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Novel method of powder-based processing of copper nanofoams for their potential use in energy applications

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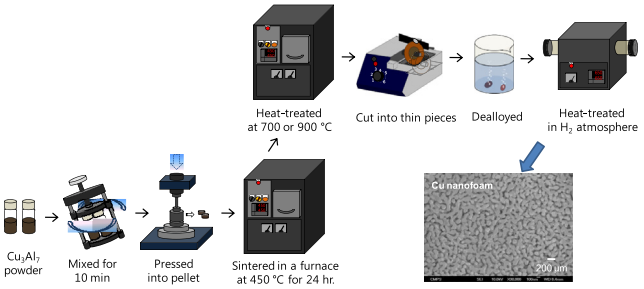
HIGHLIGHTS

- Cu nanofoams are fabricated using a simple powder-metallurgy method.
- This method is useful for producing thin Cu nanofoams with potential energy applications.
- Cu foams with multiscale pores can also be fabricated by slightly modifying the processing route.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper discusses a new method of powder-metallurgy processing to produce regular-structured Cu nanofoams or irregular-structured Cu foams containing both micropores and nanopores. Coarser Cu nanofoam struts (approximately 2.5 times larger) formed in the ribbon samples of the foams subjected to additional sintering at 900 °C after initial lower-temperature sintering at 450 °C than those formed in the ribbon samples of the foams subjected to additional sintering at 700 °C. Furthermore, a much higher degree of strut continuity was observed in the Cu nanofoam sintered at 900 °C, which should improve the ductility and structural integrity of the Cu nanofoam. This study can be considered as a framework for using a simple method of powder-based dealloying to produce nanoporous and micro/nanoporous metallic foams for a variety of energy-based applications requiring metallic foam materials with a high density of specific surface area. Although the dealloying process of achieving Cu nanofoams is not new, this powder-based method has significant implications because often a difficult and expensive material shaping process can be avoided by forming the precursor alloy with a near-net shape geometry in the method.

1. Introduction

In order to obtain a nanoporous structure that exhibits a high density of specific surface area for energy or functional applications, a majority of earlier studies have been confined to organic or inorganic materials [1,2], because it is generally more difficult to

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produce a nanoporous metallic structure owing to the relatively poor oxidation and corrosion resistance of metallic materials. Despite such disadvantages, some successful attempts have recently been made to take advantage of the great potential that nanoporous metallic structures have for use in functional applications such as substrates for heat-exchanger applications, catalysts, sensors, actuators, fuel cells, and microfluidic flow controllers [3–6]; nanoporous metallic structures generally have relatively better mechanical properties and long-term operational reliability. Indeed, recent studies have focused considerable attention on processing and characterizing high-performance nanoporous noble metals through dealloying; that is, the selective dissolution during anodic corrosion in which less noble metal is dissolved out of an alloy and more noble metal remains nanoporous [7]. Moreover, since the earlier reports on nanoporous Au foams dealloyed from silver–gold alloys [8–10], there have been numerous follow-up studies on the processing, characterization, and mechanical properties of nanoporous noble metals [11,12]. For example, Chen et al. used X-ray nanotomography and microbeam diffraction to study the structural evolution of nanoporous gold produced from Ag–Au [13]; Qian and Chen produced ultrafine nanoporous Au from Ag–Au by dealloying at lower temperatures [14]; and Ateya et al. produced nanoporous Au from Cu–Au alloy [15].

The latest reports, on the other hand, have focused on methods of producing non-noble nanoporous metallic foams. For example, nanoporous Ti foams were produced using a new dealloying method based on an attractive force among the constituent elements in a metallic melt [16], nanoporous Ni foams were produced by leaching manganese in a single-phase solid solution of face-centered cubic (fcc) Ni-γMn [17], and nanoporous Cu alloy foams were produced by dealloying in an alkaline solution to extract Al from $CuAl_2$ or Cu–Al–Zn alloy systems, namely Raney copper [18–20].

The previously reported methods of producing nanoporous metallic structures are all based on complete melting processing, whereas this paper presents a novel powder-based processing method of producing the precursor alloys, which is simpler because a much lower processing temperature is required and a near-net shape geometry can be achieved directly without an additional machining or deposition process. This is important because if the nanoporous metallic foams are to be used as an electrode in batteries, die-sensitized solar cells, or fuel cells, they must be prepared in the form of a thin film with a thickness of tens to hundreds of microns; for example, anode material to be used in a typical coin cell should be a foil with a thickness of $\sim$100 μm. Therefore, use of this powder-based dealloying method makes it possible that one can avoid a difficult and costly additional material shaping process by obtaining the precursor alloy with near-net shape geometry.

