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Preparation of hierarchical porous metals by two-step liquid metal dealloying

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ABSTRACT

A hierarchical porous metal has been prepared by two-step liquid metal dealloying using an alloy precursor containing two soluble components and two metal baths. After the first dealloying step, one of the soluble components is dissolved and a coarse porous structure is formed. After a shorter dealloying step in another melt, the other soluble component is dissolved and a fine porous structure is formed within the previously formed coarse ligaments. The resultant porous metal presents a hierarchical morphology with a bimodal pore distribution, resulting in a higher porosity and surface-area-to-volume ratio than what can be formed by one-step dealloying methods.

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The dealloyed nanoporous metals [1–3] are attracting much attention due to their excellent performance as catalyst, electrode, optical and sensing materials [4–5]. Generally, the functional properties of dealloyed nanoporous metals are attributed to their extremely large surface area and unique three-dimensional (3D) bicontinuous nanostructure. Therefore, it is important to optimize the porous structure characteristics such as pore and ligament sizes, porosity and specific surface area depending on the target application. For example, for electrode applications [4], a specific design of the porous structure is required to obtain the desired performance: large pores are necessary to facilitate the penetration of the electrolytic solution in the foam, while small pores are also essential to increase the surface area and improve the electrochemical reaction. Such seemingly contradictory properties can be simultaneously achieved by developing a hierarchical porous structure. In a hierarchical porous structure, pores with two (or more) distinct sizes are present and the properties associated to each pore family can be controlled by changing independently the different pore size.

A typical approach to prepare such hierarchical porous metals is to perform a two-step dealloying in an aqueous solution. In Refs [6–8], an Au–Ag alloy precursor was dealloyed in HNO₃ aqueous solution to form fine porous Au, followed by thermal treatment to coarsen the porous structure. Subsequently, an Ag plating was applied on the surface of the coarsened porous Au and a heat treatment was applied to homogenize the ligament composition through bulk diffusion. Finally, it was

dealloyed again in HNO₃ to form finer pores within the ligaments. The resulting porous metal presents a bimodal pore size distribution with large and small scale pores formed at the first and second dealloying steps, respectively.

Because dealloying in aqueous solution is a corrosion phenomenon, this technique is mostly limited to noble metals [1–8], although some exceptions were reported [9]. In a recent breakthrough, we have developed an innovative dealloying technique using liquid metal instead of an aqueous solution [10]. By immersion of the alloy precursor in the liquid metal bath, a component of the precursor alloy is selectively dissolved from the solid/liquid interface and the remaining component reorganizes at the solid/liquid interface. This reorganization is attributed to an interfacial spinodal decomposition [11], leading to the formation of a 3D porous structure. The dealloying reaction results from a thermodynamical equilibrium taking place between the solid and liquid phase at the dealloying front. It can also come along with structural phase transitions (FCC to BCC in the case of Fe–Ni dealloyed in Mg) and the possible nucleation of intermetallic compounds. Because this reaction occurs in the liquid metal, it can be applied to less-noble metals that could not be dealloyed in an aqueous solution. By use of this technique, a large variety of less-noble metal based porous or composite materials with outstanding electrochemical or mechanical properties have been fabricated: Ti [10,12,13], Nb [14], V, Fe [15,16], Cr [15], Ta [11,17,18], Si [19,20] and C [21].

In the present work, a hierarchically porous Fe–Cr alloy presenting a bimodal pore size distribution was prepared by two-step liquid metal dealloying for the first time. The strategy of this method is schematically shown in Fig. 1. A multicomponent A–(B₁, B₂) alloy precursor and two

