of the more noble gold atoms from the alloy NPs was also achieved by cyclic voltammetry (CV) in sodium chloride. The silver was oxidized first to cohesive silver chloride, and then gold dealloying to soluble HAuCl\(_4\) occurred at higher potentials. Chen et al. [52] developed a novel converse dealloying method to fabricate free-standing nanoporous silver (np–Ag). One remarkable characteristic of the new dealloying method is that inert component (Au) is selectively removed from Au–Ag alloys while active component (Ag) is left undissolved. Thiourea plays a key role in the formation of a free-standing porous Ag framework since it not only leads to anodic dissolution of Au component but also causes the surface passivation of Ag component.

In addition, halide ions also play a significant influence on the formation of nanoporous metals during dealloying of precursors in halide ion-containing solutions. It is generally accepted that the addition of halide ions into the solution could accelerate the surface diffusion of the more noble element during dealloying. It has been found that the electrochemical dealloying mechanism of Al\(_2\)Au in the neutral NaCl solution can be explained based upon pourbaix diagram and chloride ion effect [53]. During the dealloying process, a self-acidifying effect is triggered due to the dissolution and instant hydrolysis of Al\(^{3+}\)/Al, which is assisted by chloride ions in the electrolyte. The dissolution of Cu to form soluble CuCl\(_2\)^- complex also

Fig. 2.8  a Series of X-ray transmission images showing the dealloying front propagation with ex situ imaging (sample A). The dealloying front is highlighted with a *dashed line*. b Cross section of tomographic reconstruction of the selected volume marked in yellow in (a); the dealloying front is highlighted with *arrows*. (Reproduced from Ref. [45]. Copyright 2013, Elsevier)
contributes to the dealloying of MgCu2 and the formation of nanoporous copper [54]. Hakamada and Mabuchi [55] reported the spontaneous formation of NPG prism microassembly with highly dense skins, which was caused by the chloride ion enhanced surface diffusion of gold atoms in concentrated hydrochloric acid. Renner et al. [56] have also argued that chloride additives enhance the surface diffusion and respective morphologies are observed earlier during electrochemical dealloying of Au3Cu single crystal.

We systematically investigated the electrochemical dealloying of single-phase Al2Au alloy in sodium halide aqueous solutions at different temperatures [57, 58]. The Al2Au alloy is passivated in NaF solution but can be dealloyed in NaCl, NaBr, and NaI solutions, leading to typical NPG. The open-circuit potential is susceptible to the halide species, and the amount and pattern of cracks in the obtained NPG as well as the sizes and homogeneity of ligaments are remarkably affected by the halide ions. It has been found that the surface diffusivities of gold adatoms increase with the increase of temperature in a given halide solution, and also increase following the sequence of Cl− < Br− < I− at a given temperature. Besides, the activation enthalpy decreases following the sequence Cl− > Br− > I−. The open-circuit potential of the single-phase Al2Au alloy markedly decreases with increasing electrolyte concentration, as well as the corrosion potential of Al2Au. The steady-state current density markedly increases, and the dealloying time visibly decreases with increasing chloride ion concentration in the NaCl solutions. There exists a good linear relationship between the surface diffusivities of Au adatoms and the electrolyte concentration, and the activation energy visibly decreases with increasing chloride ion concentration in the electrolyte at the given overpotential. Ankah et al. [59] also found that the additions of halides (Cl−, Br−, I−) have a pronounced effect on the dealloying process of Cu3Au (111) in acidic solutions and lead to peculiar changes in the resulting surface morphologies.

If multiple phases exist in the alloy, Pugh et al. [60] argued that porosity formation of any individual phase would follow the same requirement for a single phase, and hence typically only the A-rich phase would dealloy (Here A is the less noble element). In this case, dealloying would be isolated to only surface grains unless a mechanism existed for the penetration of the electrolyte throughout the alloy; for example, the A-rich grains form a percolating path through the alloy. As for a two-phase alloy, we have found that the dealloying process depends not only upon the activity difference of the constituent elements, but also on the composition, activity, defect (for example vacancy) concentration and electrochemical properties of each phase in the alloy [49, 61–67]. According to the reactions (being excavated, dealloyed, or retained) of the constitutive phases in a biphasic alloy during dealloying, six types of dealloying are classified, Table 2.1 [49]. Three scenarios (type II, IV, and V) involve the formation of nanoporous structure during dealloying of a two-phase alloy. Moreover, it is suggested positively by type II and IV that the dealloying of bi-phasic alloys is quite versatile and effective in fabricating nanoporous metals with controllable morphologies (bimodal pore size distribution and nanoporous composites). Also in the case of type II and IV, the excavation or dealloying of the less noble phase probably has an obvious catalytic effect on the
dealloying of the more noble phase. For example, the dealloying of $\alpha$-Al accelerates the dealloying of Ag$_2$Al in the biphasic Al-35–50 Ag alloys composed of $\alpha$-Al and Ag$_2$Al. Eventually, the single-phase Ag$_2$Al is totally inert in the same dealloying solution. This catalytic effect is particularly important for the dealloying of bulk samples. As shown in Fig. 2.9a, b, the Al phase can be completely etched away in an alkaline solution like NaOH, leaving large channels. The electrolyte can quickly penetrate into the inner part of the sample through these large channels, and the dealloying front can move forward much faster than the scenario of the homogeneous solid alloy like AuAg. Through this design of the precursor alloys, one could fabricate bulk nanoporous metallic samples with sizes of up to centimeters, Fig. 2.9c. Additionally, strictly speaking, the scenario of type III does not belong to the scope

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<th>Type number</th>
<th>$\alpha$</th>
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<td>I</td>
<td>Excavated</td>
<td>Excavated</td>
<td>Al-Zn in HCl</td>
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<tr>
<td>II</td>
<td>Excavated</td>
<td>Dealloyed</td>
<td>Al-20 Au, Al-30 Au</td>
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<td>III</td>
<td>Excavated</td>
<td>Retained</td>
<td>Al-Sn in dilute HCl (at room temperature)</td>
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<td>IV</td>
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<td>Pt$<em>{40}$Ag$</em>{60}$ in HCl</td>
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Table 2.1 A classification for biphasic alloys (composed of $\alpha$ and $\beta$ phases) based on the dealloying behaviors of constitutive phases in the 1 M NaCl aqueous solution. (Reproduced from Ref. [49]. Copyright 2010, The Royal Society of Chemistry)

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**Fig. 2.9** a, b Schematic illustration of dealloying in two-phase or multiphase precursor alloys (like Al—Ni). c Bulk nanoporous Ni rods dealloyed from Al$_{75}$Ni$_{25}$ in alkaline media
of dealloying-driven nanoporous metals, because no surface diffusion on the atomic scale and no nanoporosity evolution occur during the dealloying process. Although one can obtain nanoporous metals (Fig. 1.7 in Chap. 1) through dealloying of this type of two-phase precursors, the formation of this porous structure is due to one phase simply being excavated out of a two-phase material.

