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Bendable nanoporous copper thin films with tunable thickness and pore features

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ABSTRACT

Three dimensional nanoporous copper (NPC) films with tunable thickness ranging from ~230 nm to ~2.2 μm were fabricated by dealloying Cu–Zr–Al metallic glasses. The ductile-to-brittle transition behavior of the NPC was firstly explored. Moreover, by systematically investigating the influence of Cu content and dealloying temperature on nanoporosity, it was found that, as the Cu content increased, the pore size significantly decreased. In addition, decreasing the dealloying temperature could result in the formation of ultrafine nanoporous structure. Our current work provides bendable ultrathin NPC films with tunable nanoporosity, which is promising for functional applications in micro/nano electromechanical systems.

1. Introduction

Nanoporous metals with three dimensional (3D) bi-continuous network produced by electrochemical or chemical dealloying methods constitute a new class of advanced functional materials for various technological applications in heterogeneous catalysis [1–3], sensing [4], optics [5], energy storage [6,7] and medical treatment [8] due to their high specific surface area and low density. A number of nanoporous metals, such as nanoporous gold, silver and palladium, have been extensively studied. In particular, nanoporous copper (NPC) with continuous porosity, high electrical and thermal conductivity has recently attracted great interest due to its low cost of precursor materials, high catalytic activity and surface enhanced Raman scattering (SERS) performance [9–12].

Dealloying is one of the most promising ways to produce nanoporous metals, which is selective leaching one or more active components out of a precursor alloy by microscopic-scale galvanic corrosion mechanism [13]. The dealloying process occurs when an alloy is immersed in an electrolyte under chemical or electrochemical force, by which the active components dissolve while the noble components remain, resulting in the formation of continuous open nanopore structure. It is known that morphologies of nanoporous metals can be tailored by tuning alloy compositions and dealloying conditions [14–16]. The nanoporous metals with desirable uniform continuous structures are often obtained from binary solid-solution alloys, typically the Au–Ag, Cu–Mn alloys [17,18]. Recently, metallic glasses (MGs) emerge as a new kind of precursor alloys to produce nanoporous metals by electrochemical or chemical dealloying. Compared with the crystalline precursor alloys, MGs have unique advantages for obtaining uniform nanoporous structure due to their monolithic amorphous microstructure which is free from element segregations and crystallographic defects, such as grain boundaries and dislocations. More importantly, many MGs have a wider composition range with respect to the crystalline solid-solution alloys, which provide a larger adjustability to tune the nanoporosity. Therefore, numerous attempts have been conducted to fabricate nanoporous metals by dealloying MG precursors.

In addition to the fabrication of noble nanoporous metals by dealloying noble-metal-based MGs, such as nanoporous palladium [19], gold [20] and silver [21], NPC has also been prepared by dealloying various Cu-bearing MGs, such as Mg–Cu–Y [22], Cu–Hf–Al [23] and Al–Cu–Mg alloys [24]. However, these fabricated NPC products usually suffer from brittleness and are thus difficult to be utilized for actual devices. In this paper, we investigated the relationship between film thickness and flexural toughness of the

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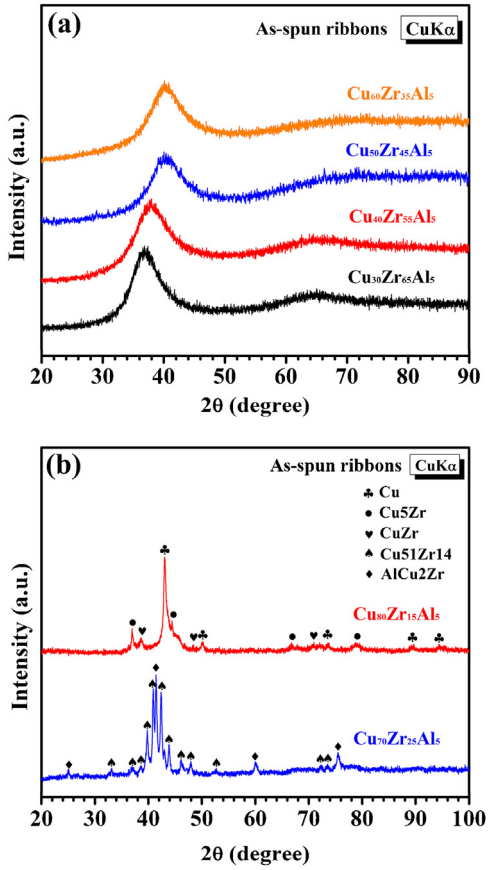

Fig. 1. (a) XRD patterns of the as-spun $Cu_{30}Zr_{65}Al_5$, $Cu_{40}Zr_{55}Al_5$, $Cu_{50}Zr_{45}Al_5$ and $Cu_{60}Zr_{35}Al_5$ glassy ribbons, and (b) XRD patterns of the as-spun $Cu_{70}Zr_{25}Al_5$ and $Cu_{80}Zr_{15}Al_5$ ribbons.

resultant NPC and revealed a ductile-to-brittle transition behavior of the NPC. Then, bendable NPC thin films with tunable thickness were fabricated in our current work. The reason for selecting Cu–Zr–Al MGs as the model alloys is because they exhibited high glass-forming ability in a wide composition range [25], which enables us to systematically study the effects of chemical composition on the microstructure evolution and stability of the NPC. Moreover, we have also studied dependence of the size of ligaments and pores of the resultant NPC on dealloying temperature, especially at the low temperature side.

