Fabrication, microstructure and properties of nanoporous Pd, Ni and their alloys by dealloying

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Abstract

Nanoporous metals can be fabricated by dealloying, which is one of the reactions that occur during the corrosion of alloys. Nanoporous gold has been widely investigated for several decades, and it has recently been found that other metals such as platinum, palladium, nickel and copper can form nanoporous structures through the dealloying of binary alloys. This article mainly shows fabrication and properties of nanoporous palladium and nickel after introduction of nanoporous metals by referring to nanoporous gold as an example. It is necessary to select binary alloys with suitable elements, in which the dissolution of the less noble element and the aggregation of the nobler element at the solid/electrolyte interface are simultaneously allowed. Postprocessing by thermal or acid treatment alters the nanoporous structure. Various properties of nanoporous metals (including mechanical, catalytic, piezoelectric, hydrogenation and magnetic ones) are different from those of bulk and nanocrystalline materials and nanoparticles because of their specific three-dimensional network structures consisting of nanosized pores and ligaments. Hydrogenation and magnetic properties are reviewed in terms of lattice strain at curved surfaces. These new metallic nanomaterials are now being investigated from the viewpoint of functional applications, and provide much room for study in various fields.

Keywords: nanoporous metals, dealloying, corrosion, pore size, surface

Title for running head: Nanoporous metals fabricated by dealloying

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1. Introduction

Materials with a porous (or foamed or cellular) structure intrinsically provide many functions.[1–5] In particular, nanoporous structures, which consist of a network of nanosized pores and ligaments, are common in oxide ceramics[6–8] and carbon materials,[9,10] and offer several important functions for the synthesis and processing of materials. On the other hand, nanoporous metals with an interconnected open-cell structure can be easily fabricated through self-organization by dealloying,[11–14] which is one of the fundamental corrosion reactions. Nanoporous metals, similarly to other nanoporous materials, have a high surface area and are promising materials for electrode, sensor and catalytic applications. During the last decade, increasing research attention has been paid to nanoporous metals, although the formation of nanoporous structures itself has been known and utilized since the 1920s, during which nanoporous Raney-type catalysts were patented.[15,16]

Figure 1 shows a schematic illustration of the use of dealloying to fabricate nanoporous metals. The scheme is simple and as follows. First, a starting binary alloy is prepared. Second, one of the elements in the starting alloy is selectively dissolved in an electrolyte. During the dissolution of this element, the other element spontaneously forms a nanoporous structure. This spontaneity in dealloying is similar to spinodal decomposition,[12] in which entwined two phases gradually forms without nucleation

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and growth during the equilibration of two-elemental solids, and markedly different from the so-called template, replication or spacer method,[17–19] where the pores (in metals and other materials) are created by the removal of spacing materials such as particles and wires from metal-spacer composites. Thus, this self-synthetic nature of nanoporous metals is attractive for the efficient production of high-surface-area metallic components.

The atomic behavior considered to occur at the solid/electrolyte interface during dealloying is schematically shown in Fig. 2, where element A is chemically nobler (more stable) than element B. Two processes are equivalently involved in the formation of nanoporous metals: one is the dissolution of the less noble element B into the solution and the other is the aggregation of the nobler element A at the interface.[11,12] At the initial stage of dealloying of the A-B alloy, B first dissolves into an electrolyte, leaving vacancies and less-coordinated A atoms at the solid surface. Then the less-coordinated, and thus less stable, A atoms diffuse at the interface to form islands consisting of a number of A atoms. The aggregation of A atoms exposes the underlying A-B alloy to the electrolyte, allowing the subsequent dissolution and removal of B. Thus, the repetition of B dissolution and A aggregation at the solid/electrolyte interface results in the final nanoporous structure.

As shown later, the size and morphology of pores and ligaments can be controlled by thermal and/or acid treatments, which induce the reorganization of the

nanoporous structure. Figure 3 shows a comparison of the range of controllable pore and ligament sizes with various substances having submicron-scale length. The smallest pores are under 5 nm while the largest pores are above 1000 nm. The ability to adjust the pore size over such a wide range is one of the characteristics of nanoporous metals fabricated by dealloying.

The fabricated nanoporous metals have a large surface area due to their small ligament sizes. The surface area is almost comparable to that of nanoparticles; however, the interconnected three-dimensional nanoligaments in nanoporous metals are expected to exhibit properties different from those of individual and aggregated nanoparticles.

In this review we review the fabrication of various species of nanoporous metals by dealloying, followed by a description of their properties.

2. Nanoporous gold

Dealloying and the subsequent formation of nanopores have been reported most frequently for gold (Au).[11,12] Actually, several good and comprehensive review papers on nanoporous Au have been already published.[13,14,20–23] This is because the investigation of nanoporous Au started much earlier than that of other nanoporous metals. Mechanisms related to the fabrication and properties of nanoporous Au have been thoroughly investigated and are documented well; for further details, see the review papers.[13,14,20–23] In this section, a brief description of nanoporous Au will be

given to only introduce the key fundamentals of nanoporous metals.

2.1 Fabrication

A typical initial alloy used for the fabrication of nanoporous Au is Au-Ag since

Ag dissolves into HNO_3 and $HClO_4$. Because of the high inertness of Au and the

sufficiently high solubility of Ag in these electrolytes, which can be understood by the

comparison of standard electrode potentials (E_0 (Au^{3+}/Au) = +1.50 V vs standard

hydrogen electrode (SHE), and E_0 (Ag^+/Ag) = +0.80 vs SHE),[24] it is easy to fabricate

nanoporous Au from Au-Ag alloy. When alloyed with each other, Au and Ag form a

face-centered-cubic (fcc) solid solution at all compositions; hence, the resulting pore

characteristics such as porosity and pore size can be tuned over a wide range, and the

discussion of the relationship among the processing conditions, pore characteristics

and properties of the nanoporous metal is straightforward. The Ag content in the initial

Au-Ag alloy must be larger than approximately 0.55 for the production of nanoporous

Au;[25] otherwise the dissolution of Ag stops after minimal dissolution of Ag from the

outermost surface of the alloy. The other combinations of Au-Cu[26,27] and Au-Al[28,29] are

possible, although these alloys intrinsically contain ordered intermetallic compounds,

which may make the discussion complicated and limit the range of processing

conditions.

Figures 4–7 shows scanning electron microscopy (SEM) images of various

nanoporous Au structures fabricated by the dealloying of Au-Ag alloy in HNO_3 or $HClO_4$.[30–33] These figures clearly demonstrate that the pore size and morphology strongly depend on the processing conditions including the acid or thermal treatments after dealloying.

5   In free corrosion, which is the simplest dealloying technique, the initial Au-Ag alloy is immersed in a concentrated electrolyte such as HNO_3. Pore and ligament sizes increase with the immersion time, as shown in Fig. 4, owing to the diffusion of Au atoms at the solid/electrolyte interface.[33–35] Free corrosion at lower temperatures leads to smaller pore and ligament sizes (Fig. 4d) because of the suppression of Au atom

10   diffusion.[35]

On the other hand, dealloying under an anodic electrochemical potential results in nanoporous structures as fine as 5–10 nm (Fig. 5a). In general, the imposition of a higher anodic potential results in smaller pores.[33,36] The anodic electrochemical potential, in general, causes a significant volume reduction during the dissolution of Ag

15   and leads to macroscopic crack formation (Fig. 5b).[30,36]

Careful investigation showed that nanoporous Au can be synthesized by dealloying of Au-Ag in electrolytes with neutral pH under anodic potentials.[37,38] Residual Ag, which can be in the alloyed or oxide forms depending on pH, considerably affects the kinetics of dealloying. As a result, pH of the electrolyte and

20   potentials are quite important for not only pore/ligament size control but the residual

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amount of less noble element.[38] This aspect should be investigated extensively to other initial alloy systems and electrolytes for facile control of nanoporous structure and residual less noble elements.