Normally, the minor residual of the less noble element is inevitable in the resultant nanoporous metals formed by dealloying, but less attention has been paid to the retention of the less noble element during dealloying. Recently, Liu et al. [68] have investigated factors controlling the less noble metal retention in nanoporous structures processed by electrochemical dealloying, taking Ag–Au as an example. It has been found that while the dealloying critical potential is generally independent of pH, the dissolution rate is strongly affected by the solution acidity. pH substantially affects Ag retention in both the oxide and alloy forms. They have found that the pH and dissolution rate affect more significantly the amount of Ag retained in the form of oxide (AgO), while the dealloying potential has a stronger impact on Ag trapping. In addition, it is generally accepted that the residual less noble element can not be completely removed but asymptotically reaches a limit at exhaustively long etching times (up to 100 h) [23].

At present, although people have known some aspects in dealloying-driven formation of nanoporous metals, the intrinsic physical and chemical mechanisms involved in the dealloying process need to be further clarified using both experiments and computer simulations. For example, it has been found that Cu3Pt nanoparticles underwent surface dealloying to form core–shell structure under electrochemical conditions, while volumetric dealloying would occur to form a nanoporous structure under chemical dealloying conditions [69]. But the underlying reason for these phenomena is still unclear. On the one hand, people should know how to understand and determine the parting limit and the critical potential of each precursor alloy. On the other hand, people should also unveil some processes possibly occurring during dealloying, including the selective dissolution of the less noble element(s), the surface diffusion/reorganization (or dissolution–redeposition) of the more noble element(s), the penetration of the electrolyte into the precursor, the nucleation/growth of the ligaments, and so forth. Based upon these, novel precursor alloy systems suitable for dealloying could be explored, and nanoporous metallic materials with ideal morphologies/compositions/structures could be designed and fabricated.

2.3 Microstructure and Characterization of nanoporous Metals

Nanoporous metals possess a unique porous microstructure and combine the properties of both metals and nanostructured materials. In this section, we mainly outline the methods to characterize the microstructures of nanoporous metals.
It is known that the formation of nanoporous metals normally undergoes the surface diffusion and reorganization of the more noble element(s) during dealloying. And thus, phase transformation also takes place in the dealloying process. XRD is the most efficient and also facile method to identify the phase constitution of the precursors and the as-dealloyed samples. For example, Fig. 2.10 shows the phase constitutions of the rapidly solidified Al-based binary precursor alloys and the corresponding nanoporous metals [70]. It can also be seen that digit camera can easily capture the appearance (color) of both the monolithic precursors and the as-dealloyed samples. In addition, it should be noted that the combination of XRD with other methods like TEM and selected area electron diffraction (SAED) can exactly determine the phase constitution of nanoporous metals. Coherent diffraction imaging (CDI) is a method by which the transmission function of a nonperiodic object is recovered from its XRD pattern. X-ray CDI offers nondestructive three-dimensional characterization of electron-dense materials at nanometer length scales beyond the resolution of current x-ray lenses, and access to the full complex refractive index of the material. Kim et al. [71] have demonstrated the use of physically justified object constraints in X-ray Fresnel CDI on NPG, enabling highly reliable imaging of the sample’s shape and pore structure.

Normally, the microstructure and morphology of nanoporous metals can be simply characterized by SEM and TEM (see Fig. 1.1 of Chap. 1). It can be clearly seen from SEM/TEM that NPG (taken as an example) appears to be completely irregular in morphology for both empty pore channels and solid metallic ligaments.

![Fig. 2.10](image)
comprising the nanostructure. The distribution of solid gold ligaments and empty pore channels, if assumed as two separate phases, is analogous to the microstructure produced by traditional spinodal decomposition. In addition, the combination of TEM with SAED can determine the phase constitution and crystalline nature (single crystalline or polycrystalline) of nanoporous metals. However, plan-view SEM and TEM cannot probe the internal microstructure nanoporous metals. Fujita et al. [72] employed electron tomography along with a number of algorithms to quantitatively characterize the complex 3D nanoporous structure of NPG (Fig. 1.1c, e in Chap. 1). They found that gold ligaments and nanopore channels are topologically and morphologically equivalent, i.e., they are inverses of each other in three-dimensional space. In addition, through energy dispersive X-ray analyzer (which is normally attached to SEM), the overall composition of nanoporous metals can be determined, but the errors may be as large as \( \sim 1 \text{ at.\%} \).

Besides conventional SEM and TEM, high-resolution TEM (HRTEM) and fast Fourier transform (FFT) have also been utilized to document the microstructure of nanoporous metals. From HRTEM images and corresponding FFT patterns, one can clearly see the lattice features (fringes) of the nanoporous structure within the framework of observation, and further discern the single crystalline or polycrystalline nature of nanoporous metals. For example, NPG dealloyed from Ag–Au or Al–Au alloys generally inherits from the crystalline orientation and grain size of the precursor [70, 73]. One can clearly see lattice fringes extending throughout all of the ligaments shown in the HRTEM image (Fig. 1.13 of Chap. 1). Furthermore, crystal defects sometimes appear in the resultant nanoporous metals due to the stress generated during dealloying, especially potential-driven electrochemical dealloying. Through HRTEM observations, people can obtain the information on lattice defects in nanoporous metals, including dislocations, twins and stacking faults (see Fig. 1.14 of Chap. 1).

By using spherical-aberration-corrected TEM, one can probe the structural information of nanoporous metals on the atomic size. For example, Fujita et al. [74] revealed atomic origins of the high catalytic activity of NPG dealloyed from Ag–Au films through spherical-aberration-corrected TEM and environmental TEM. Figure 2.11 shows the scanning TEM (STEM) images under a high-angle annular dark field (HAADF) mode. The Z-contrast STEM image can well show the porous structure of nanoporous metals (here, NPG, Fig. 2.11a). The curved surfaces with a high density of atomic steps and kinks can be observed from STEM images (Fig. 2.11b–d). Low-index (100) and (110) facets as well as stepped high-index planes, such as (310) and (410), can be recognized from the nanopore surface. Unlike the (111) and (100) surfaces, the (110)-terminated facets do not form ordered terraces (Fig. 2.11d). They further performed in situ environmental HRTEM observations of NPG catalyzing CO oxidation. They found that NPG containing 1.2 at.\% Ag begins to show catalytic activity along with significant surface reconstruction (faceting), and higher Ag content (20 at.\%) could effectively suppress the faceting dynamics.

