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Dealloying solution dependence of fabrication, microstructure and porosity of hierarchical structured nanoporous copper ribbons

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ABSTRACT

The monolithic hierarchical structured nanoporous copper ribbons (HSNCRs) have been facilely fabricated by one-pot chemical dealloying of dual-phase Al 27 at.% Cu alloy with hypereutectic structure. The results show that dealloying solution has a key influence on fabrication, microstructure and porosity of products. The HSNCRs are composed of interconnected large-sized maze/river-shape channels with laminated/uniform porous channel walls upon dealloying in acidic/alkaline medium. The specific surface area of samples by dealloying in alkaline solution is two times larger than that in acidic solution. Additionally, microstructure (morphology, sizes and distribution) and porosity of products can be tuned effectively by changing dealloying solution.

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1. Introduction

Nanoporous metals (NPMs), as novel functional materials, have recently attracted considerable interest in a wide variety of applications including catalysis, sensors, actuators, fuel cells, microfluidic flow controllers, and so forth [1–4]. Since it has been found that chemical/electrochemical dealloying can be used to yield a broad range of porous metals, during the latest decades, lot of efforts have been directed towards the investigation of NPMs through dealloying [5–8]. Currently, one of the most important issues on research of NPMs is synthesis. Typically, methods to fabricate porous metals with controlled channel sizes result in synthesis of materials with unimodal channel size distributions. Obviously, the properties of NPMs with hierarchical channel size distributions can be optimized through adjusting channel size and distribution. For instance, for microfluidic-based sensors, a hierarchical channel size distribution is desirable in order to achieve faster response time and higher sensitivity, in which large-sized channels are useful in microfluidic flow control, while small-sized channels are beneficial for increasing device surface area as required for sensor applications [9].

To this end, Ding and Erlebacher [9] have reported on a two-step dealloying strategy to make free-standing noble metal membranes with a typical hierarchical channel size distribution by performing a annealing/redealloying cycle on Ag-plated nanoporous gold (NPG). However, the cycle prolongs the production time and increases the cost. Obviously, avoiding cycling treatment and achieving facile synthesis of hierarchical structured NPMs are crucial for its wider applications, which urgently need to be investigated.

It is well recognized that porosity evolution during dealloying involves etching of the base metal coupled with coarsening of the noble metal by surface diffusion [7,10]. Recently, our group developed an effective one-pot dealloying route to fabricate NPMs with controlled hierarchical channel size distributions via modulating surface diffusivity of more noble atoms along alloy/solution interfaces [11]. Compared to the previous two-step strategy, the one-pot route has evident advantages of simplicity and economy. Obviously, aside from modulation of surface diffusivity of the noble metal element, it could be easy to consider that adjusting and controlling the etching-related process of the base metal during dealloying, such as the constituent design of initial alloy or subsequent etching condition, is also an effective idea to achieve it.

In this paper, the well-designed Al 27 at.% Cu alloy with hypereutectic structure (eutectic point composition: 16.5 at.% Cu; meanwhile, also avoiding the possibility of disturbance of pseudoeutectic and divorced eutectic structure) was taken to

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synthesize the monolithic nanoporous copper ribbons with hierarchical channel size distributions through one-pot chemical dealloying. The experimental results show that the dealloying solution has a significant influence on fabrication, microstructure (including surface morphology, ligament/channel sizes and distribution) and porosity of resultant porous products. The HSNCRs are composed of interconnected large-sized maze/river-shape channels with laminated/uniform porous channel walls upon the dealloying in the acidic/alkaline medium. Intriguingly, by dealloying in the acidic solution, the surface of small-sized ligaments is stacked of nanoparticles in comparison with the smooth edges obtained in the alkaline environment. The Brunauer–Emmett–Teller surface area of samples upon the dealloying in the alkaline solution is two times larger than that in the acidic solution. Based on our current understanding of dealloying process of multi-phase alloys, their formation mechanism has been discussed in detail. Additionally, the microstructure and porosity of resultant products can be tuned effectively by changing the dealloying solution.

2. Experimental

Al–Cu alloy with nominal composition of 27 at.% Cu was prepared from pure Al (99.99 wt.%) and pure Cu (99.999 wt.%). Voltaic arc heating was employed to melt the charges in a copper crucible under an argon atmosphere, and then the melt was cooled down into ingots in situ. By use of a single roller melt spinning apparatus, the Al–Cu ingots were remelted in a quartz tube by high-frequency induction heating and then melt-spun onto a copper roller at a circumferential speed of ∼1500 rpm in a controlled argon atmosphere. The alloy ribbons obtained were typically 10–20 μm in thickness, 4–6 mm in width, and several centimeters in length. Energy dispersive X-ray (EDX) analysis showed the atomic percentage of Cu and Al in the Al–Cu alloy ribbons was quite closely to the initial designed chemical composition, indicating the alloy ribbons can be further used in the following study (see supplemental material for the EDX results, Table S1). Subsequently, the melt-spun Al–Cu alloy ribbons were dealloyed in a 5 wt.% HCl aqueous solution at 75 °C or 10 wt.% NaOH aqueous solution at room temperature (RT, 20 °C) until no obvious bubbles emerged, respectively. After dealloying, the samples were rinsed with distilled water and dehydrated alcohol. The as-dealloyed samples were kept in a vacuum chamber to avoid oxidation. Microstructural characterization and analysis of the melt-spun Al–Cu alloy ribbons and as-dealloyed samples were made using X-ray diffraction (XRD, Rigaku D/Max-2400) with Cu Kα radiation, scanning electron microscopy (FESEM, Hitachi S-4800), transmission electron microscopy (TEM, JEOL JEM 2100F) with selected-area electron diffraction (SAED) and an EDX analyzer.