Acid treatment by concentrated HCl after dealloying under an electrochemical potential leads to the formation of peculiar prismlike structures with the nanoporosity coarsened to 300–500 nm (Fig. 6).[30] That is, nanoporous Au prisms with dense walls are created throughout the entire specimen. At the top surface of the specimen, nanoporous walls, whose ligament sizes are increased to 300–500 nm, separate the surface of the specimens into "plots", whose interiors are hollow (Figs. 6a and 6b). At the bottom surface of the specimens, on the other hand, the nanoporous structure is enclosed inside highly dense walls (Fig. 6c). The ligament size of the inner porous structure is 300–500 nm, and the thickness of the enclosing walls is approximately 1 µm. Each plot has side lengths of 5–20 µm and extends toward the inside of the specimens, forming nanoporous prismlike structure with dense walls (Fig. 6d). The dense walls break down further into the sample thickness. These prisms are approximately perpendicular to the specimen surface. The microassembly of nanoporous Au prisms, which is due to heterogeneous coarsening of the porous structure, appears to be related to the macroscopic cracks in the as-dealloyed sample before the HCl treatment (Fig. 5b).

Thermal treatment also coarsens the nanoporous structure,[32,39] while maintaining

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the open-cell porous structure. Higher heating temperatures lead to larger pore and ligament diameters (up to 1.2 µm), as shown in Fig. 7. The thermally-coarsened nanoporous structures with characteristic length scale above approximately 150 nm can be observed by transmission X-ray microscopy.[40] Compared with the melting of

5   nanoparticles at temperatures lower than the melting point of bulk Au,[41] the coarsening of nanoporous Au by thermal treatment alters the nanostructure at much lower temperatures. Differential scanning calorimetry results for nanoporous Au exhibit an exothermic peak (Fig. 8), which indicates that solid-state reorganization processes, rather than melting, are responsible for the coarsening of heated nanoporous Au.

10   Several observations by transmission electron microscopy (TEM) have revealed that typical nanoporous metals, including coarsened ones, have a grain size much larger than the pore and ligament sizes;[34,36] therefore, the exothermic peak is unlikely to be caused by recrystallization, although the dependence of pore/ligament size on heating temperature is similar to that of the grain size in nanocrystalline Au.[32] Thermal

15   coarsening in nanoporous Au is an efficient means of controlling the pore size over a wide range, although it turns unsuitable when nanoporous Au is to be applied in high-temperature environments.

2.2 Properties

20   Many researchers have revealed peculiar properties of nanoporous Au, which

have already been documented in published papers including review articles.[13,14,20,27,31,39,41–49] For example, the mechanical strength of nanoporous Au increases with decreasing pore and ligament sizes.[28,40] Marked strengthening upon reducing the pore size has not been observed in conventional macroscopic porous materials with millimeter- and micrometer-scale pores and ligaments.[1] This suggests that the dislocation activity, which is responsible for the plastic deformation of metals, is strongly affected by the nanoporous structure. Dou and Derby summarized the mechanical properties of nanoporous Au uncovered by many researchers and emphasized the peculiar microstructures of microtwins and partial dislocations localized at bent nodes in the nanoporous architecture during deformation.[47]

The catalytic properties of nanoporous Au have also been reported, although bulk Au itself is not always a catalytic material.[27,48] The effect of nanosized pores and ligaments with possible surface strain may be similar to the case of Au nanoparticles supported on porous oxides.[50] Kameoka and Tsai reported enhanced CO oxidation on nanoporous Au fabricated by dealloying Au-Cu alloy.[27] Wittstock et al. also revealed CO oxidation on nanoporous Au fabricated by dealloying Au-Ag alloy and attributed the catalytic properties to the residual Ag segregated at the surface.[48] The catalytic effect of nanoporous Au on other reactions such as the oxidation of CH_3OH has also been reported.[49]

The piezoelectric properties of nanoporous Au, which are related to its large

surface area, become apparent in an electrolyte[51,52] and under an atmosphere of specific gases.[53] This piezoelectric nature of nanoporous materials was originally reported for platinum black[54] and may be useful for applications to sensors and actuators. In addition, nanoporous Au exhibits optical properties including

5 surface-enhanced Raman scattering, which can be used for sensing applications.[13,55–57]

3. Nanoporous palladium

Palladium (Pd) is one of the platinum group metals and known for its chemical inertness, catalytic properties and hydrogen storage capacity. Hence, Pd nanostructures

10 (including nanoparticles) with high surface area have been intensively developed for catalytic devices and sensors.[58,59] However, less attention has been paid to the fabrication of nanoporous Pd through dealloying, although Kabius et al. reported its formation by dealloying Pd-Cu alloy in 1986.[60]

15 *3.1 Fabrication*

Recently, dealloying of Pd-containing alloys to fabricate nanoporous Pd has been extensively examined by the present authors.[61–63] Iron (Fe), cobalt (Co) and nickel (Ni) were selected as candidates for the sacrificial elements in Pd-containing starting alloys for two reasons; one is that the standard electrode potentials of Fe, Co and Ni are much

20 lower than that of Pd (as summarized in Table 1) and the other is that Fe, Co and Ni

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forms single-phase solid solution when alloyed with Pd. However, the anodic polarization behaviors of these alloys, where the alloys were used as working electrodes in H_2SO_4 electrolyte, significantly differed, as shown in Fig. 9. Pure Fe, Co and Ni exhibited monotonic increases in current with increasing potential and no passivity was observed. This suggests that passive surface oxide films of Fe, Co and Ni do not form upon electrolysis in H_2SO_4. $Pd_{0.2}Co_{0.8}$ alloy also exhibited a similar trend in its anodic polarization curve (Fig. 9(b)), although the measured current was smaller than that of pure Co. The monotonic current increase in the anodic polarization curve of $Pd_{0.2}Co_{0.8}$ is similar to those for Au-Ag alloys, which produce nanoporous Au upon electrolysis.[64] On the other hand, $Pd_{0.2}Fe_{0.8}$ and $Pd_{0.2}Ni_{0.8}$ clearly had regions of passivity at high potentials, at which a low constant current was detected. The constant-potential electrolysis of $Pd_{0.2}Fe_{0.8}$, $Pd_{0.2}Co_{0.8}$ and $Pd_{0.2}Ni_{0.8}$ in H_2SO_4 (Fig. 10) showed that a large current was detected during the constant-potential (+0.6 V vs saturated calomel electrode (SCE)) electrolysis of $Pd_{0.2}Co_{0.8}$, suggesting the considerable dissolution of Co into the electrolyte; however, very little current was observed in the cases of $Pd_{0.2}Fe_{0.8}$ and $Pd_{0.2}Ni_{0.8}$.

