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Properties and Application of Nanoporous Metals Fabricated by Dealloying

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ABSTRACT

Dealloying, that is, selective dissolution of less noble elements from binary alloys, can create nanoporous metals with three-dimensionally interconnected nanopores and nanoligaments. Various metals such as Au, Pt, Pd, Ru, Cu and Ni can be made nanoporous through the dealloying of simple single-phase binary alloys. The aggregation of nobler element atoms via diffusion at solid/electrolyte interface is necessary for the evolution of nanoporosity during dealloying. The open-cell metallic nanoporous structure offers various properties (including mechanical, magnetic and catalytic ones) distinguished from those of other nanomaterials such as nanoparticles, nanowires etc. For example, nanoporous metals clearly show the catalytic decoloration of azo dye solution without light irradiation, while bulk counterpart metals do not. The defective structure and straining at the surface of nanoligaments are important for the peculiar properties of nanoporous metals.

1. INTRODUCTION

Materials with a porous (or foamed or cellular) structure intrinsically provide many functions. In particular, nanoporous structures, which consist of a network of nanosized pores and ligaments, are common in oxide ceramics (Corma 1997, Yang 1998, Soler-Illia 2002) and carbon materials (Ryoo 2001, Lee 1999), 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 (Forty 1980, Erlebacher 2001, Ding 2009, Weissmüller 2009), 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

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formation of nanoporous structures itself has been known and utilized since the 1920s, during which nanoporous Raney-type catalysts were patented (Raney 1927, Raney 1927). 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 presentation the fabrication of various species of nanoporous metals by dealloying is shown. Also, their peculiar properties are shown.

2. FABRICATION

Fig. 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 (Erlebacher 2001), in which entwined two phases gradually forms without nucleation and growth during the equilibration of two-elemental solids, and markedly different from so-called template, replication or spacer method (Wijnhoven 2000, Attard 1997, Hakamada 2005), 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.

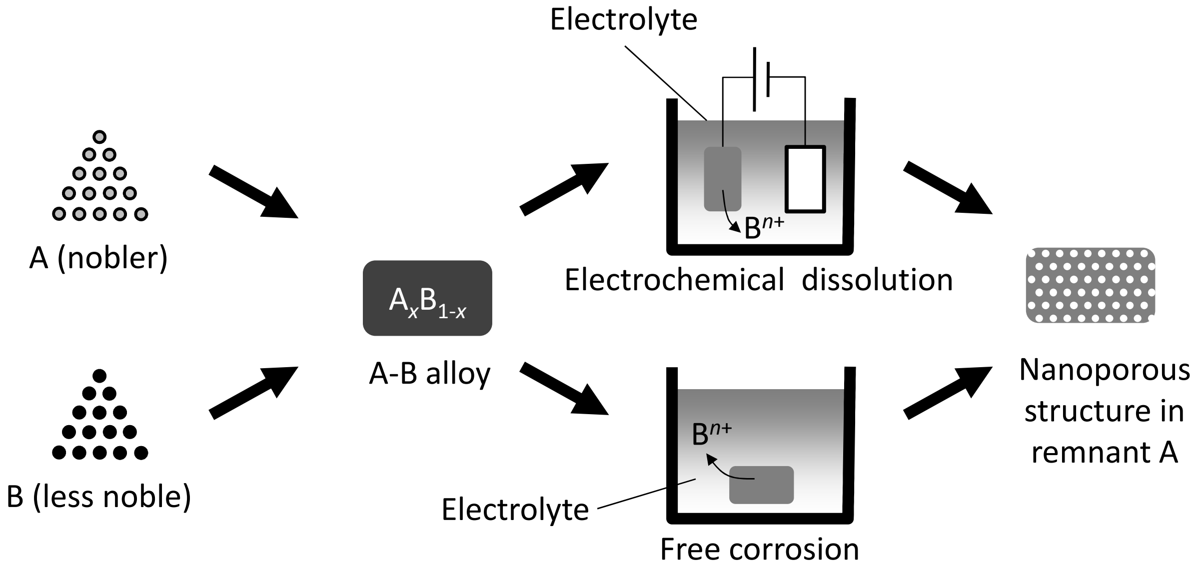


Fig. 1 Schematic illustration of use of dealloying to fabricate nanoporous metals

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 (Forty 1980, Erlebacher 2001). 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. Various nanoporous metals are currently being developed, as exemplified in Fig. 3.

