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Fabrication and characterization of bulk nanoporous copper by dealloying Al–Cu alloy slices

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ABSTRACT

Bulk NPC (nanoporous copper) were fabricated by dealloying xAl(100−x)Cu (x = 60, 70 at.%) alloy slices in NaOH solutions (10, 20 and 30 wt.%) under free corrosion conditions. The results show that Al–Cu alloy slices can be completely dealloyed. The synergetic dealloying of Al_2Cu and AlCu results in the formation of uniform NPC with small-sized channels. The dealloying of α-Al and Al_2Cu plays an important role in the formation of NPC with two kinds of structures of both small-sized uniform ligaments–channels and hierarchical skeleton-like (large-sized channels with highly porous walls) structure, and these two structures form layer-cake structure.

1. Introduction

Nanoporous materials have attracted extensive attentions because of their promising applications in catalysis, sensors and fuel cells [1–6]. Among various methods including template method [7], hydrothermal method [8], dealloying method [9], etc., dealloying has been approved to be a simple and effective way to fabricate nanoporous materials with a three-dimensional bi-continuous interpenetrating ligaments–channels structure by selective dissolution of the most electrochemically active elements out of crystalline alloys [9–12], amorphous alloys [13] and metallic glasses [14]. And many alloy systems have been applied to prepare nanoporous structures metals through dealloying process such as Au–Ag [9], Ti–Cu [10], Al–Au [15], and Al–Cu [16].

In comparison with expensive nanoporous gold (NPG), platinum (Pt) and palladium (Pd) it is more suitable for mass production of cheaper NPC which also works well in area of catalysis [17]. NPC has been successfully fabricated by dealloying Al–Cu [16,18], Mg–Cu [19] and Zn–Cu [20] alloys. The precursors, however, as reported are usually ultrathin ribbons of about 20–40 μm in thickness. Generally, researchers spin the high-temperature melt onto a copper roller in a single-roller melt spinning apparatus under a controlled argon atmosphere [21,22]. Whereas, large amount of this kind of ribbons would not be fabricated by this method, and industrial application will be limited.

To date, less attention has been paid to the synthesis of nanoporous structures by dealloying bulk alloys. Mao et al. [20] has obtained bulk NPC with a three-dimensional continuous interpenetrating ligament–channel structure by dealloying a 2.0 mm thick Zn–Cu slice that annealed at different temperatures in HCl (or HCl + NH_4Cl)solution. In addition, Changchun Zhao also has mentioned that $Mg_{50}Cu_{50}$ can serve as precursor to fabricate bulk NPC under diluted hydrochloric acid condition but he did not describe the microstructure in detail [23]. In this work, 1.0 mm thick xAl(100−x)Cu (x = 60, 70 at.%) slices were applied to obtain bulk NPC through chemical dealloying at free corrosion conditions. The experimental results show that slices can be completely dealloyed across all given compositions. Uniform NPC can be obtained simply from synergetic dealloying 60Al40Cu slices which comprise two phases of Al_2Cu and AlCu, and hierarchical skeleton-like structure (large-sized channels with highly porous walls) can be fabricated by dealloying Al-rich 70Al30Cu. The hierarchical skeleton-like structure forms layer-cake structure with uniform NPC. In addition, the mechanism of the layer-cake structure is studied.

2. Experimental

xAl(100−x)Cu (x = 60, 70 at.%) alloy casts were prepared by arc-melting Cu and Al with purities of 99.9 wt.% in an argon atmosphere, then the casts were cut into slices of 1.0 mm in thickness by wire cut electrical discharge machine (WEDM). The slices were cleaned in an ultrasonic cleaner then dried in vacuum chamber. Then chemical dealloying experiments were conducted at room

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temperature in the open air, and Al–Cu slices were immersed in NaOH solutions with a concentration of 10 wt.%, 20 wt.% and 30 wt.%, respectively. They were numbered sequentially from sample 1–6 (Table 1). When no obvious bubbles emerged any longer and the solutions became clear again the dealloying process stopped. The residues were taken out of beakers and well rinsed with distilled water and dehydrated alcohol to remove the residual NaOH solutions and metal ions.

The phase distributions in precursors were observed using an M-4XC metallographic microscope. The phases present in the Al–Cu alloys were confirmed by X-ray diffraction (XRD, D8 ADVANCE) with a Cu Kα irradiation. The morphology and structure of the dealloyed samples were characterized by a scanning electron microscope (SEM, FEI QUANTA FEG 250) coupled with an energy dispersive X-ray spectroscopy (EDS). Electrochemical experiments were carried out to study the microstructure evolution under a conventional three-electrode electrochemical workstation (GU/07345C) at room temperature. The electrochemical cell consisted of a platinum needle as the counter electrode and saturated calomel electrode (SCE) as a reference electrode, 0.05 M NaOH solution was applied as electrolyte. All potentials quoted are on the SCE scale unless otherwise stated.

3. Results and discussion

Fig. 1 shows the XRD patterns of as-prepared Al–Cu alloy slices and a prototypical as-dealloyed bulk sample. The XRD results show that 70Al30Cu alloy is almost totally composed of Al_2Cu phase and a trace Al_4Cu_9 phase also can be detected. However, AlCu phase emerges when the content of Al decreases to 60Al40Cu. It is obvious that the Al_2Cu phase is dominant in the 70Al30Cu alloys, and the amount of Al_2Cu is comparable to that of AlCu in the 60Al40Cu alloy, and these are in accordance with their diffraction peak intensities [20]. A prototypical XRD pattern of as-dealloyed sample is present at the top of Fig. 1. After dealloying, all of Al_2Cu, AlCu and Al_4Cu_9 can be fully dealloyed in NaOH solution and a face centered cubic (fcc) Cu phase can be identified in the as-dealloyed bulk samples. Additionally, a minor amount of Cu_2O that maybe caused by oxidation during preservation is detected in the as-dealloyed samples.