Figures 11 (a)–(c) are the SEM images of $Pd_{0.2}Fe_{0.8}$, $Pd_{0.2}Co_{0.8}$ and $Pd_{0.2}Ni_{0.8}$ after the constant-potential electrolysis. $Pd_{0.2}Co_{0.8}$ alloy exhibited an open-cell nanoporous structure (Fig. 11 (b)). The ligament and pore sizes were approximately 20 nm. However, $Pd_{0.2}Fe_{0.8}$ and $Pd_{0.2}Ni_{0.8}$ had featureless microstructures after the

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electrolysis (Figs. 11 (a) and (c)). The passivity indicated in Fig. 9 clearly prevents the

formation of nanopores. Thus, Pd-Co is a promising starting material among the three

alloys for fabrication of nanoporous Pd. The compositional effect on the

current/potential behavior of Pd-Co alloy ingots in 0.1 mol/l H_2SO_4 solution is shown

5   in Fig. 12. For all the Pd-Co alloys tested, the current density monotonically increased

with the potential increase. Dealloying critical potentials, which can be determined as

the potential corresponding to a current density of 1 mA cm^{-2},[64] were +0.17, +0.04 and

+0.00 V for $Pd_{0.2}Co_{0.8}$, $Pd_{0.15}Co_{0.85}$ and $Pd_{0.1}Co_{0.9}$ alloys, respectively. The dealloying

critical potential decreased with increasing content of less noble element (Co). This

10   trend is reasonable and agrees with the electrochemical behavior of Au-Ag alloys.[64]

To investigate the mechanism that governs the nanoporosity evolution from the

Pd-containing alloys, two surface elemental analyses with different detection depth

were conducted on the alloy surfaces before and after the electrolysis. One is

energy-dispersive X-ray spectroscopy (EDXS) with typical detection depth of 1–10 µm

15   and the other is X-ray photoelectron spectroscopy (XPS) with the detection depth of <

2 nm; thus EDXS and XPS give the information on bulk and near-surface composition,

respectively. EDXS suggested that Co dissolves into H_2SO_4 from $Pd_{0.2}Co_{0.8}$ during the

constant electrolysis, while bulk composition does not change after the constant

electrolysis of $Pd_{0.2}Fe_{0.8}$ and $Pd_{0.2}Ni_{0.8}$ (Fig. 13). However, XPS analyses (Fig. 14)

20   showed that Fe and Ni near the surface (within the detection depth of XPS) of

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$Pd_{0.2}Fe_{0.8}$ and $Pd_{0.2}Ni_{0.8}$ disappear after the electrolysis. XPS also revealed the surface enrichment of Co at the surface of $Pd_{0.2}Co_{0.8}$ occurs during the electrolysis; that is, core-shell-like structure with Pd core and Co shell is generated in the ligaments.

As stated in Introduction, the dissolution of less noble element (Fe, Co or Ni in this case) in the electrolyte and the aggregation of noble adatoms (Pd in this case) through diffusion at the solid/electrolyte interface are equivalently important for the formation of nanoporous structure. Without the aggregation of Pd adatoms, the accumulated Pd atoms would block further dissolution of less noble elements after the initial dissolution at the surface, and after approximately 10 monolayers of the alloys had dissolved, the dissolution would stop and no nanopores would form.[12] The exposure of internal atoms of Fe, Co or Ni to H_2SO_4 due to the aggregation of Pd is necessary for the subsequent dissolution of less noble elements and the formation of nanopores in remnant Pd. The EDXS and XPS (Figs. 13 and 14) suggest that the aggregation of Pd adatoms at the solid/electrolyte interfaces on $Pd_{0.2}Fe_{0.8}$ and $Pd_{0.2}Ni_{0.8}$ is considerably inhibited, and after the initial dissolution of Fe and Ni at the surface layers (Figs. 14(a) and (c)), Pd atoms are accumulated at the surface without exposing internal Fe and Ni to the electrolyte. As a result, no nanoporosity forms during the electrolysis, as schematically shown in Fig. 15a. On the other hand, Pd adatoms readily aggregate into islands at the solid/electrolyte interfaces on $Pd_{0.2}Co_{0.8}$. Similar situation is suggested for well-known nanoporous Au fabricated from Au-Ag alloy, where the

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surface segregation of residual Ag is observed even after thorough removal of Ag by dealloying in HNO_3.[48] Thus, exposed Co atoms successively dissolve to the electrolyte, and consequently, nanoporosity forms in remnant Pd (Fig. 15b). These results experimentally demonstrate that the factors other than standard electrode potentials of elements in initial alloys have significant influence on occurrence or nonoccurrence of nanoporous structure in Pd.

To date, free corrosion of Pd-Co alloy for the fabrication of nanoporous Pd has not yet been successful. Figure 16 shows the FE-SEM image of the $Pd_{0.2}Co_{0.8}$ sample after 17-day immersion in H_2SO_4. Even after 17-day immersion in the concentrated H_2SO_4 electrolyte, no nanoporous structure (like Fig. 11(b)) was observed. The situation was the same when concentrated HNO_3 was used instead of H_2SO_4. This is quite different from those for the free corrosion of Au-Ag alloy,[12,34] in which Ag readily dissolves in HNO_3 or $HClO_4$ without the electrochemical potential and nanoporous Au is spontaneously obtained. The surface segregation of Pd may be responsible for the inertness of the $Pd_{0.2}Co_{0.8}$ alloy under free corrosion condition, although further investigation is needed to elucidate the mechanism.

It has been found that other Pd-containing alloys such as Pd-Al and Pd-Ni-P can be dealloyed to fabricate nanoporous Pd, although these initial alloys have stoichiometric intermetallic and glass phases, respectively.[65,66] Pd-Co alloy described above is a simple fcc binary alloy at any composition; thus the porosity can be widely

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tuned by altering the composition, which is one of the advantages of Pd-Co alloy. Furthermore, combined with Co electrodeposition and thermal alloying, dealloying of Pd-Co can develop nanoporous structure on the surface of bulk Pd, increasing the surface area by up to 300 times.[61] Recent careful examination showed that $Pd_{0.2}Ni_{0.8}$ is also a good candidate of nanoporous Pd under a limited electrochemical condition.[67] Raney-type Pd-Al systems can be dealloyed to nanoporous Pd as well.[68–73]

3.2 Properties: hydrogen storage

Pd is an intrinsic hydrogen-storage metal, and many studies on hydrogen storage in Pd have been conducted.[74] Hydrogen storage properties of nanostructured Pd such as nanocrystalline and/or nanoparticle Pd have been extensively investigated because the surface and grain boundaries are expected to offer peculiar hydrogen absorption sites. Hydrogen storage properties of nanoporous Pd are quite important because nanoporous structures obtained by dealloying are different from that of the aggregation of nanoparticles; that is, the complex surface curvature including concavity (with negative curvature) as well as convexity (with positive curvature) in nanoporous Pd may offer surface properties distinguished from those of nanoparticles. This section briefly describes the hydrogen storage properties of nanoporous Pd.[75]

Pressure-composition isotherm (PCT) measurement, which is the conventional measurement standard of hydrogen storage properties of materials, was conducted on

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nanoporous Pd fabricated by dealloying $Pd_{0.2}Co_{0.8}$. Two types of nanoporous Pd, that is, as-dealloyed and annealed (at 773 K) samples, were subjected to the PCT measurements to elucidate the ligament size effect. The as-dealloyed and annealed samples had average ligament diameters of 20 and 140 nm, respectively (Fig. 17).

5   The PCT curves of the nanoporous Pd are shown in Fig. 18. The three distinct regions were found in both as-dealloyed and annealed samples. In the initial region, the H_2 pressure steeply increased at low hydrogen concentrations, in which H dissolves in the metallic α-phase. The subsequent plateaulike region with nearly constant pressures corresponds to α-to-β phase transition. The second pressure increase region at high

10   hydrogen concentrations indicates the H dissolution in the hydride β-phase. Higher measurement temperatures increased the plateau pressures in both samples, but the plateau pressures themselves were not affected by the ligament size. The as-dealloyed nanoporous Pd with a small ligament size showed a narrower miscibility gap of H between α- and β-phases (corresponding to the storable H) than the annealed one,

15   which is similar to that observed for the nanoparticle Pd.[76,77] Furthermore, the hysteresis in PCT curves of the as-dealloyed nanoporous Pd was much smaller than that of the annealed one. This vanishing trend of hysteresis in PCT curves with the decrease in ligament size is similar to that observed for Pd black.[78]

        The difference from the PCT behaviors of nanoparticle Pd[76] can be seen in the

20   shoulders of the curves where the α-to-β phase transition starts. The hydrogen

solubility in the α-phase hardly increases, although the as-dealloyed nanoporous Pd

had a ligament size as small as 20 nm; that is, the shoulders of the PCTs at the initial

stage are angulated. In other words, the plateau behavior can still be observed at low

hydrogen concentrations in the present nanoporous Pd. This is different from the PCT

5   behavior observed for nanoparticle Pd, where the hydrogen solubility in the α-phase

increases and then the shoulder becomes vague.[76] On the other hand, the β-phase

formation in the present nanoporous Pd, which is shown as the second pressure

increase in the PCT curves, is still similar to that observed in nanoparticle Pd, where

the pressure gradually increases with hydrogen concentration. These results suggest

10   that the nanoporous structure affects the hydrogen dissolution in Pd (α-phase) and

Pd-H (β-phase).