In addition, this paper demonstrates that the powder-based dealloying method can be used to produce nanoscale Cu foams with the pore size on the order of a few hundreds of nanometers and can also be slightly modified to produce multiscale Cu foams containing a mixture of nanopores and micropores from Cu–Al alloys precursors.

2. Experimental

Nanoscale copper foams were synthesized using a novel powder-metallurgy process and Cu and Al powders (Cu: 99.9%, mean particle size: 1 μm, Metal Chem Tech; Al: 99.0%, mean particle size: 1 μm, Alfa Aesar, USA). A powder mixture composed of 30 at.% Cu and 70 at.% Al was blended using a simple mixing machine (8000-D Mixer Mill, SPEX CertiPrep) for approximately 10–30 min prior to compaction at room temperature. The selected composition of 30 at.% Cu and 70 at.% Al corresponds to a composition of 49.7 wt.% Cu and 50.3 wt.% Al, which is expected to yield a theoretical porosity of 76.6% on the basis of the theoretical densities of Cu and Al (Fig. 2) [21]. An air presser (DBP-6P, DONG-JIN Machine, Republic of Korea) was then used to press the powder mixture into pellets, which were subsequently sintered in an air furnace at 450 °C for 24 h. This relatively low-temperature sintering step, which was planned on the basis of the melting temperatures of Al and Cu (660 and 1085 °C, respectively, Fig. 2), was intended to serve as a 'pre-heat-treatment' process and provide a weak solid-state consolidation prior to the subsequent higher-temperature heat-treatment. One of two different follow-up processing routes was then applied to different samples of pellets in order to produce both nanoporous Cu foams and multiscale porous Cu foams containing a mixture of micropores and nanopores (Fig. 1): They are henceforth named "Cu nanofoam" and "Cu multiscale foam," respectively. For the first processing route, the pressed pellets were subjected to additional sintering at either 700 or 900 °C for 8 h to compare their microstructural features prior to dealloying in a 5 wt.% aqueous NaOH solution for 5 h. The additional higher-temperature heat-treatment was applied to ensure the achievement of a homogenous microstructure throughout the sample through the occurrence of a partial-liquid sintering, since both temperatures of 700 and 900 °C are higher than the melting temperature of Al (Fig. 2). A diamond cutting machine (Isomet low speed saw, Buehler, USA) was used to cut the specimens into thin pieces, which were subsequently polished down to a thickness of 200–250 μm in preparation for selective etching. The second processing route was as same as the first processing route until the initial low-temperature sintering at 450 °C for 24 h; however, the order of the additional higher-temperature sintering and dealloying was switched. That is, the samples were dealloyed prior to the additional higher-temperature heat-treatment (Fig. 1), which was performed at 650 °C for 2 h in a tube furnace (MSTF11-500, Myung-Sung Engineering, Republic of Korea) under H_2 atmosphere to prevent the samples from oxidizing. This final heat-treatment in H_2 atmosphere was also carried out for the sample that had been subjected to the first processing route to remove any remaining impurities. The microstructures of the Cu nanofoam and Cu multiscale foam were characterized and analyzed using scanning electron microscopy (SEM, JSM7401F, JEOL) combined with an energy dispersive X-ray spectroscopy (EDS) analyzer. X-ray diffraction (XRD, Rigaku Ultima III X-ray diffractometer) with Cu Kα radiation (λ = 1.5406 Å) was also used to determine alloy phases between Al and Cu. The mean strut size was experimentally measured using standard metallographic methods. More than ten random struts were selected on the examined fracture surface to obtain the mean strut size. For elongated struts that had an aspect ratio greater than unity, the mean size of the Cu strut was defined as the average of the largest and smallest diameters. The degree of continuity (C_S) of the Cu nanofoam strut was metallographically assessed using the contiguity parameters of N^{SS} and N^{SP}, which were determined using simple intercept measurements by drawing ten random lines of unit length on the fracture surface examined for each microstructure.

3. Results and discussion

It is generally recognized that ideal nanoporous structures can be obtained by chemically dealloying single-phase solid-solution binary alloys [18,19]. Nevertheless, to ensure a higher volume density of porosity and specific surface area, this study used a precursor alloy at a composition of 30 at.% Cu–70 at.% Al with a slightly higher Al at.% than the single-phase alloy, θ, at 33 at.% Cu–67 at.% Al [21]. It is possible to dealloy Al out of the Al–Cu system because of the large difference in the standard potentials of Al and Cu (−1.662 V *vs.* standard hydrogen electrode (SHE) for Al/Al^{3+} and