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Relationship between dealloying conditions and coarsening behaviors of nanoporous copper fabricated by dealloying Cu-Ce metallic glasses

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ABSTRACT

Monolithic nanoporous copper (NPC) with tunable ligament size (107–438 nm) was synthesized by dealloying a new Cu-Ce binary glassy precursor in dilute H_2SO_4 aqueous solution. The effects of the dealloying conditions on the morphologies of NPC were evaluated comprehensively. The results show that the ligaments of NPC can significantly coarsen with the increase of acid concentration, elevation of reaction temperature or prolongation of immersion time. These coarsening behaviors can be well described by a diffusion based growth kinetic model. Moreover, the surface diffusivity and activation energy for diffusion of Cu atoms were also estimated to investigate the formation mechanism of NPC, which is mainly governed by dissolution of Ce element in the glassy precursor coupled with nucleation and growth of Cu clusters via the precursor/solution interface. In the experiment of the degradation of methyl orange (MO) dye, the NPC fabricated by Cu-Ce metallic glasses exhibits superior sono-catalytic activity.

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1. Introduction

Nanoporous metals, as the novel functional materials with three-dimensional (3D) bi-continuous interpenetrating ligament-channel nanostructure, have recently attracted considerable interest in a wide variety of applications including catalysis, sensors, actuators, fuel cells, microfluidic flow controllers and surface plasmon resonance, etc [1–6]. In comparison with the other nanoporous noble metals (nanoporous palladium [7], platinum [8], gold [9] and silver [10]), nanoporous copper (NPC) is more attractive owing to its cost-effectiveness, low density and high catalytic activity, which can be used as high-active substrates for surface-enhanced Raman scattering and attractive catalysts in the water-gas shift reaction [11,12].

In recent decades, a variety of chemical and physical methods have been proposed to synthesize NPC, such as template, hydrothermal and dealloying method [13–15]. Among them, dealloying has been demonstrated to be a very promising strategy, which is a simply chemical or electrochemical process of selective dissolution of the less noble elements out of a precursor alloy [16]. So far, various binary alloys systems have been developed to pre-

pare NPC by dealloying, for instance, Al-Cu [17], Mn-Cu [18], Mg-Cu [19], Zn-Cu [20], Zr-Cu [21] and Ti-Cu [22], etc. The microstructure of these alloys plays an important role in the formation of the final nanoporous structure because ligaments are formed usually via a self-organized process through surface diffusion without the involvement of any single recrystallization [23]. It is reported that the typical characteristics of intermetallics and phase segregations in the crystalline alloys can be reflected by the final porous structure in Al-Cu binary alloys [24]. Compared to crystalline alloys, metallic glasses are free from crystallographic defects (mostly grain boundaries, dislocations and segregations), which exhibit a unique disordered atomic structure [25–27]. Therefore, metallic glasses, as ideal supersaturated solid solutions with high chemical homogeneity, are readily available for fabricating uniform nanoporous copper by dealloying. Dan et al. [28] have synthesized monolithic nanoporous copper with a pore size of 25–380 nm and a ligament size of 46–338 nm through dealloying of the Cu-Ti glassy alloys. Deng et al. [29] have prepared homogeneous NPC with tunable pore sizes (20–50 nm) via chemical dealloying $Mg_{65}Cu_{25}Gd_{10}$ amorphous ribbons. Wang et al. [30] have fabricated uniform NPC with the ligament width of 16–140 nm by dealloying $Cu_{52.5}Hf_{40}Al_{7.5}$ metallic glasses. The results suggest that amorphous alloys are really ideal starting materials for the synthesis of monolithic NPC.

Recently, we have prepared NPC by dealloying new Cu-Ce amorphous ribbons in dilute H_2SO_4 solution. Compared to other binary

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alloy systems (Al-Cu, Mn-Cu, Mg-Cu, Zn-Cu, Zr-Cu and Ti-Cu), novel Cu-Ce metallic glasses are very ideal precursors for dealloying. This is because Al-Cu, Mn-Cu, Mg-Cu and Zn-Cu alloys could not be formed in amorphous state, while for Zr-Cu and Ti-Cu alloys, the standard electrode potentials of active elements (Zr for Zr-Cu, Ti for Ti-Cu) are relative high, which could not promise a large driving force for dealloying (NPC can only be well prepared by dealloying these alloys in highly toxic hydrofluoric acid (HF) solution, which could pollute the human environment and threaten people's health). By contrast, Cu-Ce amorphous alloys not only have high glass forming ability (GFA), but also have active element Ce with low standard electrode potential. Thus, the standard electrode potentials of Ce and Cu differ as much as 2.678 V (-2.336 V vs. the standard hydrogen electrode (SHE) for Ce/Ce³⁺ and 0.342 V vs. SHE for Cu/Cu²⁺), which promises to be a large driving force for selective leaching of Ce from Cu-Ce amorphous alloys in dilute H₂SO₄ solution. Furthermore, as binary amorphous precursors, Cu-Ce alloys have simple elemental components, which is beneficial to tune the morphologies of NPC and clarify the dealloying mechanism.

In order to fabricate nanoporous metals with 3D bi-continuous interpenetrating ligament-channel structure, the contents of active elements in the precursor alloys have to exceed a threshold [31]. Given this realization, many researchers designed low atomic percent of the noble elements (25%–60%) in their precursors for dealloying [32–37]. However, this work shows that homogeneous nanoporous copper can be synthesized by dealloying Cu₇₄Ce₂₆ amorphous ribbons, whose noble element (copper) concentration can reach as high as 74%, thus indicating that 3D bi-continuous interpenetrating nanoporous metals can be prepared by dealloying a precursor alloy with low atomic percent of the active elements while whose mass percentage is still modest. It is known that many ideal alloy precursors can only be formed in amorphous state at their precious metal-rich compositions. Unfortunately, they have been ignored because the contents of active elements do not exceed a threshold. Consequently, this research sets a good example and provides a very constructive sight for designing more novel ideal amorphous precursors for dealloying, which has extremely vital significance for the preparation of uniform nanoporous metals.

