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On the Benign One-Pot Preparation of Nanoporous Copper Thin Films with Bimodal Channel Size Distributions by Chemical Dealloying in an Alkaline Solution

W.B. Liu*, S.C. Zhang†, X.X. Lu‡

School of Materials Science and Engineering, Beihang University, Beijing 100191, China

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Nanoporous copper (NPC) thin films with bimodal channel size distributions can be benignly fabricated by one-pot chemical dealloying of dual-phase Al 27 at % Cu alloy with hypereutectic structure in the NaOH solution. The microstructure of these NPC thin films was characterized using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis. The results show that these NPC thin films are composed of interconnected large-sized channels (100s of nm) with highly porous channel walls (10s of nm), in which large-sized channels resulting from entire dissolution of solid solution while small-sized those deriving from part corrosion of intermetallics. Both large- and small-sized channels are 3D, open, and bicontinuous.

Keywords: Nanoporous Copper, Chemical Dealloying, One-pot Preparation, XRD, SEM.

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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, a lot of efforts have been directed towards the investigation of NPMs through dealloying [5-8]. Currently, investigations of NPMs have been mainly focused on 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 multimodal channel size distributions can be optimized through adjusting channel size and distribution. For instance, for microfluidic-based sensors, a bimodal channel size distribution is desirable in order to achieve fast response time and high sensitivity, in which large-sized channels are useful in microfluidic flow control, while small-sized channels are useful for increasing device surface area as required for sensor applications [9].

To this end, Ding et al. [9] have reported on a two-step dealloying strategy to make free-standing noble metal membranes with a typical bimodal 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. 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 elements along alloy/solution interfaces [10]. Compared to the previous two-step strategy, however, the porous structure by one-pot route is still not good enough although simplicity and economy would be an advantage. Therefore, avoiding cycling treatment and further optimizing structure of NPMs are crucial for its wide applications, which urgently need to be investigated.

Inspired by porous glasses [11], it could be easy to consider that, for a dual-phase alloy with hypereutectic structure, nanoporous strucuture with bimodal channel size distributions would be achieved by a combination of rapid solidification and one-pot dealloying techniques, in which large-sized channels resulting from entire dissolution of solid solution while small-sized those deriving from part corrosion of intermetallics. To test this hypothesis, Al 27 at % Cu alloy (eutectic point composition: 16.5 at % Cu) was taken as an example to synthesize the NPC thin films with bimodal channel size distributions through rapid solidification and one-pot chemical dealloying in an alkaline solution. The results show that the NPC thin films are composed of interconnected large-sized channels (100s of nm) with highly porous channel walls (10s of nm). Both large- and small-sized channels are 3D, open, and bicontinuous.

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 ~3000 rpm in a controlled argon atmosphere. The alloy thin films obtained were typically 10-20 μm in thickness, 4-6 mm in width, and several centimeters in length. The rapidly solidified (RS) Al-Cu thin films were dealloyed in a 10 wt % NaOH aqueous solution at

* liuwenbo_8338@163.com (W.B. Liu)
† csc@buaa.edu.cn (S.C. Zhang)
‡ zjgpku@163.com (X.X. Lu)

room temperature (RT) until no obvious bubbles emerged. 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 RS Al-Cu alloy thin films 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) with energy dispersive X-ray (EDX) analyzer.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the initial RS Al 27 at % Cu alloy thin films and their as-dealloyed samples upon dealloying in the NaOH solution. The filled circles, squares and triangles in Figure 1 stand for α-Al, Al_2Cu and Cu, respectively. As can be seen from part a of Figure 1, the Al 27 at % Cu alloy is composed of two phases: α-Al and Al_2Cu, and the amount of Al_2Cu is obviously dominant in the initial alloy. After dealloying in the NaOH solution, only a face-centered cubic (f.c.c.) Cu phase can be identified in the as-dealloyed samples (parts b of Figure 1).

Figure 2 shows the microstructure of the NPC thin films by dealloying of the RS Al 27 at % Cu alloy in the 10 wt % NaOH solution. The large-sized channels (100s of nm) can be clearly seen on the surface of NPC thin films (part a of Figure 2). The section view of the NPC thin films demonstrates that the large-sized channels continuously penetrate throughout the whole films (part c of Figure 2). The large-sized channel walls exhibit an open, bicontinuous interpenetrating ligament-channel structure with length scales of 10-20 nm in the section- and fracture-view SEM images at a higher magnification (part b and d of Figure 2). Additionally, EDX analysis shows only Cu can be identified and nearly all of Al was etched away during dealloying by the NaOH solution (part e of Figure 2). In contrast, NPG (by dealloying of Ag-Au alloys) normally contains some residual at % Ag. The residual Ag is expected to be trapped inside the Au ligaments based upon the dealloying mechanism [12, 13]. Moreover, the residual Ag can not be removed but asymptotically reaches a limit at exhaustively long etching times (up to 100 h) [12].

