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Formation mechanism and characterization of nanoporous silver with tunable porosity and promising capacitive performance by chemical dealloying of glassy precursor

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ABSTRACT

In this study, nanoporous silver with tunable porosity was fabricated by chemically dealloying Ag-based metallic glasses in HCl solution. By systematically investigating the dynamic change in pore characteristics of the nanoporous silver with dealloying condition, the correlation between ligament size and dealloying parameter was successfully established. It was also found that the evolution behavior of the ligament size can be well described by a diffusion based growth kinetic model. In addition, our study of the capacitive performance of the nanoporous silver shows that these newly developed materials are promising for applications as electrode/substrate materials in electrochemical supercapacitors.

1. Introduction

Nanoporous metals, a new family of functional materials, have recently attracted considerable attention in wide applications including catalysis, optics, sensor, and supercapacitors, due to their unique mechanical, physical and chemical properties [1–4]. For example, nanoporous gold with excellent thermal and chemical stability has been exploited as an attractive substrate for surface enhanced Raman scattering because of their large specific surface area and bi-continuous nanoporous structure [5]. Lang et al. [6] reported that nanoporous gold/oxide shows extraordinary specific capacitance, energy density and cyclic stability, which make them viable for high performance electrochemical supercapacitors.

Over the past decades, a few approaches have been proposed to fabricate nanoporous metals. Among them, the dealloying method which is referred to selective dissolution of one or more components out of a precursor alloy has the advantage for producing nanoporous metals with bi-continuous open nanoporosity in three dimensions (3D) [7,8]. Recently, various nanoporous metals such as gold, platinum, copper, palladium and nickel were fabricated by chemical or electrochemical dealloying [9–13].

It is known that, to form uniform nanoporosity by dealloying, the precursor alloy with a monolithic phase is required because nanopores are formed usually via a self-organized process through surface diffusion, instead of a simple excavation of extra phases from polycrystalline master alloys [7,14]. Currently, fabrication of nanoporous metals by dealloying mainly focuses on solid solution alloys, typically the Au–Zn, Al–Cu, Cu–Mn, and Al–Au alloys [15–18]. In addition, it was confirmed that the microstructure of precursor alloys has great effects on the nanoporosity of dealloyed products. Crystalline defects such as grain boundaries and dislocations in precursor alloys are not favorable for forming homogeneous nanoporosity [19,20]. Alternatively, metallic glasses which possess a homogeneous atomic structure and are free from crystallographic defects have apparent advantages to be utilized as precursor alloys for fabricating nanoporous metals. Meanwhile, the adjustable constituent elements and relatively wide composition ranges of metallic glasses are also beneficial for achieving desirable pore characteristics and overall properties. Actually, several attempts to fabricate nanoporous metals by dealloying metallic glasses have been conducted. For example, Chen et al. [21] have fabricated nanoporous palladium with open pores (5–60 nm) through electrochemical dealloying of the $Pd_{30}Ni_{50}P_{20}$ glassy alloy. Luo et al. [22] have fabricated nanoporous copper through

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electrochemical dealloying of Mg–Cu–Y glassy alloys in acid aqueous solutions.

Nanoporous silver materials with specific surface morphology and bi-continuous 3D nanoporosity are of great importance for applications in molecular detection, heterogeneous catalysis and medical materials [23,24]. Recently, Zhang et al. [25] have fabricated porous silver through dealloying Zn–Ag alloys in diluted HCl solutions and NaCl solutions. In our previous work, we have also successfully prepared nanoporous silver with superior surface enhanced Raman scattering performance by electrochemically dealloying Ag–Mg–Ca metallic glasses [26]. However, dynamic change in the pore characteristics of the nanoporous silver has not been investigated systematically. As a result, the related formation mechanism of nanoporous silver during dealloying Ag-based metallic glasses is still not clear. In this work, effects of dealloying conditions including leaching time, concentration of acid solution, and temperature on the nanoporosity were studied in detail. Formation mechanism of the nanoporous silver was discussed and the ligament growth kinetic was also analyzed. Moreover, the capacitive performance of the nanoporous silver based electrode was explored.

2. Experimental

Alloy ingots with a nominal composition of $Ag_{45}Mg_{35}Ca_{20}$ (at.%) were prepared by induction-melting pure elements (Ag: 99.99 wt.%, Mg: 99.99 wt.%, Ca: 99 wt.%) in a quartz tube with corundum crucible. The ingots were re-melted by a high-frequency induction furnace in a quartz tube and then rapidly quenched into a copper wheel to form glassy ribbons with the thickness of 10–15 μm and width of 2–4 mm using a single-roller melt-spinning apparatus under pure argon atmosphere [26,27]. The diameter and linear speed of the copper wheel are 20 cm and 31 m/s, respectively.