The morphologies of nanoporous metals can be tuned by changing the dealloying conditions, e.g. electrolytes (kinds and concentration), temperature and immersion time. Luo et al. [38] found that the ligaments of NPC by dealloying Mg-Cu-Y amorphous ribbons can be significantly coarsened with prolongation of leaching time or elevation of reaction temperature. Jin et al. [39] showed that the morphology of nanoporous silver (NPS) can be controlled by changing the Ag concentration in Ag-Ca metallic glasses. Dursun et al. [40] reported the coarsening behavior of ligaments in nanoporous gold (NPG) with the addition of other halides into HClO₄ electrolyte. However, few attempts have been made to estimate the influence of all the dealloying conditions on ligament size of NPC by dealloying the same alloy.

In this work, the morphologies and corresponding formation mechanism of NPC by dealloying Cu₇₄Ce₂₆ amorphous ribbons was investigated. The effects of the acid concentration, temperature and leaching time on ligament size of NPC were evaluated systematically. Furthermore, the surface diffusivity and activation energy of NPC were also calculated. The results will give a constructive reference for clarifying the dealloying mechanism. In addition, the NPC prepared by dealloying Cu-Ce metallic glasses was applied in the sono-catalytic degradation for methyl orange (MO) dye, which displayed enhanced catalytic activity than the commercial copper foil. To the best of our knowledge, there is no report about nanoporous metals prepared by dealloying a precursor alloy with such a low atomic percent of the active elements (just 26 at.%). Not only that, but there is little report about the sono-Fenton-like

process of nanoporous copper (NPC) on the degradation of the dye [41].

2. Experimental

The ingot of Cu₇₄Ce₂₆ was fabricated by arc melting a mixture of pure Cu (99.99 wt%) and Ce (99.95 wt%) elements in a Ti-gettered Ar atmosphere. Then, the ingot was remelted in a quartz tube by high frequency induction and rapidly quenched into a copper wheel to form corresponding glassy ribbons with a thickness of 20–30 μm and a width of 2 mm.

Chemical dealloying Cu₇₄Ce₂₆ amorphous ribbons was performed in dilute H₂SO₄ aqueous solution, the different concentration of electrolytic solution was adopted to estimate the influence of acid concentration on the microstructure of NPC, i.e. 0.04, 0.1, 0.2, 0.4 mol L⁻¹, respectively. Cu₇₄Ce₂₆ amorphous ribbons were leached in the acid solution with different concentrations at 333 K for 90 min. Besides, the effect of temperature on the ligament growth of NPC obtained from Cu₇₄Ce₂₆ glassy ribbons was investigated by leaching them in 0.1 mol L⁻¹ H₂SO₄ aqueous solution for 90 min at various temperatures of 313, 323 and 333 K. Furthermore, the immersion time was used to study the growth and evolution of the nanoporous structure. Cu₇₄Ce₂₆ amorphous ribbons were leached in 0.1 mol L⁻¹ H₂SO₄ electrolytic solution at 333 K for different immersion time (90, 120, 240, 270 and 360 min). After dealloying, all the ribbons were rinsed with distilled water and dehydrated alcohol, then kept in vacuum chamber until characterizations.

The phase composition of the as-spun and as-dealloyed ribbons was characterized by X-ray diffraction (XRD) using a D8-Discover diffractometer with Cu-K_α radiation (wavelength λ = 0.15406 nm), the accelerating voltage and the applied current were 30 kV and 20 mA, respectively. The microstructures of obtained NPC specimens were investigated by FEI-3D scanning electron microscopy (SEM) operating with an accelerating voltage of 10 kV, and transmission electron microscopy (TEM) using a G2-20 instrument operating at 300 kV. The size of the ligament was statistically measured by a single length chord method over 200 sites of SEM/TEM morphologies.

The sonocatalytic activities of the samples were estimated by the degradation of MO. The initial MO concentration was 20 mg L⁻¹. In this experiment, 100 mL MO solution, 50 mg catalyst of NPC (produced by dealloying Cu₇₄Ce₂₆ metallic glasses in 0.1 mol L⁻¹ H₂SO₄ aqueous solution at 333 K for 90 min) and 0.5 mL 30 wt% hydrogen peroxide (H₂O₂) were put into a 250 mL erlenmeyer flask. Then, the degradation reactions were conducted in a serial-ultrasonic apparatus (KH-300DB, Kunshan Ultrasonic Apparatus Company, China) with a frequency of 40 kHz and output power of 240 W at 333 K. Prior to irradiation, the whole suspension was stirred for 30 min to ensure the establishment of the adsorption-desorption equilibrium. Afterwards, 3 mL of the suspension was extracted every 5 min during the sonocatalytic process to test the residual concentrations of MO. The concentration of MO solution was evaluated by measuring the change in maximum absorbance through TU-1810 UV-vis spectrophotometer. The absorbance peak at 464 nm was selected, and the residual concentration was obtained by evaluating the intensity ratio between the residual and original MO solutions.

3. Results and discussion

3.1. Effects of dealloying conditions on the microstructure of NPC

Fig. 1 shows XRD patterns of Cu₇₄Ce₂₆ amorphous ribbons and corresponding sample after dealloying in 0.1 mol L⁻¹ H₂SO₄ solution at 333 K for 90 min. The as-spun Cu₇₄Ce₂₆ ribbons present a

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