It is known that the H solubility in the α-phase of nanocrystalline Pd[79,80] and

nanoparticle Pd[76] is higher than that of bulk Pd. This is because hydrogen can dissolve

at grain boundaries in nanocrystalline Pd and in the surface and subsurface regions in

15   nanoparticle Pd, in addition to typical octahedral sites. Likewise, nanoporous Pd must

have such additional sites on the surface and subsurface regions. However, the

complex nanoporous structures, which have a negative curvature as well as positive

one, may offer lattice expansion and contraction according to the Laplace equation.[81,82]

When a lattice constant of metallic matrix is reduced, it becomes difficult for hydrogen

20   to occupy interstitial sites[80,83] in the metallic matrix and the hydrogen solubility around

this region decreases (and vice versa). High-resolution transmission electron microscopy (HR-TEM) images of surface of nanoporous Pd are shown in Fig. 19. It is obviously observed that some crystal lattices are expanded (Fig. 19a), whereas others are contracted (Fig. 19b) near the surfaces. Dislocations are also present as shown in

5 Fig. 19b. As exemplified in Figs. 19a and 19b, the lattices on the surface and subsurface regions are significantly disordered, although macroscopic lattice constants are almost the same as that of bulk Pd (as determined by X-ray diffraction (XRD) analyses).[75]

The coexistence of lattice expansion and contraction at the surface of nanoporous

10 Pd is worth noting. To elucidate the effect of lattice constants on the hydrogen adsorption behavior on the Pd surface, first-principles calculations were conducted. The calculations revealed the relationship between hydrogen adsorption energy ΔE_{ad} and lattice strain ε, as shown in Fig. 20. The absolute value of ΔE_{ad} increases with ε. This monotonic relationship between ΔE_{ad} and ε suggests that lattice expansion and

15 contraction, in the range of $-0.05 < \varepsilon < +0.05$, promotes and inhibits the hydrogen adsorption on the Pd (111) surface, respectively. Comparison of density of states (DOS) for the H-adsorbed surface models with different lattice strains (Fig. 21) shows that hydrogen adsorption induces a split-off state below the Pd $4d$ band. In particular, Fig. 21 reveals that the energy difference $(\delta\varepsilon)$ between the bottom of the Pd band and

20 the split-off H-Pd bonding state monotonically increases with lattice strain ε. The

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energy difference $\delta\varepsilon$ is closely related to the bond strength between Pd surface and adsorbed H.[84] Thus this result is in good agreement with the trend of the hydrogen adsorption energy ΔE_{ad}. These calculations qualitatively indicate that the hydrogen dissolves more preferably on Pd surfaces with larger lattice strain.

5   The nanoporous Pd has surface lattice disorder including both lattice expansion and contraction. Lattice expansion enhances the hydrogen solubility at the surface; however, lattice contraction reduces the solubility. These effects cancel each other in the nanoporous Pd owing to the coexistence of the lattice expansion and contraction. The resulting total hydrogen solubility in the α-phase of nanoporous Pd may be nearly

10   the same as that of bulk Pd. Thus, unique PCT behaviors of the nanoporous Pd seems to be much related to the complex nanoporous structure.

4. Nanoporous nickel and nickel-copper

       Raney-Ni and copper (Cu) with nanoporous structures have been already used as

15   a variety of chemical catalysts.[85–87] Synthesis schemes of Raney-Ni and Cu catalysts are the dealloying of Ni-Al and Cu-Al alloys in alkali-leaching etchant (such as NaOH and KOH) without electrochemical potential, respectively.[88,89] However, nanoporous structure in Raney catalysts is irregular,[85] perhaps because of intermetallic compounds in the initial Ni-Al and Cu-Al alloys.

20

4.1 Fabrication

Ni-manganese (Mn) binary phase diagram reveals that a single-phase solid solution of fcc Ni-γMn can be produced by homogenization at a suitable temperature and subsequent rapid quenching. Furthermore, Ni-Cu-Mn ternary phase diagrams indicate that Ni, Cu and Mn form a single-phase solid solution with a wide compositional range at a high temperature. Ni and Cu are nobler elements than Mn; therefore, Mn can be readily dissolved from the starting Ni-Mn and Ni-Cu-Mn alloys, which results in the formation of nanoporous Ni and Ni-Cu.[90]

Figure 22 shows the anodic polarization curves for $Ni_{0.3}Mn_{0.7}$, $Ni_{0.15}Cu_{0.15}Mn_{0.7}$ and $Cu_{0.3}Mn_{0.7}$ alloys measured in 1 mol/L $(NH_4)_2SO_4$. The current density almost monotonically increased with the applied potential for all tested alloys. This trend is similar to the typical anodic polarization behaviors of alloys for fabrication of nanoporous metals including Pd-Co (Figs. 9 and 12). Thus, the common dealloying mechanism (described in the Introduction) is operative in the present Ni-Mn, Ni-Cu-Mn and Cu-Mn alloys in the electrolyte.

TEM images of nanoporous Ni and Ni-Cu fabricated by dealloying of $Ni_{0.3}Mn_{0.7}$ and $Ni_{0.15}Cu_{0.15}Mn_{0.7}$ are shown in Fig. 23. Nanoporous structures with the typical length of approximately 10 nm can be obtained by the dealloying. Combined with XRD analyses, the ligament sizes *d* are estimated and plotted as a function of Ni/(Ni+Cu) molar ratio in the initial alloys in Fig. 24. It can be clearly seen that the

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ligament size decreases with the increase in Ni composition. The diffusion at the solid/electrolyte interface plays a major role in nanopore coarsening. Hence, at the solid/electrolyte interface, Ni had a lower diffusivity than Cu, which results in the smaller pores and ligaments after dealloying. From another viewpoint, pore and

5   ligament sizes of nanoporous Cu can be reduced by the addition of Ni in the initial alloy.

Thermal treatment of nanoporous Ni (preferably under reducing atmosphere) increases pore and ligament sizes up to approximately 300 nm as shown in Fig. 25. The XRD patterns of the as-processed and annealed nanoporous Ni are shown in Fig. 26,

10   showing the peaks of metallic Ni. Inspection of the XRD patterns (Fig. 26 (b)) reveals that the diffraction angle for Ni 111 peak is significantly lowered by the nanoporous structure. As annealing temperature and thus ligament size increase, the peak angle approaches the value for bulk Ni (approximately 44.51° for Cu-Kα radiation). That is, nanoporous structure as fine as 10 nm in Ni is likely to have strong effect on crystal

15   lattice spacing, although the quantitative evaluation is difficult because of the peak broadening.