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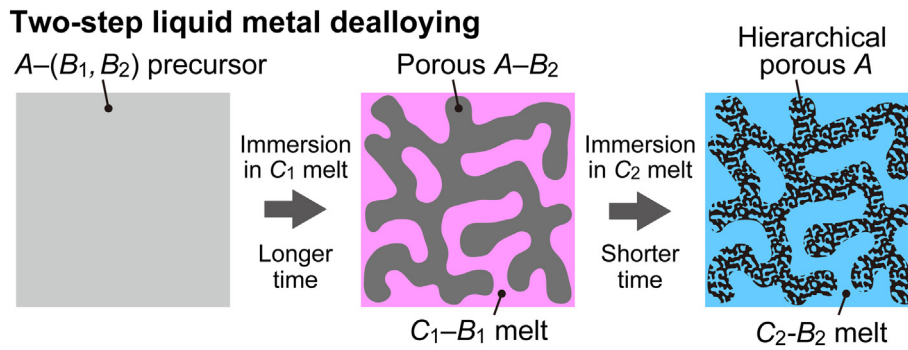


Fig. 1. Schematic illustrations showing the formation of hierarchical porous A by two-step dealloying of A-(B₁, B₂) precursor in C₁ and C₂ liquid metal baths.

metallic baths denoted C₁ and C₂ are used (A, B₁, B₂, C₁ and C₂ denote elements). These elements are selected to satisfy the following conditions: A is immiscible in both C₁ and C₂, B₁ is miscible in C₁, B₂ is miscible only in C₂. In the first dealloying step in the C₁ melt (for a longer time), B₁ component is selectively dissolved into C₁ and a porous structure of A-B₂ alloy with a unimodal pore size distribution is expected to form. In the second dealloying step in C₂ melt, B₂ component is selectively dissolved into C₂ and a porous structure of A is expected to evolve within the ligaments of the initial structure. Since the ligament size increases with the dealloying time [15,18], the second dealloying step is chosen to be much shorter than the first one in order to produce a hierarchically microstructured material with a bimodal pore distribution. By extending this method to more steps, hierarchical porous metals with multimodal pore size distribution can in principle be obtained.

In this paper, the preparation of porous Fe-based alloy with a bimodal pore size distribution is demonstrated. Our previous work revealed that by immersing a (Fe, Cr)-Ni alloy precursor in Mg melt, Ni is dissolved selectively in the Mg melt and a porous Fe-Cr alloy forms owing to the miscibility of Mg-Ni and immiscibility of Mg-(Fe, Cr) [14]. This dealloying reaction was extended to two-step dealloying by adding Mn in the precursor and employing Bi melt as the second bath.

A $(\text{Fe}_{0.8}\text{Cr}_{0.2})_{0.3}\text{Mn}_{0.7}\text{Ni}_{40}$ (at.%) ingot was prepared by induction melting using pure Fe, Cr, Mn and Ni metals (purity >99.9 mass%) in a boron nitride crucible under He gas atmosphere. The ingot was cold-rolled into a sheet with a thickness of ~200 μm and cut into a rectangular shape of 8 mm × 8 mm. The samples were sealed in quartz tubes under vacuum (10^{-3} Pa) and annealed in an electric furnace at 1173 K for 2 h for homogenization. Pure Mg (50 g, 99.9 mass%) and Bi (150 g, 99.99 mass%) melt bath were inductively heated in a graphite crucible of cylindrical shape (inner diameter: 35 mm, height: 40 mm) at 1023 K under He gas atmosphere (~0.1 MPa). The loss of Mg due to the evaporation was within 1% during the dealloying treatment.

Firstly, the Fe-Cr-Mn-Ni sheet precursor was immersed in the Mg melt bath for 20 min. Secondly, the sample was immersed in the Bi melt for 1 min. After the two immersions, the sample was immersed in a HNO₃ solution (about 8 mol/l) to remove the metallic baths components, followed by rinsing in pure water. The microstructure and chemical composition were analyzed using a scanning electron microscope (SEM, Ultra55, Zeiss, Germany) equipped with an energy dispersive X-ray spectroscope (EDX, Xflash, Bruker, Germany). The porosity, pore and ligament sizes and specific surface area were determined by image analyses on cross-sectional SEM image using Fiji software. The cross-section was fabricated by Ar ion milling (E-3500, Hitachi, Japan). The phase of the sample was analyzed by X-ray diffraction (XRD, D8 Advance with CuKα source, Bruker, Germany).