With the combination of STEM with EDX (spot analysis, line scanning and area analysis), one can also obtain the compositional information of nanoporous metals,
especially for nanoporous nanostructures (nanoparticles, nanowires or nanotubes). In addition, the morphology and atomic scale elemental distribution of nanoporous metals can be determined by aberration-corrected STEM equipped with electron energy loss spectrometer (EELS). Moreover, STEM 3D tomography reconstruction can be used to directly visualize the three-dimensional porous network of nanoporous metals [69, 75]. For example, Fig. 2.12 shows three-dimensional tomographic reconstruction of a chemically dealloyed nanoparticle (spongy) at two different viewing directions [69]. A series of consecutive slices through the isosurfaces of such nanoparticle clearly show the nanoporous networks of the nanoparticle. Hovden et al. [76] recently proposed a three-dimensional imaging

Fig. 2.11 STEM images viewed along [001] of NPG dealloyed from Ag–Au. a The labeled squares indicate the areas characterized by HAADF-STEM in the following observations. b HAADF-STEM image of a high-index (310) plane with atomic kinks. c Concave (100) plane area with flat terraces and atomic kinks. d Concave (110) plane with a non-level edge. The Inset is the color-enhanced image of the area in the dashed rectangle. (Reproduced from Ref. [74]. Copyright 2012, Nature Publishing Group)
method by combining through-focal depth sectioning and traditional tilt-series tomography to reconstruct extended objects, with high resolution, in all three dimensions (Fig. 2.13). A through-focal reconstruction over a 390 nm 3D carbon support containing over 100 dealloyed and nanoporous PtCu catalyst particles revealed with sub-nanometer detail the extensive and connected interior pore structure that is created by the dealloying instability.

Corcoran [77] explored the use of small angle neutron scattering (SANS) as potential tools for sorting out the mechanisms involved in porosity formation and characterizing the microstructure of nanoporous metals. Figure 2.14 shows the scattering intensity for dealloying times of 3–21 h. A well-defined peak indicates that the porous structure contains a well-defined average pore size. The average pore size is related to the inverse of the peak position, thus the shifting of the peak to lesser values of Q corresponds to an increasing pore size, i.e., the porosity is coarsening at room temperature during the dealloying process. In addition, STM can not only probe the dealloying process of some single crystal intermetallic compounds (such as Cu$_3$Au, Au$_3$Cu, etc.), but also characterize the microstructure of the obtained nanoporous metals [56]. Erlebacher and McCue [78] proposed a hybrid fairing method for geometric characterization of nanoporous metals, and

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Fig. 2.12 Three-dimensional tomographic reconstruction of a chemically dealloyed nanoparticle (spongy) at two different viewing directions. The arrows indicate channels connecting to the exterior surfaces. A series of consecutive slices through the isosurfaces of such nanoparticle, showing the porous networks. (Reproduced from Ref. [69]. Copyright 2012, American Chemical Society)
found that the method is useful for tracking the morphological evolution of nanoporous metals toward the Wulff shape, in particular to calculate the relative surface fraction of various facet orientations and the interfacial shape distribution.

It has been recognized that the characteristic length scale of nanoporous metals is an important factor that controls their physical, chemical, and mechanical properties. Therefore, a precise measurement of the length scale of NPMs (or even identifying the relevant length scale metric) is essential for modeling the size-related properties and for correctly understanding the relationship between microstructures and properties of nanoporous metals. First, one can roughly determine the average length

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**Fig. 2.13**  Simplified diagram illustrating through-focal STEM tomography. a A stack of images at different focal planes is acquired at one specific tilt. This is repeated over a range of specimen tilts. b The through-focal image stacks acquired at every tilt angle contain lateral and depth information allowing for a high-resolution reconstruction of extended objects with fewer tilt angles. (Reproduced from Ref. [76]. Copyright 2014, Elsevier)

**Fig. 2.14**  In situ scattering data for the spontaneous corrosion of Ag$_{0.7}$Au$_{0.3}$ in concentrated HNO$_3$. The dealloying time associated with each curve is indicated. Adapted from Ref. [77]
scale of nanoporous metals from high-resolution SEM and/or TEM images. For example, the average ligament/channel sizes, defined by the equivalent diameters of ligaments/channels in nanoporous metals, could be determined manually by identifying a minimum of 50 ligaments/channels, making measurements across the shortest distance of each ligament/channel and then averaging [79]. Secondly, the average pore size of the as-dealloyed NPG can also be calculated from the SANS data (the inverse of the peak position) [77]. Third, Fujita et al. [72] proposed a rotational FFT method to evaluate the characteristic length scale of nanoporous metals. The resultant Fourier space spectrum can provide a scattering peak corresponding to the characteristic length scale of the bicontinuous structure. Additionally, the combination of tomographic reconstruction from HAADF-STEM images with 3-D stereological analysis can give quantitative information on the size distribution of both ligaments and nanopores in nanoporous metals [75].

The specific surface area is another important parameter for modulating the microstructures, properties and applications of nanoporous metals. Although developing a standard procedure for the surface area determination is essential for a better understanding of the materials properties influenced by the delocalized surface atoms, there is a lack of general agreement in the characterization of surface area of nanoporous metals. Several methods have been proposed to evaluate the specific surface area of nanoporous metals, and here we summarize as follows. (I) Gas adsorption method [80]. The adsorption isotherms are first obtained through measurements at low temperature (using liquid N2, normally at 77 K). Thus the specific surface area can be determined by the Brunauer–Emmett–Teller (BET) analysis. The shortcomings of this method include the limited sensitivity, and the need for sample heating in order to obtain accurate measurements. The latter may result in coarsening of nanoporous metals and a decrease of the measured surface area with respect to the actual value. (II) Redox method [81]. The method is applicable to metals (such as Au, Pd, etc.) showing well-developed regions for oxide monolayer formation and reduction. For example, the cathodic peak will appear on the CV curve in the back scan, corresponding to the reduction of Au oxide monolayer which is formed during the forward scan. By calculating the involved charge, the specific surface area can be determined through dividing by the reference charge (390 ± 10 μC cm⁻² for polycrystalline Au [81]). (III) Hydrogen adsorption/desorption method [81]. The method is used as a rule with a few transition metals (for example, Pt) showing hydrogen adsorption in potential regions prior to massive H₂ evolution. The charge under the voltammetric peaks for hydrogen adsorption or desorption (or associated with the appropriate section of the potential-time curves) corrected for double-layer charging, is assumed to correspond to adsorption of one hydrogen atom on each metal atom of the surface, and the charge associated with a one-to-one H-M correspondence per unit surface area is 210 μC cm⁻² for polycrystalline Pt. For the methods II and III, one should take care when measuring the specific surface area of Au-based or Pt-based alloys because the addition of other alloying element(s) may change the monolayer nature of Au oxide or hydrogen adsorption/desorption. (IV) The double-layer capacitance method [82]. The double-layer capacitance could be derived by the analysis of electrochemical impedance spectroscopy (EIS). The ratio
between the double-layer capacitance measured on porous and flat electrodes from the same metal correlates directly with the surface area development. EIS is a powerful technique but the recording of impedance spectra is complicated with nanoporous samples and the EI spectra analysis is a complex procedure depending on critical assumptions. (V) Underpotential deposition (UPD) method [82, 83]. The Pb UPD and Cu UPD have been developed to determine the specific surface area of NPG. The specific surface area of nanoporous metals could be evaluated via the formation and stripping of a Pb or Cu monolayer using either CV or chronoamperometry (CA) [82, 83]. The authors also compared the UPD method with other techniques, and found that Cu UPD and Au oxidation/reduction methods yielded surface area values in good quantitative agreement, but estimates based on EIS measurements were 1.5–1.75 times larger. (VI) CO stripping method [84]. In some cases, the CO adsorption/stripping method is used to determine the specific surface area of nanostructured Pd. It is believed that CO could form monolayer adsorption when the Pd electrode is potentially held in the CO saturation electrolyte, and the CO monolayer will be stripped during the subsequent CV scan. Through calculating the involved charge of the CO stripping peak, the specific surface area of the Pd electrode could be determined.