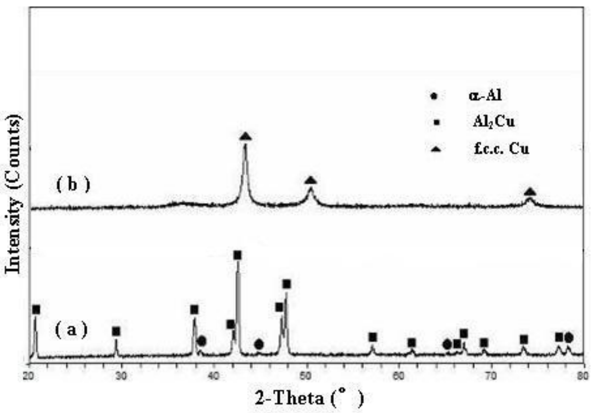

Fig. 1 – XRD patterns of melt-spun Al 27 at % Cu alloy thin films (a) before and (b-c) upon dealloying in the 10 wt % NaOH solution at RT

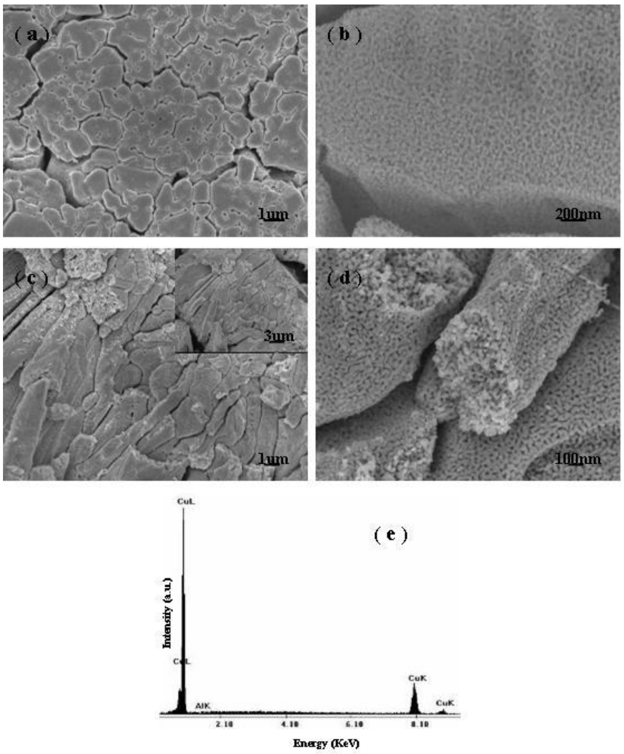

Fig. 2 – SEM images showing the microstructure of NPC by dealloying of the RS Al 27 at % Cu alloy in the 10 wt % NaOH solution at RT. Parts a and b are the plane views; parts c and d are the section views. Inset in part c shows the entire section-view image at a lower magnification

It is generally recognized that ideal bicontinuous nanoporous structures are obtained from binary alloy families with a single-phase solid solubility across all compositions by chemical/electrochemical dealloying. The formation mechanism of nanoporous structures during dealloying has been described in the literature [8]. It has been shown that ligaments form as a result of an intrinsic pattern formation during which aggregation of chemically driven noble metal atoms occurs. The process started with selective dissolution of base metal atoms from the outermost alloy surface, leaving behind noble metal atoms that diffused along alloy/solution interfaces and agglomerated into the ligaments. Thus, porosity evolution forms dynamically during dissolution and is not due to one active component simply being excavated out of a binary solid solution alloy [14].

However, if multiple phases exist in an alloy, a more complicated process will occur during dealloying. Typically, in a dual-phase alloy, if one phase can be entirely dissolved and another just is partly corroded, the dealloying of it could lead to the formation of NPMs with bimodal channel size distributions. The present Al-Cu alloy is composed of a combination of α-Al and Al_2Cu. As a result, the synergetic dealloying of α-Al and Al_2Cu in the dual-phase alloy could result in the formation of NPC with bimodal channel size distributions. The formation mechanism is discussed detailedly in the following part.

According to the binary Al-Cu alloy phase diagram [15], during the rapid solidification of Al 27 at % Cu alloy, eutectics of α-Al and Al_2Cu phases can directly nucleate and continually grow from the initial liquid after the precipitation of primary Al_2Cu phase, namely hypereutectic structure, characteristic of an two-phase interconnected network. During the etching, the excavation of the interconnected α-Al phase from the microstructure contributes to the formation of the large-sized channels in the resultant NPC, like the case for porous glasses [11], while the dealloying of the Al_2Cu intermetallics results in the nanoporous structure of the channel walls. Obviously, this is in good agreement with the SEM observations, indicating the microstructure of NPC thin films strongly depends on the phase constitution of the initial alloy.

Based on our present work, it can be proposed that one can employ this simple and effective one-pot route to obtain NPC with bimodal channel size distributions from dual-phase alloys with hypereutectic structures via chemical dealloying in an alkaline solution regardless of the complicated cycling treatment in the literature. It will have important implications for fabricating novel NPMs with more complex structures from multiphase alloy families.

4. CONCLUSIONS

We present a simple and facile one-pot synthesis of NPC thin films with bimodal channel size distributions through chemical dealloying of dual-phase Al 27 at % Cu alloy with hypereutectic structure in the NaOH solution. The microstructure of NPC thin films strongly depends on the phase constitution of the initial alloy. These NPC thin films are composed of interconnected large-sized channels with highly porous channel walls, in which large-sized channels resulting from entire dissolution of solid solution while small-sized those deriving from part corrosion of intermetallics. Both large- and small-sized channels are 3D, open, and bicontinuous.

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