Fig. 2(a) shows the cross-sectional SEM image and corresponding EDX elemental maps (Fe, Cr, Mn, and Ni) for the cold-rolled Fe-Cr-Mn-Ni alloy sheet precursor. The SEM image shows no observable contrast difference in this area, except for the presence of elongated pores. In the EDX maps, Fe, Cr, Mn and Ni are uniformly distributed and no concentration fluctuation was detected, indicating that the sample is a

solid solution with uniform composition. The XRD pattern shown in Fig. S1 in the Supplementary information also confirmed that the precursor sample is a single phase of the face-centered cubic structure. Fig. 2(b) shows a cross-sectional SEM image and EDX maps for the Fe-Cr-Mn-Ni precursor immersed in Mg melt at 1023 K for 20 min. The immersed sample shows a fine bicontinuous microstructure typical of the liquid metal dealloying, in which bright ligaments are embedded in a dark matrix phase. The EDX maps reveal that the ligaments are enriched in Fe, Cr, Mn with a small content of Ni, while the remaining matrix contains mostly Mg. The average chemical composition of the ligaments is Fe_{27.2}Cr_{7.5}Mn_{63.6}Ni_{2.0} (at.%). It should be noted that the composition ratio of Fe:Cr:Mn after immersion is kept almost the same than the original precursor, while a drastic depletion of Ni is detected, indicating that selective dissolution of Ni occurred in accordance with the reaction design. Fig. 2(c) shows histograms of the size of ligaments and remaining matrix, respectively. The curves drawn with solid lines show fitted log-normal distributions. Both phases display a unimodal size distribution. Statistical image analyses show that the volume fraction and average size (mode value) are 57.4% and 2.4 μm for the ligament and 42.6% and 1.5 μm for the remaining matrix, respectively.

The (Fe-Cr-Mn)/Mg composite sample was subjected to the second step immersion in a Bi melt at 1023 K for 1 min. Upon immersion, the Mg phase in the composite sample dissolves into the Bi melt due to the miscibility of Bi-Mg. Fig. 3(a) shows a cross-sectional SEM image and EDX maps for the yellow square region in the sample after the second dealloying step. The SEM reveals that the macroscopic bicontinuous structure formed during the first dealloying step was mostly preserved, while the individual ligaments were further dealloyed and a finer bicontinuous structure of submicron length developed within the ligaments. From the EDX maps, it was identified that the finer ligament is mostly enriched in Fe, Cr with a small amount of Mn and the remaining matrix region is enriched in Bi mostly with a small amount of Mg. The intermediate gray-scale contrast phase enriched in Bi and Mn is also observed in the matrix region which is likely the Bi-Mn compound precipitated during the solidification of the Bi melt bath.

This (Fe-Cr-Mn)/Bi composite was immersed in a HNO₃ solution for 2 h to remove Bi-rich phase. The Bi metal reacts with the HNO₃ solution to form Bi nitrate that is soluble in the concentrated solution of pH < 0 [22]. The Fe-Cr-Mn ligament, of which the composition is similar to the Cr-Mn stainless steel, is expected to display excellent corrosion resistance in HNO₃ solution due to the formation of a passive film [23]. Therefore, the porous Fe-Cr-Mn could be extracted by etching in nitric acid, although the standard electrode potential of Bi is higher than those of Fe, Cr and Ni. The overall structure of the resulting sample is shown in Fig. 3(b) where the hierarchical porous structure with a bimodal distribution of pores can be clearly seen. The porosity and the surface-area-to-volume ratio of the porous sample, obtained by image analyses are about 80% and $1.4 \times 10^6 \text{ m}^2/\text{m}^3$, respectively, being higher than those formed by normal one-step liquid metal dealloying using a similar alloy precursor [15]. The average composition of the ligaments

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