2.4 Microstructural Regulation of Nanoporous Metals

To tune their properties and meet the requirements for various applications, microstructural regulation is a crucial issue for development of nanoporous metallic materials. On the basis of the understanding of the formation mechanisms, kinds of strategies could be utilized for microstructural regulation of nanoporous metals, including design of precursors for dealloying, controlling over the dealloying parameters and post-dealloying treatment, and further modification of nanoporous metals. In the following, we will detailedly discuss these three aspects.

2.4.1 Design of Precursors for Dealloying

Erlebacher [27] has proposed that alloy systems that form porosity upon dealloying share a number of characteristics, and there are four basic common characteristics that an alloy typically possesses if it has a chance of becoming nanoporous during dealloying: (i) the difference in potential required to dissolve the alloy component in its pure form must be separated by a few hundred millivolts, with one element being more noble and the other less noble; (ii) the composition is usually rich in the less noble component (the content of the more noble element is below its parting limit); (iii) the alloy must be homogeneous with no phase separation prior to dissolution. Porosity evolution thus forms dynamically during dissolution and is not due to one phase simply being excavated from a two-phase material; (iv) diffusion of more
noble atoms at the alloy/electrolyte interface must be sufficiently fast. The Ag–Au system is the prototype precursor for dealloying and has received much attention [1]. Based upon the above criteria, many other precursor systems have also been explored, such as Al-based alloys [70], Zn-based alloys [85], Mg-based alloys [64, 86], Mn-based alloys [87], Cu-based alloys [30], Ni-based alloys [88], and so forth.

**Composition** In general, there exists a parting limit for a precursor alloy suitable for dealloying [27]. According to the above common criteria, the precursors for dealloying-driven nanoporosity evolution normally have the more noble element with the content of less than its parting limit. The dealloying critical potential will increase with increasing content of the more noble element. The higher the more noble element in the precursors (below the parting limit), the better mechanical integrity (the less cracks) of the obtained nanoporous samples would preserve [63]. Sometimes, however, the dilute precursors with the more noble element content well below its parting limit, could be adopted to fabricate nanoporous metals with unique morphologies and compositions. For example, nanoporous Pt–Co alloy nanowires could be synthesized by electrodeposition of Co-rich Pt1Co99 alloy into anodic aluminum oxide (AAO) membranes, followed by a dealloying treatment in a mild acidic medium [89]. Qi and Weissmüller [90] reported an electrochemical dealloying strategy that yields bulk samples of porous gold with a hierarchical microstructure starting from a dilute Ag95Au5 solid solution. Most recently, Qiu et al. [91] fabricated aligned bimetallic Pt–Cu microwires with a three-dimensional nanoporous structure, tunable composition, and high catalytic activity by dealloying a dilute Pt3Cu97 precursor (Fig. 2.15).

**Fig. 2.15** SEM images of the dealloyed sample: a plane-view image, b section-view image, c image of a mildly crushed one. d TEM and high-angle annular bright field STEM (e, low magnification; f, high magnification) images of the np-PtCu microwires. Inset in part d is the corresponding SAED image. (Reproduced from Ref. [91]. Copyright 2015, American Chemical Society)
Phase Constitution The precursor alloy may be a single-phase solid solution or intermetallic phase. The single-phase structure is ideal to fabricate nanoporous metals with a homogeneous microstructure. The dealloying of a two-phase or multiphase precursor is complicated, but also provides a versatile and flexible choice to prepare nanoporous metals with multilevel and multiscale morphologies (bimodal pore size distribution [61], composite structure [62], etc.). Moreover, the two-phase microstructure is crucial to the complete dealloying of bulk precursor samples (Fig. 2.9). The two-phase precursors may be comprised of two solid solutions, or two intermetallic phases, or the combination of a solid solution with an intermetallic phase, as summarized in Fig. 2.16. Thus one can design the phase constitution of the precursors in order to obtain nanoporous metals with a desired microstructure. Of course, the scenario will be more complicated for multiphase precursor alloys.

Crystalline Nature In most cases, the precursors for dealloying are crystalline. The widely used Ag–Au alloys (for example, commercially available alloy leaves) are polycrystalline and have a grain size of up to tens of microns. The rapidly solidified Al-based alloy ribbons also have grains with the size of tens of microns [70]. In contrast, single crystalline intermetallic precursors (such as Cu₃Au, Au₃Cu, etc.) are normally adopted to probe the initial corrosion mechanisms during dealloying [30]. Due to the unique microstructure (single phase, no grain boundaries, homogeneous), amorphous alloys (also called as metallic glasses) are another type of precursors for dealloying, such as Pd-based alloys [92], Au-based alloys [92], Ti-based alloys [93], Ag-based alloys [94], and so forth. Moreover, amorphous alloys are normally multicomponent, which are also beneficial to the design and fabrication of nanoporous alloys with better electrocatalytic activities. In addition, quasicrystalline alloys can also be used as precursors for the preparation of nanoporous metallic materials by dealloying. For example, magnetic nanoporous Cu (NPC)/(Fe,Cu)₃O₄ composites with tunable magnetism and excellent conductivity were fabricated by dealloying of rapidly solidified Al–Cu–Fe alloys containing

Fig. 2.16 Phase constitution of a two-phase precursor alloy
quasicrystalline Al$_{65}$Cu$_{20}$Fe$_{15}$ phase [95]. In addition, it has been found that lattice defects (vacancies) in the precursors also play an important role in controlling over the dealloying process and the formation of nanoporous metals [65, 96]. Figure 2.17 summarizes the crystalline/quasicrystalline/amorphous nature of precursors for dealloying.

**Addition of the Third Element (Microalloying)** It is well recognized that the surface diffusivity of the more noble element along the alloy/solution interface during dealloying has a significant influence on the length scale of ligaments/channels in nanoporous metals [27]. The incorporation of the third element with a lower diffusivity into the precursor alloy could markedly suppress the coarsening of ligaments/channels during dealloying. For example, the nanoporous alloy dealloyed from Ag–Au–Pt precursor has a pore size of less than 5 nm, much smaller than the characteristic length scale (normally above 15 nm) of NPG dealloyed from Ag–Au. Moreover, the addition of Pt to precursor Ag/Au alloys could stabilize the morphology of the nanoporous alloy even in harsh chemical and thermal environments [97]. It has been found that proper elemental doping has no influence on the phase constitution of rapidly solidified Al–Au–Pt, Al–Au–Pd, and Al–Au–Pt–Pd alloys, and all these precursor alloys are composed of a single Al$_2$Au-type intermetallic compound [Al$_2$(Au,Pt), Al$_2$(Au,Pd), and Al$_2$(Au,Pt,Pd)]. A certain amount of Pt and/or Pd addition exhibits a superior refining effect and the length scale of ligaments/channels in the as-obtained np–Au alloys can reach ~3 nm for the Pt doping or Pt/Pd codoping. Due to the intrinsic catalytic properties, the introduction of Pt and/or Pd into np–Au could generate novel bi/trimetallic nanoporous functionalized alloys with enhanced electrocatalytic activities [98]. Similarly, due to the intrinsic magnetism of Ni and Co, the addition of Ni and/or Co leads to the formation of novel magnetic nanoporous alloys with ultrafine ligament/channel sizes [99]. In the light of the above analysis, the incorporation of element(s) with proper amount and properties into the precursors can not only refine/stabilize the

![Fig. 2.17](image.png)

**Fig. 2.17** The crystalline/quasicrystalline/amorphous nature of precursors suitable for dealloying
nanoporous morphology/structure of the as-dealloyed samples, but also lead to the formation of nanoporous alloys/composites with functionalized properties.