2. Experimental

The pre-alloy ingots with a nominal composition of $Cu_xZr_{95-x}Al_5$ (x = 30, 40, 50, 60, 70 and 80 at.%) were prepared by arc-melting a mixture of pure Cu (99.99 wt.%), Zr (99.99 wt.%) and Al (99.99 wt.%) under a Ti-gettered argon atmosphere. The Cu–Zr–Al ingots were then remelted in a quartz tube by high frequency induction heating and then melt-spun onto a rotating copper roller with a diameter of 200 mm at a linear speed of 31 m/s. The obtained ribbons were typically 20–30 μm in thickness and 5–8 mm in width.

Chemical dealloying of the as-spun Cu–Zr–Al ribbons was carried out in HF aqueous solutions concentrated from 0.001 to 0.05 mol/L under a free corrosion condition. The as-spun $Cu_xZr_{95-x}Al_5$ (x = 30, 40, 50, 60, 70 and 80 at.%) ribbons were also chemical dealloyed at room temperature for a constant dealloying time of 24 h in 0.005 mol/L HF solution to investigate effects of the alloy composition on the morphology of the prepared NPC. To evaluate effects of dealloying temperature on the microstructure of NPC, dealloying experiments for the typical $Cu_{60}Zr_{35}Al_5$ glassy ribbons at two temperatures, i.e., 0 °C and room temperature (25 °C), were conducted in the 0.005 mol/L HF aqueous solution for 24 h. The residual chemical substances within pore channels of the NPC products were rinsed with ultrapure water and dehydrated alcohol repeatedly.

Microstructures of the free side of the melt-spun ribbons and dealloyed products were characterized by X-ray diffraction (XRD, Rigaku DMAX-RB-12KW, Cu-Kα), scanning electron microscopy (SEM, Zeiss Supra 55) equipped with an energy dispersive X-ray spectrometer (EDX), and transmission electron microscope (TEM, Tecnai G2 F30). X-ray photoelectron spectroscopy (XPS AXIS-ULTRA-DLD, Kratos) with an Al Kα (mono, 1486.6 eV) anode at energy of 150 W in a vacuum of 10^{-7} Pa was employed to investigate the surface chemical state and binding energy of the NPC. The ligament size and pore size were statistically measured by a single length chord method over 120 ligaments and pores based on the SEM images, respectively.

3. Results and discussion

3.1. Formation and characterization of NPC by dealloying the Cu–Zr–Al precursors

The as-spun ribbons with a nominal composition of $Cu_xZr_{95-x}Al_5$ (x = 30, 40, 50, 60, 70 and 80 at.%) were prepared to fabricate NPC by chemical dealloying. Fig. 1 shows XRD patterns of the as-spun Cu–Zr–Al precursors, and the alloys containing 30–60% Cu, i.e., $Cu_{30}Zr_{65}Al_5$, $Cu_{40}Zr_{55}Al_5$, $Cu_{50}Zr_{45}Al_5$ and $Cu_{60}Zr_{35}Al_5$ ribbons illustrate a characteristic broad halo around 41°, along with a weak broad diffraction peak at 70–75°, indicating that these Cu–Zr–Al precursors have an amorphous structure (Fig. 1a). Further increasing the Cu content, sharp crystalline peaks corresponding to several intermetallic phases in the $Cu_{70}Zr_{25}Al_5$ and $Cu_{80}Zr_{15}Al_5$ ribbons were seen (Fig. 1b), suggesting a decrement in the glass-forming ability.

Fig. 2 shows SEM images of the surface morphologies of the $Cu_xZr_{95-x}Al_5$ (x = 30, 40, 50, 60, 70 and 80 at.%) ribbons dealloyed at room temperature for 24 h in 0.005 mol/L HF aqueous solution. It is seen that the treated $Cu_{30}Zr_{65}Al_5$, $Cu_{40}Zr_{55}Al_5$, $Cu_{50}Zr_{45}Al_5$ and $Cu_{60}Zr_{35}Al_5$ glassy samples (Figs. 2a–d) show a similar feature of continuous nanoporous structure, but the actual size of the pores and ligaments are dependent on the individual alloy composition. Specifically, as the Cu content of the glassy precursor increases, the pore size decreases while the ligament size significantly coarsens, indicating that the nanoporosity of the NPC can be tailored by modulating the Cu content in the Cu–Zr–Al MGs. For the crystalline precursors with the Cu content ranging from 70 to 80%, the corrosion process only occurred on their surface and the continuous 3D nanopore structure were not formed due to the crystalline structure effect and excessive Cu content (Fig. 2e and f), suggesting that there exists a composition threshold to form nanoporous structure in the current precursor alloy. Furthermore, grain boundary remainders on the surface of the dealloyed $Cu_{70}Zr_{25}Al_5$ ribbon (Fig. 2e) were clearly observed. It was reported previously that the morphology and orientation of the grains in the precursor could be remained into the resulting products during dealloying [26]. For the dealloyed $Cu_{80}Zr_{15}Al_5$ sample, the grain boundaries are invisible due to its large grain size (>3 μm) of the precursor alloy. The present result also demonstrates that the Cu–Zr–Al MGs which are free form boundaries and segregations have unique advantages to fabricate uniform continuous nanoporosity, as compared with crystalline precursors.