4.2 Properties: magnetism in nanoporous Ni

Nanosized materials exhibit unique magnetic properties that are greatly different

20   from those of bulk materials. For example, it is known that nanoparticles exhibit

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superparamagnetism or a very low coercivity because their coercivity strongly depends on the six power of diameter or grain size.[91,92] In addition, the nanosized materials often show a lower saturation magnetization than their corresponding bulk materials.[93–95] Nanoporous Ni fabricated by dealloying Ni-Mn is expected to have magnetic properties different from those of previous nanostructured Ni such as nanocrystalline bulk and nanoparticles owing to the complex network of nanopores and nanoligaments. The dependence of magnetic properties on the ligament size may be one of the crucial points that characterize the nanoporous structure. If the nanoporous Ni had superparamagnetism due to its extraordinarily small ligaments, it could be applied as efficient drug carrier in drug delivery system because of its porous structure might allow gradual release of drug.[96]

Figure 27 shows the magnetization curves of nanoporous Ni fabricated by dealloying Ni-Mn, which were measured using a vibrating sample magnetometer at room temperature.[97,98] These magnetization hysteresis loops are typical of ferromagnetic materials. When ligament size of nanoporous Ni is below 50 nm, the saturation magnetization (M_s) and coercivity (H_c) of the nanoporous Ni considerably decreased with decreasing ligament length, as summarized in Figs. 28 (a) and (b).[97,98] It is known that H_c of ferromagnetic nanocrystals and nanoparticles depends on D^6, where D is the grain size. However, H_c of the nanoporous Ni is proportional to $d_L^{1.2}$, where d_L is the ligament size, as shown in Fig. 26(a). The complex networking of

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nanoligaments and nanopores may alter the dimension of exchange length, assuming that a nanoligament is the minimum unit for local magnetic anisotropy.[97]

As for reduced M_s in the nanoporous Ni with small ligaments, it has been known that the ferromagnetic nanoparticles also exhibit a lower M_s than the corresponding bulks.[93–95] Even typical ferromagnetic materials, such as Ni, can possibly be stabilized in a noncollinear magnetic order under special environments.[99] The spin states at the surfaces of the nanoparticles are greatly different from those of the inside. Hence, the decrease in M_s of the nanoporous Ni may be caused by the noncollinear arrangement at its surface. Furthermore, the relationship between M_s and specific surface area (Fig. 29) reveals that M_s of the nanoporous Ni tends to be lower than that of the nanoparticle Ni[100] when the specific surface area of the former is equal to that of the latter. This suggests that the surface effect due to the noncollinear magnetic order is enhanced in the nanoporous Ni compared with that in the nanoparticle Ni. Surface complexity in nanoporous Ni may be at least one of the reasons for higher noncollinear magnetic order.

5. Other nanoporous metals

Dealloying can create nanoporous structures in various metals other than Au, Pd and Ni as described above.

After the first report of fabrication of nanoporous Cu by Min et al. in 1994,[101]

Hayes et al. succeeded in fabricating homogeneous nanoporous Cu by dealloying a single-phase fcc Cu-Mn alloy.[102] Electrolytes of HCl, H_2SO_4, $(NH_4)_2SO_4$ can be used to dissolve Mn and generate nanoporous Cu. One of the promising applications of nanoporous Cu is improvement in surface-enhanced Raman scattering.[103]

Nanoporous platinum (Pt) with extraordinarily small pore and ligament sizes (< 5 nm, as shown in the TEM image in Fig. 30) can also be fabricated through the dealloying of Pt-Cu alloy where Cu dissolves in electrolytes such as H_2SO_4.[104–106] Pt-Ni alloy is another initial alloy suitable for nanoporous Pt which shows excellent oxygen reduction capacity.[107]

Furthermore, similarly to the fabrication of nanoporous Ni-Cu fabrication described above, the dealloying of ternary alloys to form nanoporous binary alloys has been attempted, and Au-Pt[52] and Pt-Ru[108] nanoporous binary alloys have been fabricated.

6. Surface area determination

Large surface area is one of the most prominent characteristics of nanoporous metals. Most of the peculiar properties of nanoporous metals are due to the surface irregularity, as described above; thus, determination of surface area is important. Observations by SEM and TEM can provide information of pore and ligament sizes and porosity (or relative density) etc, which may be converted to the surface area by

approximating the nanoporous structure to a certain unit cell model.[33,98] However,

microscopic observations are always local and may lack comprehensiveness.

The Brunauer-Emmett-Teller (BET) method is one of the methods for surface

area measurement of a material, in which the gas (N_2 for example) adsorption on the

surface is detected. BET is often used to determine surface area of various

nanostructured materials, including nanoporous (or mesoporous) ceramics and carbon

materials. To date, there are several reports that employ BET for surface area

measurement of nanoporous metals.[27,109] BET requires several grams of a sample in

weight; however, it is sometimes difficult to prepare even one gram of nanoporous

metals by dealloying in a laboratory scale. Furthermore, samples are often preheated in

BET method to remove adsorptive water or contaminant, during which the actual

surface area may decrease because of pore coarsening.

Alternatively, electrochemical methods are effective for surface area

measurement of nanoporous metals at room temperature. Electrochemical methods

require only a small amount of sample. In the electrochemical methods, the surface

area is often represented by roughness factor (R_f), which is defined as the ratio of true

(or electrochemically active) surface area to apparent surface area (thus, $R_f = 1$ for flat

and smooth surface). R_f of nanoporous Au can be estimated by cyclic voltammetry

(CV), using the nanoporous Au as a working electrode in H_2SO_4. The charge

associated with the reduction of adsorbed oxygen (Q_{OC}), which can be calculated by

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the integration of the peak observed during a cathodic scan after the correction of double-layer charging in the CV, is proportional to the true surface area; thus the Q_{OC} of nanoporous Au is compared to that (= 390 ± 10 µC cm^{-2}) of the flat polycrystalline Au.[110] This method is applicable to nanoporous Pd as well.[61,110] On the other hand, the

5 charge corresponding to hydrogen adsorption can be used to evaluate R_f of nanoporous Pt.[106,110,111]

Liu et al. showed another electrochemical method by utilizing underpotential deposition (UPD) of Pb for surface area measurement of nanoporous Au.[112] In this study, the comparison with BET method was fairly conducted on the heat-treated

10 samples to demonstrate the availability of the proposed UPD method. Also, it was shown that the concentration of Pb^{2+} ion should be enough high to evaluate pores smaller than 8 nm.

Assessment of surface area is now gaining much importance to evaluate the catalytic and electrochemical performance of nanoporous metals. As well as peculiar

15 properties, methods of surface area measurement must be advanced and standardized for practical use of nanoporous metals.

7. Summary

Nanoporous metals are currently being developed from both fundamental and

20 application viewpoints. Dealloying is not only an important reaction related to the

corrosion of alloys, which is harmful to structural materials, but also a useful self-synthetic method for producing metallic nanoporous materials with specific functionality. The elements selected for the initial alloys must have large difference in standard electrode potential; however, in some cases (such Pd-Fe and Pe-Ni explained above) this is not a sufficient condition. There are many avenues of research that may elucidate the underlying mechanism for nanopore formation.

Ligaments and pores in nanoporous metals are as small as typical nanoparticles; thus, nanoporous metals have high surface area comparable to those of nanoparticles. In addition to the high surface area, nanoporous metals exhibit various properties different from those of nanoparticles because the complex three-dimensional network of nanoligaments and nanopores provides a different surface state from that of nanoparticles. Thus, nanoporous metals are regarded as a new type of nanostructured material emerging from nanoparticles, nanowires and nanotubes. Further functional and processing development is required for the application of these peculiar nanostructured metals.