The nanoporous structure of the bulk NPC slices is verified by scanning electron microscopy. Fig. 2 shows the plane-view and section-view microstructures of as-dealloyed 60Al40Cu alloy slices after dealloying in 10 wt.%, 20 wt.% and 30 wt.% NaOH solutions (the corresponding products are designed as samples 1–3, and the similar below), respectively. The plane-view of sample 1 shows a porous structure (Fig. 2a), the ligaments–channels structure is not obvious and many Cu nanoparticles with size of ~50 nm can be observed. Fig. 2b shows the section-view image of sample 1 at a higher magnification, a typical uniform bi-continuous interpenetrating ligaments–channels structure with size of ~50 nm can be observed. Many microcracks (tens of micrometers in length and sub-micrometer in width) can be observed on the fracture surface of the slice (insert image of Fig. 2b). For sample 2, the plane-view

Table 1
Dealloying time (h) of all samples from 1 to 6.

NO.	Alloy (at.%)	C_{NaOH} (wt.%)	Dealloying time (h)
1	60Al40Cu	10	29.33
2		20	31.83
3		30	80.0
4	70Al30Cu	10	20.33
5		20	20.33
6		30	44.0

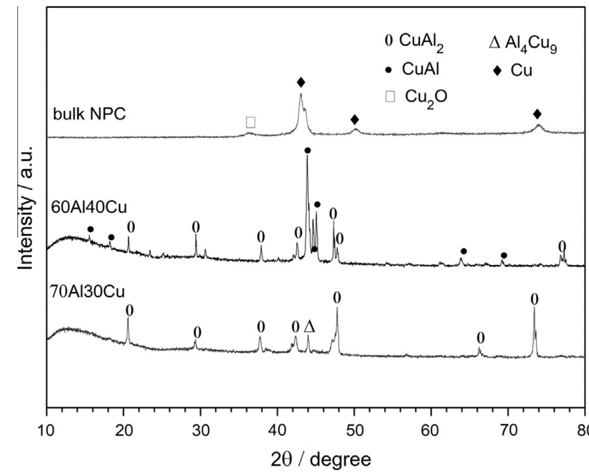

Fig. 1. XRD patterns of as-prepared Al–Cu alloy slices and a prototypical as-dealloyed bulk NPC.

and section-view images show a similar microstructure characteristic to that of sample 1. For the sample 3, Fig. 2e shows a porous structure, the ligaments–channels structure is slightly larger than that of samples 1 and 2, but the pores are still not well distinguishable. In addition, microcracks can also be observed on the surface of sample 3. However, the section-view microstructure shows a quite different structure compared with the former two samples i.e. a large sum of pores is blocked. Fig. 2 verifies that both Al_2Cu and AlCu phases can be dealloyed throughout 60Al40Cu alloy slices and nanoporous structure can be obtained. Combining with XRD result, bulk NPC can be obtained via dealloying 60Al40Cu alloy slices in NaOH solutions. Table 1 shows the dealloying time of different alloys in various NaOH solutions. Samples 1 and 2 have a similar dealloying time of around 30 h, however, that of sample 3 is 90 h, much longer than that of samples 1 and 2. Fig. 2g and h shows the microstructures of sample 3 for dealloying 70 h. Fig. 2g exhibits a prototypical open, bi-continuous interpenetrating ligaments–channels structure with length scales of ~100 nm, and the pores are obvious. A three-dimensional nanoporous structure can be observed in Fig. 2h, it is extremely different from that of sample 3. Therefore, significant coarsening occurs at later stage in concentrated alkali solution during such a long time dealloying, and that can be attributed to the fast surface diffusion [20,24]. Zhang et al. and Qi et al. have reported that length scales of ligaments–channels in nanoporous metals could be tuned by simply changing the dealloying solutions [16,21]. In this work, it is obvious that the ligaments–channels size increases with the increase of concentration (from 10 wt.% to 20 wt.%) of NaOH solution. For 60Al40Cu, finer microstructure can be obtained in 20 wt.% NaOH solution and a moderate dealloying time is required.

Fig. 3 shows the microstructure of the bulk NPC by dealloying 70Al30Cu alloy slices in 10 wt.%, 20 wt.% and 30 wt.% NaOH solutions (samples 4–6), respectively. Obviously, traditional three-dimensional bi-continuous interpenetrating ligaments–channels structure is fabricated throughout the whole alloy slices (Fig. 3b2, d1, d2 and f2). It is clear that ligaments coarse then bond to adjacent ones and the pores become vague as shown in the regions marked by the dotted ellipses in the inset image in Fig. 3a and outer parts of the irregularity closed curves in Fig. 3c. Obviously, the ligaments–channels of samples 4–6 in Fig. 3 are larger than those of samples 1–3 in Fig. 2. That indicates that the effect of alloy compositions (of the starting Al–Cu alloys) on the microstructure of bulk NPC outweighs that of dealloying solutions in case of the free corrosion of the Al–Cu alloys in the 10 wt.%, 20 wt.% and 30 wt.% NaOH solutions. It is in accordance with the