Chemical dealloying of $Ag_{45}Mg_{35}Ca_{20}$ glassy ribbons was performed in HCl aqueous solutions, and different leaching times of 2, 4, 6, 8, 10, 12, 24 and 36 h were successively applied. To investigate the effects of HCl concentration on the pore characteristics of nanoporous silver, different solutions with a concentration level of 0.025, 0.05, 0.1, 1, 5 and 12 mol/L were used. Dealloying temperature was also varied from 273, 298, 323, 348 and 368 K in the 0.05 mol/L HCl aqueous solution for 4 h. All the nanoporous silver products were rinsed with ultrapure water and dehydrated alcohol repeatedly.

Microstructures on the free side of the melt-spun ribbons and dealloyed ribbons 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). Brunauer–Emmett–Teller (BET) test was carried out on an automated surface area & pore size analyzer (Quadrasorb SI) to measure the porosity of the nanoporous silver. The ligament size was statistically measured by a single length chord method over 120 ligaments based on the SEM images.

Electrochemical properties and capacitances of the resultant nanoporous silver samples were studied by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements in a three electrode electrochemical analyzer (CHI 660D). The system was constructed using a platinum wire as the counter electrode, Ag/AgCl standard electrode (3 mol/L KCl) as the reference electrode and the nanoporous silver ribbon as the working electrode. The aqueous solution of 2 mol/L Na_2SO_4 was used as electrolyte. Before each testing, the electrolyte was deaerated by pure N_2 gas for 30 min.

3. Results

3.1. Dependence of the surface morphology on the dealloying time

The microstructure of the produced nanoporous silver is strongly dependent on the reaction parameters such as dealloying time and acid solutions. Considering the relatively inert chemical property of Ag, we chosen HCl aqueous solutions to etch the glassy precursor. Figs. 1a–f illustrate the microstructure evolution during dealloying the $Ag_{45}Mg_{35}Ca_{20}$ metallic glass at different dealloying time intervals from 2 to 36 h in the 0.025 mol/L HCl aqueous solution at room temperature. At the initial stage (Fig. 1a), only a few ligaments appeared inside the glassy matrix upon dealloying for 2 h. As the dealloying time increased to 6 h, the nanoporous microstructure started to form (Fig. 1b). The complete nanoporous structure with an average ligament size of ~81 nm was obtained by dealloying the glassy precursor for 8 h (Fig. 1c). The ligament size tends to coarsen when the dealloying time further increases (Fig. 1d). Specifically, the typical ligament length coarsened to be 90–100 nm when the dealloying time was extended to 24 h (Fig. 1e). As the dealloying time further increased to 36 h (Fig. 1f), the nanoporous structure collapsed due to the coarsening effect.

Fig. 2 shows XRD patterns of the corresponding dealloyed $Ag_{45}Mg_{35}Ca_{20}$ ribbons in the 0.025 mol/L HCl aqueous solution for different leaching time periods. It is clear to see the structure evolution from the glassy state to the face-centered cubic (*fcc*) Ag with the increase of dealloying time. Gradually, the characteristic amorphous halo of the glassy precursor diminishes and the sharp crystalline peaks of *fcc* Ag emerge with increasing the dealloying time. The XRD pattern of the sample dealloyed for 2 h shows a typical amorphous halo, indicating that the sample remains mostly a glassy state, which is consistent with the SEM observation shown in Fig. 1a. For the sample dealloyed for 6 h, the sharp peaks of *fcc* Ag develop considerably, implying formation of nanoporous Ag. The peak intensities of the *fcc* Ag become stronger as the dealloying time increases from 6 to 12 h, demonstrating the proceeding of the dealloying process. When the dealloying time extends from 12 to 24 h, however, the crystalline peaks become broader and their intensities decrease lightly, which may result from the coarsening effect and the heterogeneous surface strain [28].

3.2. Dependence of the surface morphology on the concentration of HCl aqueous solutions

To gain insights into effects of the etching solution concentration on the nanoporosity, we explored the structure evolution in different HCl solutions for a critical dealloying time when the surface dealloying process is completed. Figs. 3a–d show typical surface morphology of the dealloyed $Ag_{45}Mg_{35}Ca_{20}$ metallic glass in the HCl solutions with a concentration level of 0.025, 0.1, 1 and 12 mol/L for different critical leaching durations, respectively. Obviously, in the HCl solution with the higher concentration, the critical dealloying time for achieving a uniform nanoporous structure on the glass surface was shorter, and the pore microstructure was also finer. Specifically, the critical dealloying time dropped from 8 h to 10 min as the HCl solution concentrated from 0.025 to 12 mol/L; accordingly, the ligament size decreases dramatically from ~81 (Fig. 3a) to ~18 nm (Fig. 3d).

3.3. Dependence of the pore morphology on the dealloying temperature

In addition to the dealloying time and the concentration of the HCl solution, dealloying temperature is also an importance parameter to control the microstructure of final products. Thus, we