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Figure Captions

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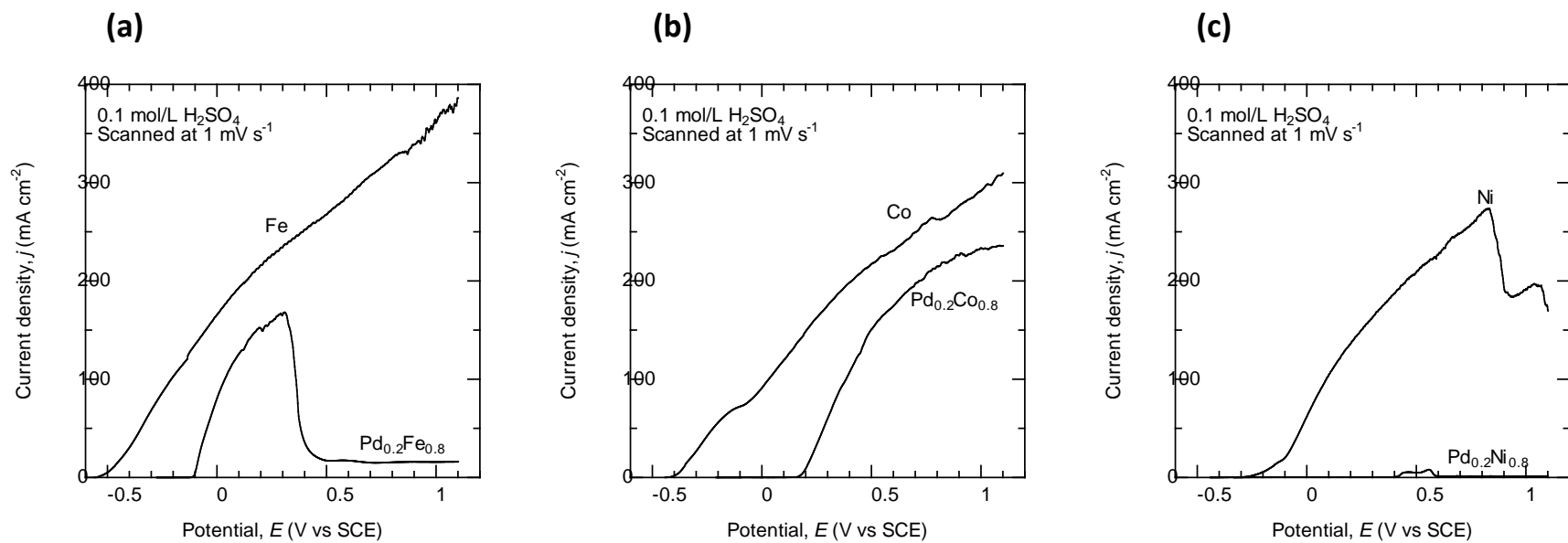
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Figure 17. Scanning electron microscopy images of (a) as-dealloyed and (b) annealed nanoporous Pd. Shown with permission from American Chemical Society (ref. 75).

Figure 18. Pressure-composition isotherms for (a) as-dealloyed and (b) annealed nanoporous Pd samples. Shown with permission from American Chemical Society (ref. 75).

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Figure 20. Relationship between hydrogen adsorption energy ΔE_{ad} and lattice strain ε calculated by first-principles calculations.

Figure 21. Surface electronic densities of states for H-adsorbed Pd surface models with lattice strains of (a) -0.05, (b) 0 and (c) $+0.05$. Shown with permission from American Chemical Society (ref. 75).

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Figure 30. Transmission electron microscopy image of nanoporous Pt fabricated by

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dealloying $Pt_{0.2}Cu_{0.8}$ in 0.1 mol/L H_2SO_4.

Tables

Table 1. Standard electrode potentials of representative reactions of selected elements used for fabrication of nanoporous Pd.[24]

Element	Reaction	Standard electrode potential, E_0 (V vs standard hydrogen electrode)
Pd	$Pd^{2+} + 2e^- \rightarrow Pd$	+0.987
Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.440
Co	$Co^{2+} + 2e^- \rightarrow Co$	−0.277
Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.250

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(a) 473 K

$d_L = 31$ nm

200 nm

(b) 573 K

$d_L = 140$ nm

400 nm

(c) 673 K

$d_L = 200$ nm

400 nm

(d) 773 K

$d_L = 440$ nm

400 nm

(e) 873 K

$d_L = 700$ nm

2 µm

(f) 973 K

$d_L = 1200$ nm

2 µm

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(a) (from Pd-Fe)　　　　**(b)** (from Pd-Co)　　　　**(c)** (from Pd-Ni)

200 nm　　　　200 nm　　　　200 nm

Figure 11. Scanning electron microscopy images of (a) $Pd_{0.2}Fe_{0.8}$, (b) $Pd_{0.2}Co_{0.8}$ and (c) $Pd_{0.2}Ni_{0.8}$ after electrolysis conducted at +0.6 V (vs SCE) in 0.1 mol/L H_2SO_4 for 1800 s at 298 K. Shown with permission from Elsevier (ref. 63).

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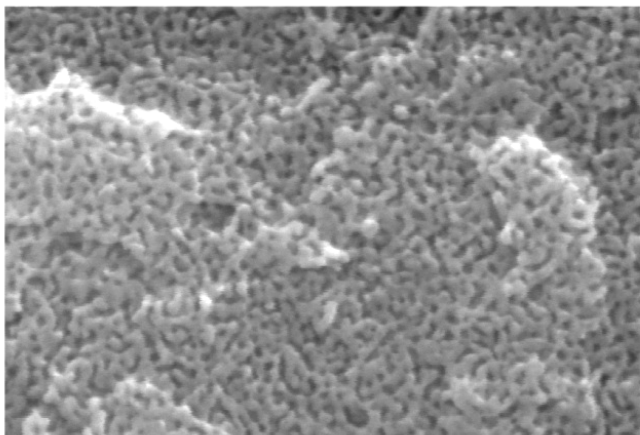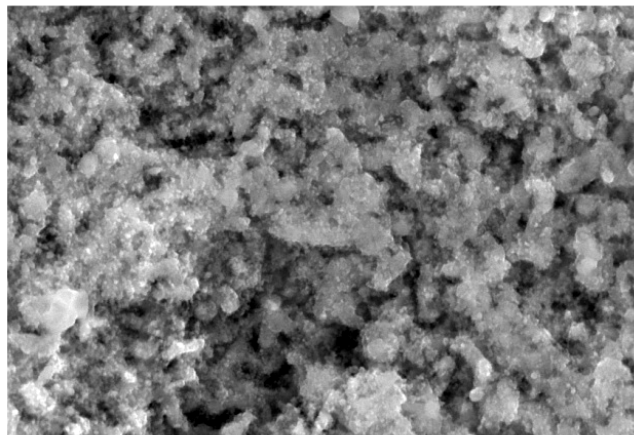
(a) As-dealloyed

(b) Annealed

200 nm

1 µm

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(a) from Ni-Mn
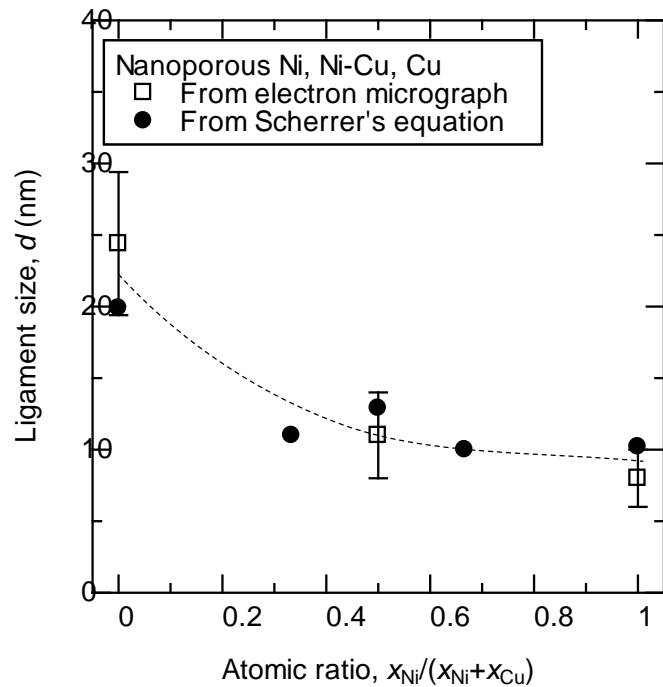
(b) from Ni-Cu-Mn