To test the electrochemical activities of α-Al and Al$_2$Cu phases in the Al 27 at.% Cu alloy, potentiodynamic polarizations studies were conducted on single-phase α-Al solid solution and Al$_2$Cu intermetallics (corresponding to Al–Cu alloy with a trace amount of Cu and Al 33 at.% Cu alloy prepared via the same technical process as the Al 27 at.% Cu alloy) under the different corrosive environments by using an electrochemical measurement unit (PARSTAT 2273). The experiments were carried out in a standard three-electrode electrochemical cell (200 mL) with a Pt plate electrode as a counter electrode, a saturated calomel electrode (SCE) as a reference electrode, and the alloy ribbon as the working electrode. Polarization scan was performed towards positive values at a scan rate of 1.0 mV s^{-1}, after allowing a steady state potential to develop. In order to evaluate specific surface areas of these NPC samples, the N$_2$ adsorption/desorption experiments were carried out at 77 K on a Nova Station A automatic surface area and pore radius distribution apparatus.

3. Results

Fig. 1 shows the XRD patterns of the initial Al 27 at.% Cu alloy ribbons and their as-dealloyed samples upon dealloying under different conditions. The filled circles, squares and triangles stand for α-Al, Al$_2$Cu and Cu, respectively. As can be seen from part a of Fig. 1, the Al 27 at.% Cu alloy is composed of two phases: α-Al and Al$_2$Cu, and the amount of Al$_2$Cu is obviously dominant in the initial alloy. After dealloying whether in the HCl or NaOH solution, only a face-centered cubic (f.c.c.) Cu phase can be identified in the as-dealloyed samples (parts b and c of Fig. 1). It should be noted that, however, the peak width of $(111)_{Cu}$, $(200)_{Cu}$, $(220)_{Cu}$ reflections of the samples by dealloying in the alkaline solution is significantly broad compared to that in the acidic solution, suggesting that the length scales of porous structure in the HSNCRs by dealloying in the NaOH solution are much smaller [12].

The plane view of nanoporous copper ribbons from Al 27 at.% Cu alloy shows that a porous structure with hierarchical channel size distributions can be obtained upon dealloying in the HCl solution and typical SEM images are shown in Fig. 2a and b. Clearly, the surface exhibits a maze-like ligament–channel structure with length scales of 150 ± 50 nm (part a of Fig. 2). The SEM image at a higher magnification shows the channel walls exhibit an open, bicontinuous interpenetrating porous network with ligament sizes of 65 ± 15 nm (part b of Fig. 2). The section view of the HSNCRs shows the large-sized channels continuously penetrate the whole samples and a typical SEM image is shown in part c of Fig. 2. Meanwhile, the high-magnification SEM image of channel walls of HSNCRs clearly exhibits a laminated bicontinuous porous network, suggesting that the nanoporous structure of channel walls is layered and 3D (part d of Fig. 2). Thus, the monolithic nanoporous copper ribbons have hierarchical channel size distributions (three levels) composed of interconnected large-sized maze-shape channels with laminated porous channel walls upon the dealloying in the acidic solution. This special kind of porous structure is very beneficial and considerably significant in the application of electrochemical catalysis or biosensors due to the unique distribution of three-level channels/pores, in which the large-sized first- and second-level channels run through the whole 3D samples in the horizontal and vertical directions, while the fine third-level pore uniformly disperses in the lamination structure.

TEM observation further verifies the porous structure of the HSNCRs by dealloying in the HCl solution and one typical TEM bright-field image is shown in part a of Fig. 3. Clearly, the high-magnification TEM image shows the small-sized ligament edges are coarse and accumulated by nanoparticles with a size of several
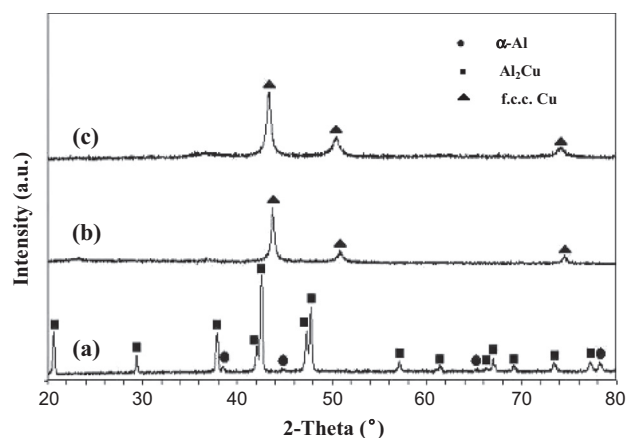

Fig. 1. XRD patterns of melt-spun Al 27 at.% Cu alloy ribbons (a) before and (b and c) upon dealloying in the 5 wt.% HCl at 75 °C and 10 wt.% NaOH solution at RT, respectively.