*Fabrication Methods of Precursors* Melting/casting is the most used method to produce the precursor alloys, and the combination with machining/rolling could prepare the precursors with different shapes/sizes (rods, cubes, foils, films, etc.). Rapid solidification (melt spinning) can often be used to produce ribbon-like precursors with thickness of tens of microns [91]. Mechanical alloying (or high-energy ball milling) could be utilized to fabricate precursor powders with multicomponent and sizes of submicron to several microns [100]. Magnetron sputtering is a power technique to produce precursor films with diverse compositions and thicknesses. For example, W–Fe thin-film materials libraries with continuous composition and thickness spreads could be co-deposited by magnetron sputtering processes on thermally oxidized Si wafer substrates, Fig. 2.18 [101]. Electrodeposition, possibly combining with annealing treatment, can also be used to produce precursor films [102, 103]. The Gasar process (metal–gas eutectic unidirectional solidification) can be utilized to fabricate lotus-type, microporous precursor alloys, which could be further dealloyed to form a hierarchically porous structure [104]. In addition, the conventional powder metallurgy processing can also be used for preparation of precursors with regular shapes [105]. It should be noted that dewetting, the normal physical phenomenon, can be used to produce precursor alloys. For example, Nguyen et al. [106] adopted the sputtering–dewetting–dealloying strategy to fabricate site-selective high activity nanoporous Au particles on highly ordered TiO$_2$ nanotube arrays. Of course, nano-sized precursors (nanoparticles, nanowires, nanotubes, nanocubes, etc.) can be fabricated by versatile methods [69, 89, 107–109].

As described above, the microstructures of the precursors have an important influence on the dealloying process and the formation of nanoporous metals. When designing the precursors, we first choose the constituent elements considering the equilibrium corrosion potential (chemical/electrochemical activity) of pure metal, the parting limit, as well as the diffusivity of the more noble element. The phase

![Fig. 2.18](image_url) a Color-coded composition map (Fe content) of the as-deposited W-Fe materials library and b film thickness map of the as-deposited W-Fe materials library. (Reproduced from Ref. [101]. Copyright 2012, Elsevier)
constitution of the precursors is another key issue, depending upon the compositions of the precursors and the processing methods. We should also control over the crystallinity (crystalline, amorphous, quasicrystalline, grain size) of the precursors. Figure 2.19 summarizes the relationships of the above factors (a novel material polyhedron of the precursor for dealloying).

2.4.2 Control Over the Dealloying Parameters and Post-dealloying Treatment

It is well recognized that the process parameters obviously affect the dealloying and the formation of nanoporous metals. The parameters include the dealloying solution (kind, concentration), the temperature, the applied potential, the dealloying duration, the dealloying step, and so on. In addition, the post-dealloying treatment (for example, annealing) could also modulate the microstructure/morphology of nanoporous metals. We will discuss these aspects in the following.

Chemical or Electrochemical Dealloying For some precursors like Ag–Au alloys, we can choose chemical or electrochemical dealloying. In both cases, NPG could be obtained. At the same time, the chemical or electrochemical dealloying will result in nanoporous metals with different characteristic length scales, and even with different microstructures. Xu et al. [110] adopted a modified dealloying by etching Ag/Au in concentrated nitric acid under applied anodic potential and obtained NPG with ligament sizes less than 6 nm. Under similar free corrosion conditions, dealloying Ag/Au foil requires extended time, which results in a coarsened structure with ligaments of ~30 nm. Wang et al. [69] found that the electrochemical dealloying of Cu₃Pt nanoparticles led to the formation of a thin Pt skin of ca. 1 nm in thickness with an ordered Cu₃Pt core structure (core–shell), while chemical
leaching of the same precursor gave rise to a “spongy” structure (nanoporous) with no ordered structure being preserved. For Al-based precursors, chemical dealloying can be performed in acidic or alkaline media. Even in neutral electrolytes like NaCl, electrochemical dealloying of Al-based alloys could well proceed, which is important for “green” fabrication of nanoporous metals. For example, nanoporous bimetallic Pt–Au nanocomposites could be produced by chemical dealloying of rapidly solidified Al–Au–Pt precursor in HCl or NaOH [111], and electrochemical dealloying of the same precursor led to bimodal nanoporous bimetallic Pt–Au alloy in a neutral sodium chloride solution [65].

The Dealloying Solution To selectively remove the less noble element(s), we should choose the dealloying solution with proper type and concentration. For the most used Ag–Au precursors, dealloying can be carried out in several solutions, such as concentrated HNO₃, [110] HClO₄, [112] neutral AgNO₃ solution [113], etc. Snyder et al. [113] have reported the electrochemical dealloying of silver/gold alloys in neutral pH silver nitrate solution to form NPG, and have found that a small pore (~5 nm) NPG is formed over a potential regime of 1.3–2.0 V versus normal hydrogen electrode. It is known that the adsorption of anions (such as Cl⁻) in the electrolyte can accelerate surface diffusion of the more noble element and thus coarsen the ligaments/channels in the resultant nanoporous structure. Dursun et al. [114] have studied the dealloying of Ag₀.₇Au₀.₃ and Ag₀.₆₅Au₀.₃₅ alloys in 0.1 M HClO₄ with the addition of either 0.1 M KCl, 0.1 M KBr, or 0.1 M KI. Without the addition of halides, a pore size of approximately 8 nm is produced while 17, 16, and 67 nm is measured in the KCl, KBr and KI containing electrolytes. In addition, it has been also found that the length scale of ligaments/channels of nanoporous metals can be modulated by simply changing the dealloying solution (from HCl to NaOH) [70]. The dealloying of Al₂Au in a 20 wt% NaOH solution results in NPG with a characteristic length scale of 10–20 nm, while the dealloying in a 5 wt% HCl solution leads to the formation of coarsened nanoporous structure with ligaments/channels of 60–80 nm [70].