40 nm

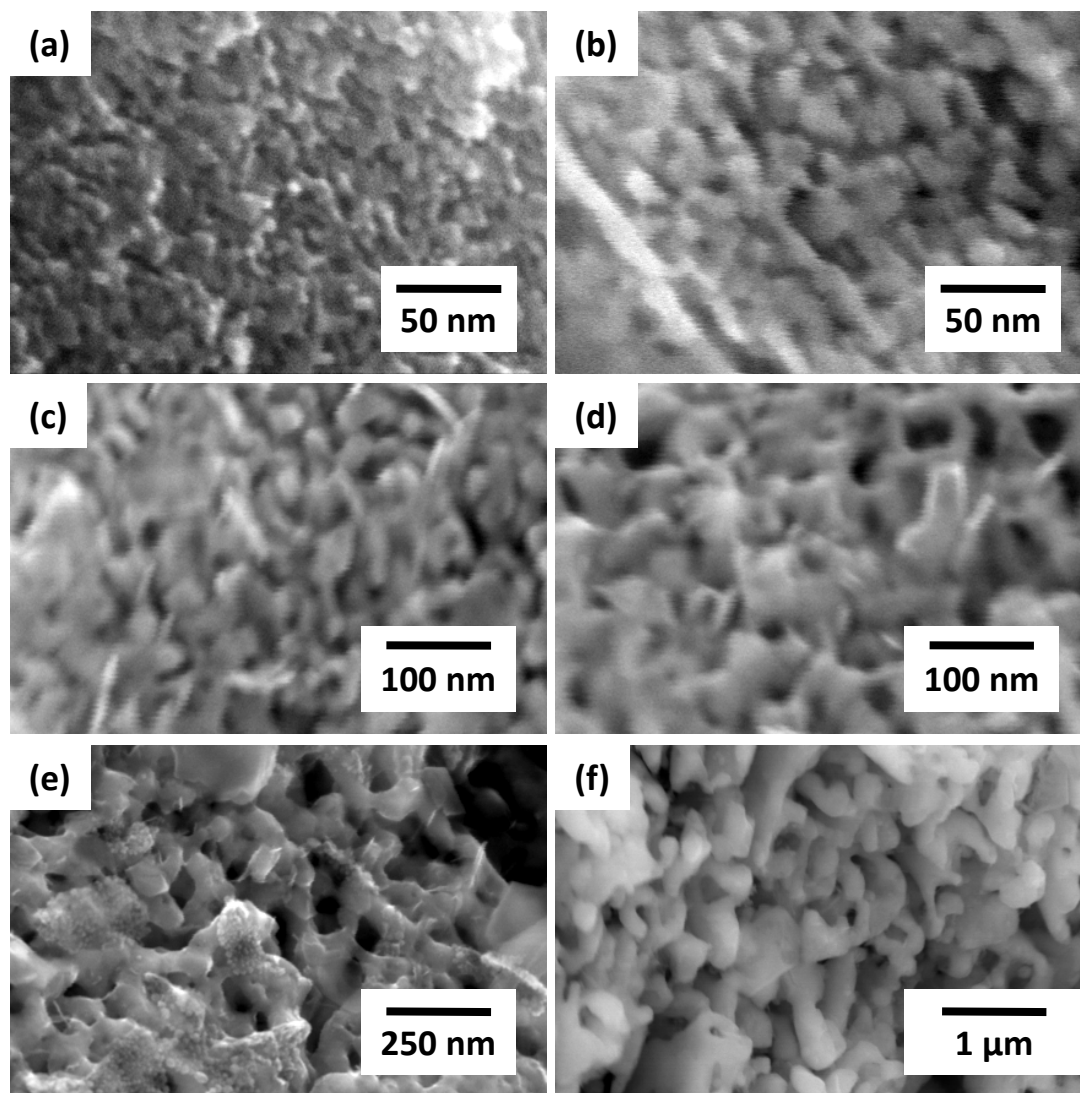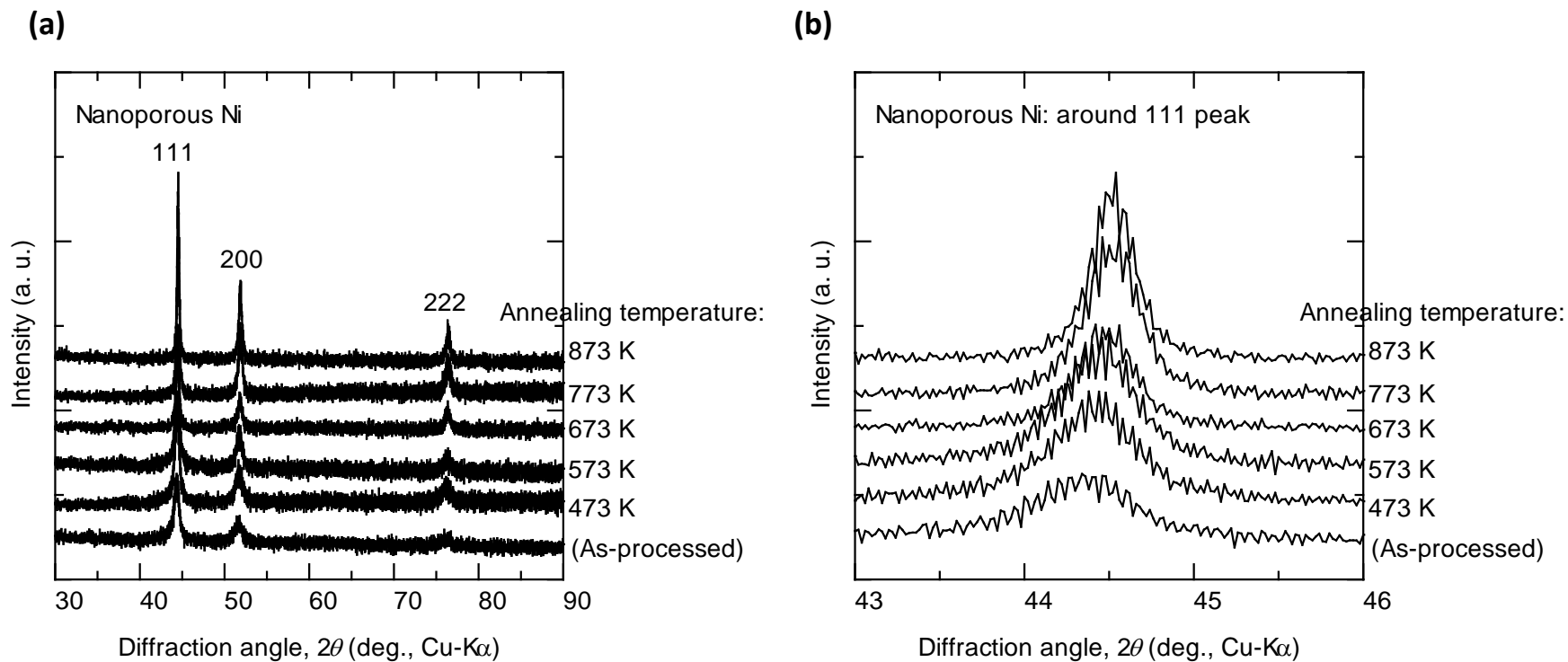40 nm