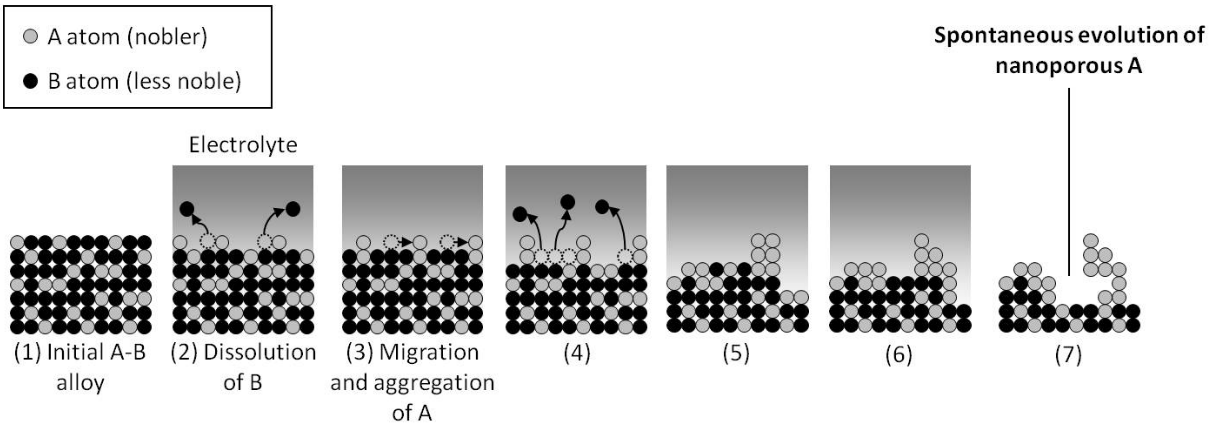


Fig. 2 Behavior of atoms at the interface between solid and electrolyte during dealloying

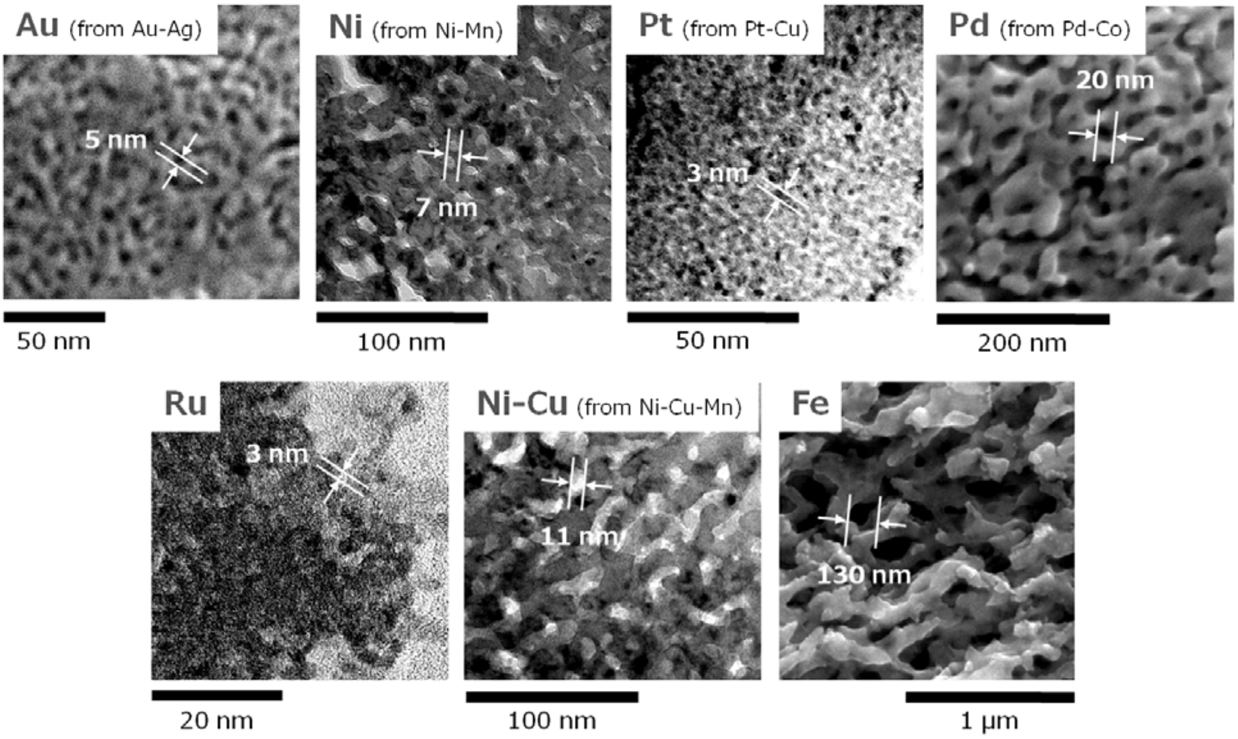


Fig. 3 Various nanoporous metals fabricated by dealloying.