The Dealloying Temperature The low-temperature dealloying treatment is an effective method to tailor the characteristic length scale of nanoporous metals. The lower the dealloying temperature, the slower the surface diffusion of the more noble element(s) is during dealloying. Thus, the smaller length scale of ligaments/channels can be obtained with higher content of the residual active element. By systematically investigating the kinetics of nanopore formation during free corrosion, Qian et al. [115] have experimentally demonstrated that the dealloying process is controlled by the diffusion of gold atoms at alloy/electrolyte interfaces, which strongly relies on the reaction temperatures. Low dealloying temperatures significantly reduce the interfacial diffusivity of gold atoms and result in an ultrafine nanoporous structure with the average pore size of ~7 nm. NPG with an average length scale of ~5.3 nm can be obtained by dealloying the rapidly solidified Al₂Au alloy in alkaline solution at 253 K, but a longer dealloying time is needed for complete dealloying and the residual Al content is a little higher [79]. Similarly, tuning the ligament/channel size of nanoporous copper could be realized by temperature control [116]. In addition, the
high dealloying temperature would coarsen the ligaments/channels of nanoporous metals but simultaneously reduce the cracks. The addition of the third element (like Pt) with lower diffusivity could significantly suppress the temperature-induced coarsening process of ligaments/channels during dealloying [117].

*The Applied Potential* During electrochemical dealloying, the selection and applying method of the applied potential would have a significant influence upon the formation of nanoporous metals. Normally, to drive the selective dissolution of the less noble element as well as nanoporosity evolution, the applied potential should be higher than the critical potential but lower than the equilibrium corrosion potential of the more noble element(s). The higher the applied potential, the faster the dealloying process proceeds and the less the dealloying duration is needed. But the dealloying could be hardly controlled, and more cracks/defects will be produced in the as-dealloyed samples. Thus, for a given precursor alloy, an appropriate dealloying potential should be applied, to balance the dealloying rate and the dealloying duration. Zhong et al. [118] have found that a complete suppression of crack formation was achieved by application of a high dealloying potential of 1.1 V versus Ag/AgCl for millimeter-sized Au25Cu75 samples. NPG films (~100 nm) with an ultrafine pore size (4–8 nm) could be fabricated by pulse electrochemical dealloying of Ag–Au films, and the pore size is much smaller than NPG obtained by chemical dealloying [119]. Wang et al. [120] have demonstrated that a critical upper limit voltage exists for creating spongy electrocatalysts from Cu3Pt ordered intermetallic nanoparticles in N2 purged 0.1 M HClO4 solution. Potential cycles from +0.05 to +1.2 V versus RHE or holding the potential at 1.0 V versus RHE for 3 h resulted in a nanoporous structure, while potential cycles from +0.05 to +1.0 V versus RHE led to the formation of core (Cu3Pt)–shell (Pt) structure. Okman and Kysar [121] carried out a set of experiments to compare the galvanostatic and potentiostatic dealloying of Ag–Au films. The NPG film obtained by potentiostatic dealloying is severely damaged, but almost no cracks are observed for NPG obtained by galvanostatic dealloying (Fig. 2.20). Vega and Newman [117] investigated the effect of the dealloying potential on the characteristics of different nanoporous structures. The ligament size in NPG increased by reducing the overpotential (Fig. 2.21a, b), which was due to the longer time available for coarsening at a lower current density. The ligament width in NPG increased from 14 nm at 550 mV to approximately 24 nm at 500 mV. The addition of 1 at.% Pt could obviously suppress the ripening process (Fig. 2.21c, d).

*The Dealloying Step (Two-Step or Multistep Dealloying)* In order to modulate the microstructures/compositions/morphologies of nanoporous metals, multistep dealloying is necessary in some cases. Xu et al. [65] reported the two-step electrochemical dealloying of the rapidly solidified Al75Pt15Au10 precursor composed of a single Al5(Pt, Au) phase with lattice vacancies inside in a neutral sodium chloride solution. It has been found that the dealloying at the low potential of ~0.4 V versus Ag/AgCl is associated with the partial dissolution of Al and the disappearance of the vacancies, leading to the formation of the stoichiometric Al5(Pt, Au). The subsequent dealloying at 0.6 V versus Ag/AgCl is related to the complete
dissolution of Al and surface diffusion of Pt/Au, resulting in the formation of the ultrafine nanoporous structure. Qi and Weissmüller [90] reported the fabrication of bulk NPG with a hierarchical microstructure by two-step electrochemical dealloying. The first-step dealloying yields nanoporous Ag–Au alloy as an intermediate product (Fig. 2.22a). After coarsening of the porous alloy to create the large ligaments of the upper hierarchy level (Fig. 2.22b), the second-step dealloying creates the fine ligaments of the lower hierarchy level (Fig. 2.22c). Moreover, the addition of 1 at.% Pt into the Ag–Au precursor could favor the formation of porous gold with a nested network architecture and ultrafine structure through the dealloying–annealing–dealloying strategy [122].

The Effect of Atmosphere on Dealloying Normally, dealloying is performed in air, without considering the influence of atmosphere. More and more investigations demonstrate that the atmosphere may have a visible effect upon the dealloying process. Gan et al. [123] reported the influence of atmosphere (air, N₂) and particle size on the chemical dealloying of PtNi₃ nanoparticles (Fig. 2.23). They have found that nanoporosity formation in particles larger than ca. 10 nm is intrinsically tied to a drastic dissolution of Ni when dealloying in air. In contrast, O₂-free acid leaching enabled the suppression of nanoporosity resulting in more solid core–shell particle architectures with thin Pt-enriched shells when dealloying in N₂.
Dealloying in Nonaqueous Solutions

In most cases, chemical or electrochemical dealloying is performed in aqueous solutions. Actually, the selection of dealloying media is quite flexible. Dealloying also occurs in organic electrolytes, metallic melts, or supercritical fluids. Chen and Sieradzki [36] examined dealloying of Li...
Li–Sn alloys in organic electrolytes and show that depending on alloy composition, particle size and dealloying rate, all known dealloyed morphologies evolve including bicontinuous nanoporous structures and hollow core–shell particles. Wada et al. [124, 125] proposed a novel dealloying method employing a metallic melt as the dealloying liquid for preparation of nanoporous metals (Ti, Fe, Cr, et al.). An atomic interaction among alloy components and metallic melt causes specific component to dissolve out from the alloy solid into the melt with self-organizing nanoporous structure by the remaining component. Morrish and Muscat [126] have demonstrated that multiphase AgCu thin films could be dealloyed using a mixture of hexafluoroacetylacetone (hfacH) and H₂O₂ dissolved in supercritical CO₂, leading to the selective dissolution of Cu.