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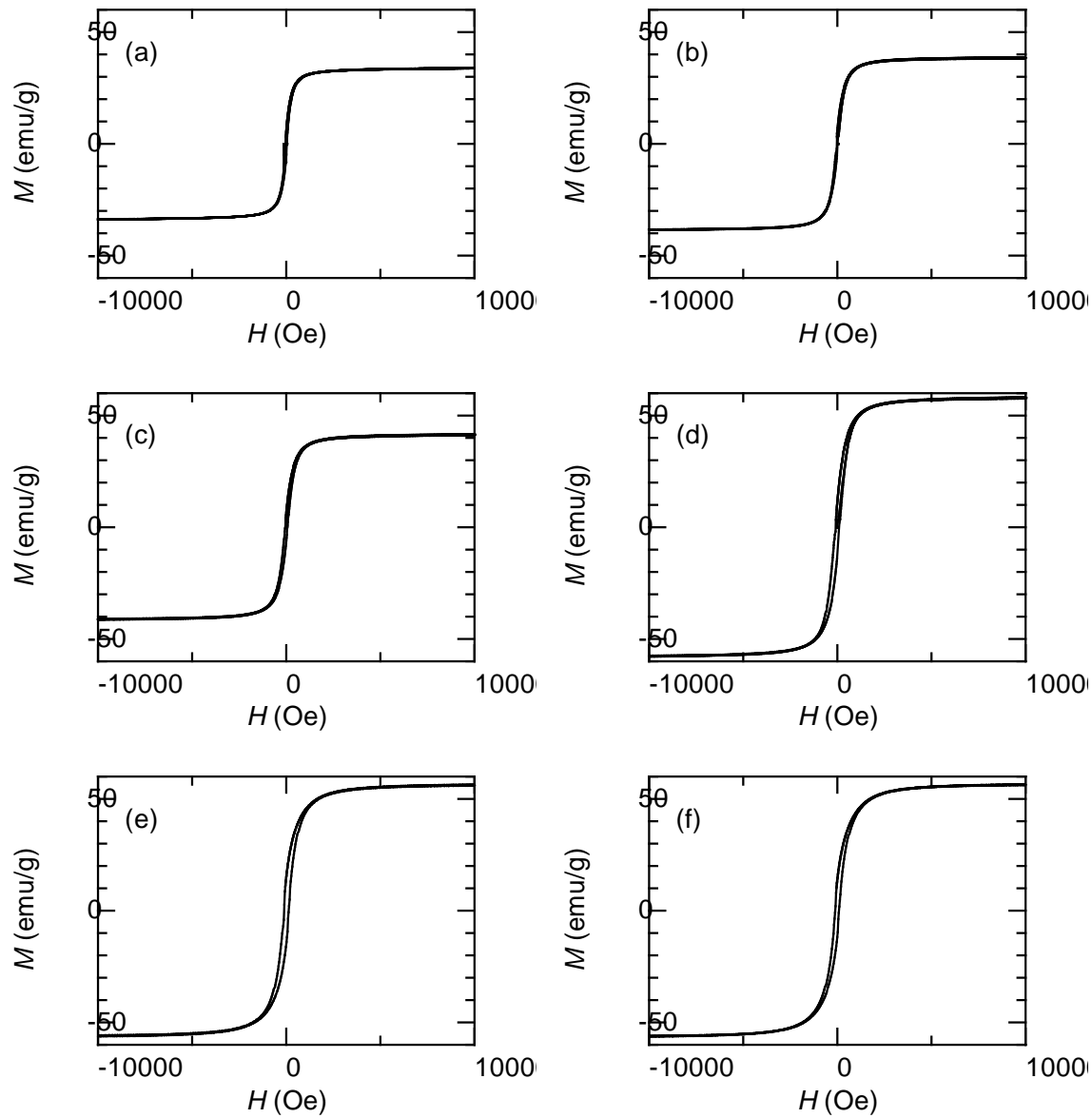
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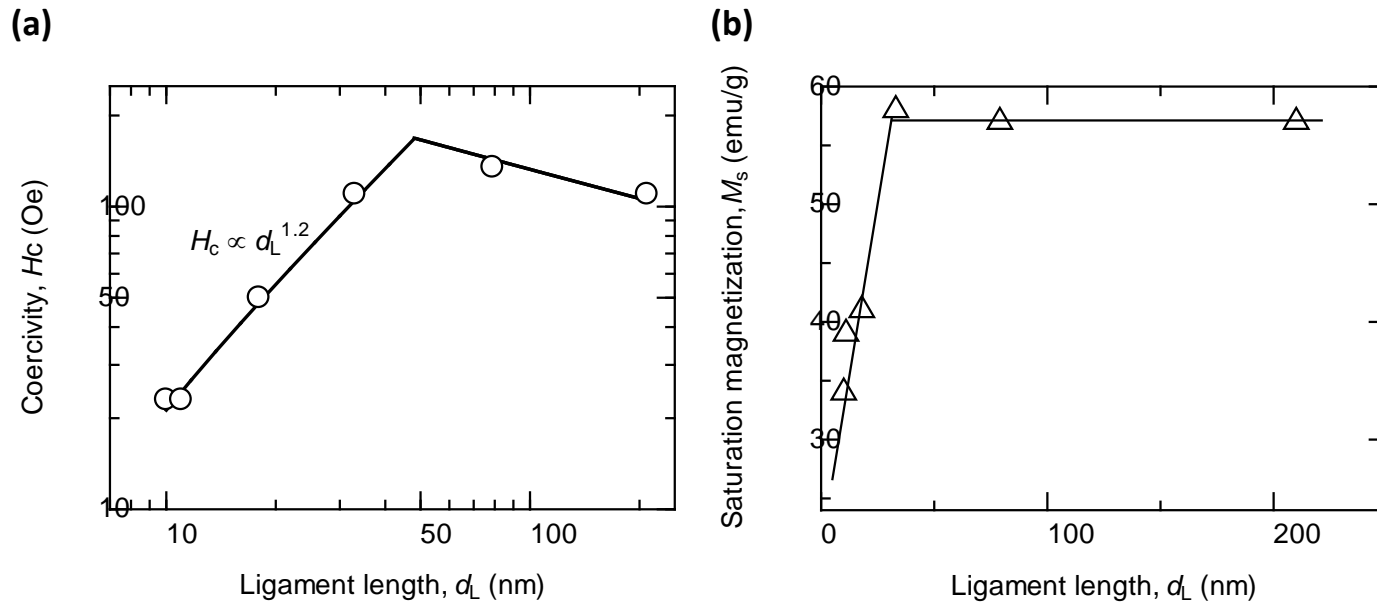
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(a)

Intensity (a. u.)

Nanoporous Ni

111

200

222

Annealing temperature:

873 K

773 K

673 K

573 K

473 K

(As-processed)

30   40   50   60   70   80   90

Diffraction angle, 2θ (deg., Cu-Kα)

(b)

Intensity (a. u.)

Nanoporous Ni: around 111 peak

Annealing temperature:

873 K

773 K

673 K

573 K

473 K

(As-processed)

43   44   45   46
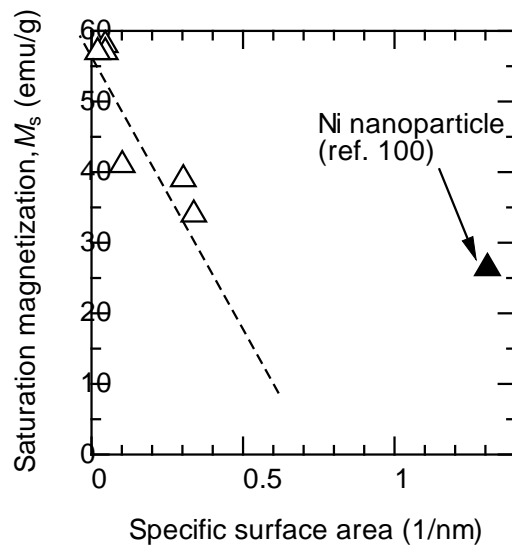
Diffraction angle, 2θ (deg., Cu-Kα)

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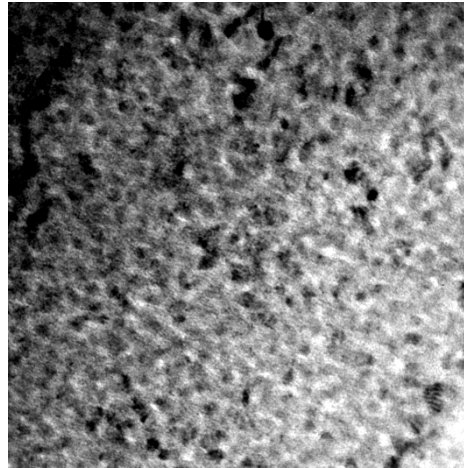
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50 nm

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