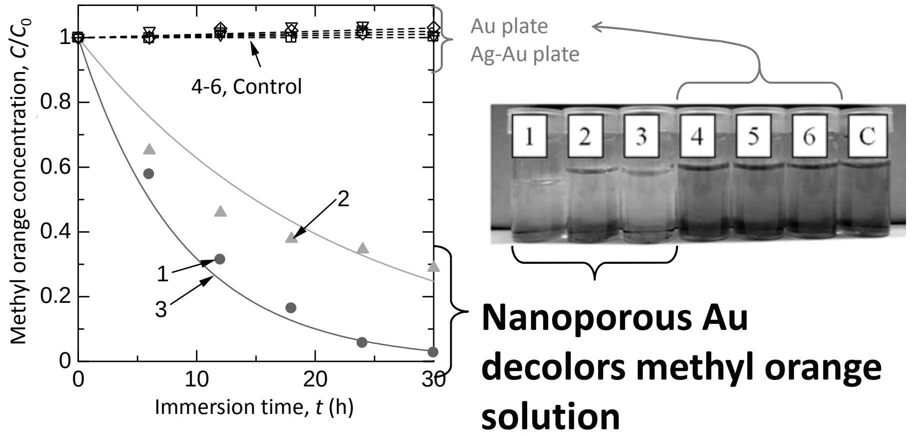
The size and morphology of pores and ligaments can be controlled by thermal and/or acid treatments, which induce the reorganization of the nanoporous structure. The smallest pores are under 5 nm while the largest pores are above 1000 nm. The ability to adjust the pore size over such a wide range is one of the characteristics of nanoporous metals fabricated by dealloying.

3. CATALYTIC PROPERTIES FOR DECOLORATION

Several studies have reported that nanoporous Au exhibits catalysis during the oxidation of CO (Zielasek 2006, Xu 2007, Kameoka 2008, Wittstock 2009) and methanol (Wittstock 2010), while its counterpart, bulk Au without a porous structure, does not. In this section, we show the catalytic degradation of a dye solution by nanoporous Au, which is distinguished from the conventional photocatalytic effect known in semiconductor oxides such as TiO_2 and ZnO.

Time variation of the MO concentration after sample immersion is shown in the left panel of Fig. 4. Nanoporous Au (Samples 1–3) significantly reduced MO concentration, whereas bulk Au, bulk $Au_{0.3}Ag_{0.7}$, and bulk $Au_{0.7}Ag_{0.3}$ had no distinguishable effect on the MO concentration. After 30-h immersion of the nanoporous Au with ligaments and a pore size of less than 10 nm (Samples 1 and 3), the MO concentration became negligible. This is also demonstrated in the right panel of Fig. 4, which shows the appearance of the MO solution after the 30-h immersion. On the other hand, TiO_2 and ZnO photocatalytic sheets were found not to decrease the MO concentration, because the tests were carried out under a dark condition with no light irradiation.

It is indicated that the defective and strained surface of the ligaments in nanoporous Au can increase the reactivity of the Au surfaces, and decrease the concentration of the MO solution. In the past, many reports have shown that nanostructured Au has a wide variety of catalytic properties (Min 2007). However, there have been no reports to date for unsupported nanoporous Au exhibiting the catalytic degradation of complicated organic compounds such as azo dyes. The catalytic or photocatalytic degradation of such organic compounds as azo dyes has required the use of an excess amount of oxidizing agents and irradiation of light (Hoffman 1995). The present results also add the information on bond-breaking capacity of gold, which has been drawing much attention (Freyschlag, 2011).



Nanoporous Au decolors methyl orange solution

Fig. 4 Decoloration of methyl orange solution by nanoporous Au.

CONCLUSIONS

Nanoporous metals are currently being developed from both fundamental and 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. There are still 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. Thus, nanoporous metals are regarded as a new type of nanostructured material emerging from nanoparticles, nanowires and nanotubes.

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