Post-dealloying Treatment To further modulate the compositions, morphologies and microstructures of nanoporous metals, post-dealloying treatment is frequently adopted, such as annealing. As early as in 1992, Li and Sieradzki [127] reported the annealing-induced coarsening of NPG. At present, annealing is still the widely used method to coarsen the ligaments/channels of nanoporous metals to different length scales [128]. Moreover, due to the unique nanoporous structure, the coarsening of ligaments/channels is a self-similar process [129]. The annealing treatment only changes the characteristic length scale of ligaments/channels, but does not alter the topological structure of nanoporous metals. Chen-Wiegart et al. [130] studied the three-dimensional evolution of nanoligaments of NPG created by Ag–Au dealloying during isothermal coarsening by X-ray nanotomography and microbeam Laue diffraction. They have argued that the distribution of orientations for the surfaces of the nanoligaments becomes more anisotropic with coarsening time, with an increasing area of the surfaces having a low surface energy, consistent with the
growth of facets. Moreover, the curvature distribution of the nanoligaments (scaled by their size) also evolves during coarsening. The evolution of both surface orientation and scaled surface curvature indicates that coarsening does not occur in a self-similar manner. Shui et al. [131] have demonstrated that a mild dealloying treatment in acid combined with an annealing treatment could make an effective Pt-rich surface layer when only a little non-noble metal is dissolved from the alloy surface. By exposing freshly dealloyed nanostructures to surprisingly low temperatures in the presence of laboratory air, the Pt segregates to the surface of the ligaments, thanks to its preferential interaction with oxygen; in contrast, in an inert atmosphere (Ar–H₂), Pt mostly remains in the bulk of the ligaments [132].

2.4.3 Modification of Nanoporous Metals

To strengthen their functions and potential applications, further modification of nanoporous metallic materials is frequently applied. In this section, we will outline the strategies used to modify nanoporous metals based upon their potential applications.

Modification for Biosensors Enzymatic reactions are crucial for applications of biosensors. Immobilization of enzyme on an appropriate support is a key step for the construction of mediator-free biosensor. Due to the good electrical conductivity, high specific surface area, good biocompatibility and support-free feature, nanoporous metals (especially NPG) are promising electrode materials for immobilization of enzyme. For example, laccase is a multicopper oxidase which contains four copper ions classified into three types (T1, T2, T3) in accordance with their spectroscopic characteristics, is able to oxidize a large number of organic and inorganic substrates with concomitant reduction of molecular oxygen to water, and thus has great potential applications in the fields of biosensors and biofuel cells. Qiu et al. [133] immobilized laccase on NPG (NPG, 100 nm in thickness) for enzyme electrode construction. Direct electrochemistry of laccase on NPG supported by glassy carbon electrode (NPG/GC) was achieved with high efficiency due to the outstanding physicochemical characteristics of the NPG. The laccase-loaded NPG/GC electrode also exhibited a strong electrocatalytic activity toward O₂ reduction and excellent stability. Feng et al. [134] used nanoporous PtCo alloy as an antibody carrier for preparation of a highly sensitive immunosensor for nonenzyme detection of zeranol, Fig. 2.24. Their results show that the immunosensor exhibited a highly sensitive response to zeranol with a detection limit of 13 pg/mL, with zeranol concentration range (0.05–5.0 ng/mL). Ding et al. [135] have demonstrated that the NPG functionalized with cysteamine allows the immobilization of carbon nanotubes on the electrode with the self-assembly technique. The carboxylated carbon nanotubes are further linked with acetylcholinesterase (AChE) for amperometric sensing of pesticides. The immobilized AChE shows excellent activity to its substrate and allows a quantitative measurement of organophosphate pesticides. Hafez et al. [136] have demonstrated that the porous gold surface is more effective
in adsorption of dodecanethiol as compared to the unetched gold alloy using cyclic voltammetric and time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis. Liu et al. [137] designed a novel sandwich-type electrochemical immunosensor for sensitive detection of human chorionic gonadotropin (hCG), using nanoporous Pd as a label. Shang et al. [138] fabricated a three-dimensional hybrid film with in- and out-of-plane pores by using porous graphene as framework structure and porous PdCu alloy nanoparticles as building blocks. Based on this hybrid film, they further developed an electrochemical sensor of melamine by further introducing melamine imprinted electropolymer of para-aminobenzoic acid. Yin et al. [139] recently developed all-solid-state polymeric membrane ion-selective electrodes by using a NPG film as solid contact.

Modification for Actuators  Nanoporous metallic actuators have shown comparable or even better reversible strain than piezoceramics, and higher strength than conducting polymer. Until now, most attention has been paid to the electrochemical actuation behaviors of nanoporous metals (Au, Pt, Pd, Ag, Ni, etc.) and their alloys (Pt–Au, etc.) in aqueous electrolytes. When being operated in an aqueous electrolyte, however, metallic muscles made of nanoporous metals may suffer from some drawbacks. For example, an aqueous electrolyte prohibits metallic muscles from operating in dry environments and hampers a high actuation rate due to the low ionic conductivity of electrolytes. In addition, redox reactions involved in electrochemical actuation may coarsen the ligaments of nanoporous metals, leading to a substantial loss in performance of the actuator. Detsi et al. [140] reported an electrolyte-free approach to put metallic muscles to work via a metal/polymer interface. By electrochemical oxidative polymerization of aniline from an aqueous solution containing aniline monomers, a nanocoating of polyaniline doped with sulfuric acid was grown onto the ligaments of nanoporous gold (NPG/PANI),
Modification for Photocatalysis Photocatalysts have attracted much attention in recent years because they allow highly efficient eco-friendly removal of organic pollutants present in our environment. Among various photocatalytic materials, considerable efforts were focused on the development of visible-light photocatalysts in order to obtain high sun light utilization efficiency. Li and Ding [141] fabricated porous AgCl/Ag nanocomposites with a facile two-step route, which involves the formation of nanoporous silver (NPS) by dealloying AgAl alloys, and a subsequent surface chlorination in a mixed solution containing $\text{H}_2\text{O}_2$ and HCl. It was found that porous AgCl/Ag nanocomposites performed very well as efficient and stable visible-light catalysts for the degradation of methylic orange (MO) dye. Yan et al. [142] synthesized porous AgBr@Ag and AgBrI@Ag plasmonic photocatalysts by a multistep route, including a dealloying method to prepare porous Ag, a transformation from Ag to AgBr and AgBrI, and a photoreduction process to form Ag
nanoparticles on the surface of AgBr and AgBrI. Both porous AgBr@Ag and porous AgBrI@Ag showed much higher visible-light photocatalytic activity than cubic AgBr@Ag for the degradation of methyl orange.

**Modification for Surface-Enhanced Raman Scattering (SERS)** SERS originates from the improved inelastic scattering of the molecules adsorbed on nanostructured metals and alloys. SERS probes bond vibrations of molecules in the proximity of metallic nanostructures. This technique has regained considerable interest stimulated by an explosive development of nanotechnology and superior sensitivity of SERS, in some cases possibly approaching the single molecule detection limit. Although NPG shows good SERS effect [143], the SERS effect could be further enhanced by modification of nanoporous metals. Qian et al. [144] employed a two-step method to create hot spots within hybrid nanostructures, which consist of self-supported NPG films with the absorbed probes and subsequent nanoparticle conjugates without surface agents or mechanical motion, Fig. 2.26. The molecules confined into 1 nm interstice exhibit \(2.9 \times 10^7\) times enhancement in Raman scattering compared to pure NPG, offering an opportunity to track spatial orientation of single molecule. Zeng et al. [145] have shown that plasmonic resonance can be significantly redshifted by up to 258 nm by the surface modification, which involves the loading of small gold nanoparticles into the pores of NPG disk. In addition, Qian et al. [146] fabricated NPG–alumina core–shell films with fixed gold skeletons and different thicknesses of alumina shells using chemical corrosion and subsequent atomic layer deposition (ALD). A 92 nm redshift of the localized surface plasmon resonance (LSPR) band is attained via its dielectric medium dependence and the comparable decay length with pore size.

**Modification for Water Splitting** It is known that efficient production of chemical fuels through solar energy is an attractive option to address the global energy challenge. Photoelectrochemical (PEC) water splitting using sunlight offers a promising solution for renewable and clean energy systems. Bak et al. [147] fabricated

![Fig. 2.26](image)

**Fig. 2.26** a Low magnification TEM image of pure NPG–nanoparticle conjugates by immersing NPG film into gold colloids with \(1.6 \times 10^{12}/\text{ml}\). b Typical SERS spectra on pure NPG film and NPG–nanoparticle conjugates. (Reproduced from Ref. [144]. Copyright 2010, The Royal Society of Chemistry)
3D-nanostructured $\alpha$-Fe$_2$O$_3$/nanoporous gold (NG) electrodes in three subsequent procedures, dealloying Au/Ag to produce a conductive 3D-NG electrode, decorating nanocrystalline $\beta$-FeOOH onto the nanopores of 3D-NG via a hydrothermal method, and converting $\beta$-FeOOH into $\alpha$-Fe$_2$O$_3$, Fig. 2.27. Great enhancement in photoelectrochemical water splitting efficiency could be achieved in hematite assisted by fast and easy transfer of electrons/holes via the 3D-NG electrode. The $\alpha$-Fe$_2$O$_3$/3D-NG electrode exhibits a maximum photocurrent density of 1.6 mA cm$^{-2}$ at 1.5 V versus RHE under AM 1.5 G simulated sunlight illumination via a photocatalytic hydrogen generation reaction, which is two times greater than that of the unmodified $\alpha$-Fe$_2$O$_3$ photoanode.

Modification for Fuel Cells The electrocatalytic activity of nanoporous metals can be further enhanced by surface modification or hybridization at both the anode and the cathode. Wang et al. [148] reported the fabrication of an ultralow-platinum-loading high-performance nanoporous electrocatalyst with nanoengineered surface structures for electrooxidation of formic acid, by means of a well-known Cu underpotential deposition (UPD) mediated process. Monolayer Pt is first deposited onto the ligament surfaces of NPG by in situ redox replacement of PtCl$_4^{2-}$ with monolayer Cu deposited by UPD. Then, an adequate amount of Au is deposited onto the Pt overlayer using the same method, where the amount of deposited Au could be effectively controlled by holding at a specific potential during the Cu UPD process or by repeating Cu UPD and Au replacement cycles. Wang et al. [149] further reported a new type of anode constructed by confining highly active nanoengineered catalysts into an ultrathin catalyst layer with thickness around 100 nm. Specifically, an atomic layer of platinum is first deposited onto NPG leaf to achieve high utilization of Pt and easy accessibility.
of both reactants and electrons to active sites. These NPG–Pt core/shell nanostructures are further decorated by a sub-monolayer of Bi to create highly active reaction sites for formic acid electrooxidation. Snyder et al. [150] incorporated a hydrophobic, protic ionic liquid, [MTBD][beti], into the pores of high-surface-area NiPt alloy nanoporous nanoparticles (np-NiPt/C + [MTBD][beti]), and the hybrid materials show enhanced oxygen reduction reaction (ORR) performance. Ke et al. [151] reported Pd-decorated three-dimensional nanoporous Au/Ni foam composite electrodes for H₂O₂ reduction. Here we just show several examples, and the detailed information on modification of nanoporous metals for fuel cells applications will be presented in Chap. 3.

Modification for Supercapacitors It is known that both transition metal oxides and conducting polymers are promising electrode materials for supercapacitors. Transition metal oxides normally suffer from poor electrical conductivity and show limited cycling performance, despite their high theoretical specific capacitance. The optimization of supercapacitor performance, i.e., high power and energy densities, relies on the simultaneous realization of several key structural parameters such as the amount of each individual electrode component, open accessibility by the electrolyte, and the interfacial structure between the electrochemically active material and current collector. Due to the three-dimensional bicontinuous porous structure, good electrical conductivity, and high specific surface areas, nanoporous metals are promising substrates for constructing hybrid electrodes, simultaneously serving as the current collector. Here we just show two examples for these aspects, and the detailed information will be given in Chap. 4. Meng and Ding [152] constructed sub-micrometer-thick all-solid-state supercapacitors with high power and energy densities from polypyrrole (PPy)-decorated NPG. Lang et al. [153] have demonstrated that hybrid structures made of NPG and nanocrystalline MnO₂ have enhanced conductivity, resulting in a specific capacitance of the constituent MnO₂ (∼1,145 F g⁻¹) that is close to the theoretical value.

Modification for Lithium Batteries Similarly, active materials can be decorated onto the ligament surface of nanoporous metals for lithium batteries. We know that tin could be used as alternative anode electrodes for lithium ion batteries (LIBs), due to its high electronic conductivity and high theoretical capacity (990 mAh g⁻¹ for Li₄.₄Sn, about three times higher than that of graphitic carbon, 372 mAh g⁻¹ for LiC₆). However, implementation of metallic tin to LIBs is greatly hampered by its poor cyclability, which can be attributed mainly to pulverization, aggregation, and loss of electrical contact at the electrode, with all of these resulting from the substantial volume changes (over 200 %) during charging and discharging. Yu et al. [154] reported a 3D nanoporous metal-supported nanocrystalline thin tin foil as an alternative anode for rechargeable LIBs with improved electrochemical performance. Zhang et al. [155] have also shown the potential of nanoporous copper as a substrate/collector to deposit a thin tin layer for LIBs. For applications in lithium batteries, the detailed information will be shown in Chap. 5.
2.5 Summary and Conclusions

In summary, we mainly discuss the formation mechanisms, microstructural characterization, and microstructural regulation of dealloying-driven nanoporous metals in this chapter. Although dealloying has a long history, it got renewed attention as novel nanostructured materials for functional applications just at the beginning of this century. Dealloying is a common corrosion process, but involves complex physical and chemical/electrochemical reactions at the alloy/solution interface. Several mechanisms have been proposed to rationalize the formation of nanoporous structures during dealloying, and the main concerns are correlated with the selective dissolution of the less noble element(s) and surface diffusion of the more noble element(s). More in situ/ex situ experiments as well as computer simulations should be explored to further clarify the underlying dealloying mechanisms. Many techniques can be adopted to characterize the microstructures (also compositions and morphologies) of nanoporous metals, and the characteristic length scale and specific surface area are two important issues. The combination of scanning TEM with energy dispersive X-ray analysis can well reveal the morphologies and compositional distribution at the nanoscale and even atomic resolution. And three-dimensional tomographic reconstruction is also powerful to reveal the interior microstructures of nanoporous metals. In the last section of this chapter, we discuss the strategies to regulate the microstructures of nanoporous metals, from three aspects: design of precursors for dealloying, control over the dealloying parameters and post-dealloying treatment, and further modification of nanoporous metals to strengthen their functional applications.

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