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Bulk hierarchical nanoporous palladium prepared by dealloying PdAl alloys and its electrochemical properties

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ABSTRACT

Bulk hierarchical nanoporous palladium (BHNPP) materials composing both bimodal porous structure and monolithic porous structure were fabricated by chemical dealloying of $Pd_{20}Al_{80}$ alloy with sub-micrometer grain size via mechanical alloying and spark plasma sintering process (MA-SPS). The different nanoporous structures were formed in the regions where the microstructure was heterogeneous. Monolithic porous structure were formed after dealloyed of monolithic grain structure mainly composed of $PdAl_3$ phase, and bimodal porous structure with both larger pore of hundreds nanometers and smaller pore of a few nanometers were obtained after dealloyed of nanocrystalline structure consist of $PdAl_3$ and Al phases, respectively. Effects of dealloying time, concentration of dealloying solutions and chloride ion (Cl^-) on the evolution of the microstructure of BHNPP were also studied. Ligament of BHNPP can be facility coarsen by add chloride rather than only raise the concentration of HCl solution. Moreover, the cyclic voltammetry results reveal that the BHNPP materials have superior ethanol oxidation ability.

1. Introduction

Nowadays, porous palladium materials have attracted intensive interest owing to their potential applications in hydrogen isotope displacement processes [1], hydrogen storage [2,3], catalytic [4–6], hydrogen sensor [7], and so on. In particularly, as a new type of nanostructure materials, nanoporous palladium materials (NPP) with bicontinuous interpenetrating ligament-channel structure and large surface area show better resistance to CO poisoning in direct ethanol fuel cell (DEFC) systems and lower cost compared with nanoporous Pt catalysis [5,6]. The rigid nanoligament network of NPP also can affect its hydrogen storage properties in a specific manner, miscibility gap in as-dealloyed nanoporous Pd whose ligament size is 20 nm can be narrowed and larger than the typical length of nanostructured Pd [3].

Recently, a great deal of effort has been directed towards the investigation of nanoporous materials prepared through dealloying method [8,9], which refers to the selective dissolution of one or more less noble components out of an alloy. The fabrication of NPP is mostly focused on the dealloying of Pd-containing metallic glass [10,11], single phase solid solution (Pd–Co) [12] and intermetallics (Pd–Al) [4,13]. Additional potential should be applied to electrochemical dealloying PdCo alloy and Pd–Cu–Ni–P metallic glass [10–12]. Unfortunately, Co and P impurities were remaining in the Pd bulk after dealloying that may lead to reduce the performance of nanoporous materials [3,11]. Phosphorus in Pd–P solid solutions will block the ethanol adsorption and led to a decrease in the electrocatalytic activity in pure Pd materials [11]. High current density was required to help the formation of NPP without P. However, it was energy cost. Intermetallics such as Pd–Al can be utilized as a precursor alloy to prepare NPP, which were mainly concerned with dealloying of PdAl ribbons prepared by a melt spinning technique [4]. However, there are few researches about the fabricating of bulk NPP materials, and the lacking of proper bulk precursor alloy is the main cause. In the former study, CuAl alloy in nanocrystalline grain were prepared by mechanical alloying and spark plasma sintering process (MA-SPS), and then bulk nanoporous copper with fine ligament and necessary strength can be obtained by chemical dealloying [14]. Thus, MA-SPS process is capable of fabricating PdAl alloy with sub-micrometer grain size, which can be used as precursor alloy to prepare bulk NPP.

In the present study, $Pd_{20}Al_{80}$ alloy with sub-micrometer grain size was prepared by MA-SPS process, and then bulk hierarchical

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nanoporous palladium materials were fabricated by dealloying of the resultant alloy. Effect of dealloying time and Cl^- on the evolution of microstructure of BHNPP materials was investigated. In addition, electrochemical properties of the prepared NPP were also studied.

2. Experimental

$Pd_{20}Al_{80}$ alloy were prepared by mechanical alloying (MA) and spark plasma sintering (SPS) process. Al (>99.9%, ~2 μm, ST NANO, China) and spongy Pd (>99.95%, ~30 μm, Northwest Institute for Non-ferrous Metal Research, China) in the composition of Al–20 at %Pd were ball milled under vacuum environment. The ball to powder mass ratio was approximately 10:1 and the angular speed of ball-milling was 300 r/min for 10 h. Then the MA powder was sintered by a Dr. Sinter SPS-1050 apparatus. A heating rate of about 70 °C/min was used from room temperature to 600 °C and a pressure of 30 MPa and a holding time of 30 min were applied during sintering. The resultant $Pd_{20}Al_{80}$ alloy was wire cutting and grinding with SiC paper to obtain a mirror surface. The chemical etching of the alloy sheet were take place in 0.1 M, 0.5 M and 1 M concentration of HCl solutions at room temperature for different time ranging from 1d to 7 days, respectively. As a contrast, dealloying was performed for 7d in mixed solutions of 0.1 M HCl and 0.9 M NaCl to investigate the concentration of Cl^- influence on the evolution of BHNPP materials. Ethanol and deionized water were used to rinse the sample, respectively. The as-dealloyed samples were kept in a vacuum chamber to avoid oxidation.

The samples were characterized with a field-emission scanning electron microscope (FESEM, XL30SFEG) equipped with an X-ray energy spectrometer (EDS) and transmission electron microscope (TEM) for microstructure and elemental analyses. X-ray diffraction patterns were recorded by an X-ray diffractometer (XRD, DX-2000) with Cu Kα radiation. The ligament sizes of resultant BHNPP materials were obtained by measuring their FE-SEM image with Image J software (100 ligaments of each were measured and averaged). Brunauer–Emmett–Teller (BET) surface areas of the resultant BHNPP materials were measured by a N_2 adsorption apparatus. Electrochemical measurements were performed in a standard three-electrode cell using a CHI600D electrochemical workstation in a three-electrode electrochemical cell (500 mL) with a Pt plate electrode as a counter electrode, Hg/HgO electrode as a reference electrode. The work electrode was coated by the as-dealloyed BHNPP materials (0.1 M HCl and 1 M HCl, 7d, designated as BHNPP-1 and BHNPP-2 respectively). The cyclic voltammograms (CV) of BHNPP-1 were obtained in 1.0 mol dm^{-3} KOH at different scan rate. Moreover, ethanol electro-oxidation performance of BHNPP-1 and BHNPP-2 were characterized in a deaerated mixture solution of 1.0 mol dm^{-3} KOH and 2.0 mol dm^{-3} ethanol. The scan rate is 50 mV s^{-1}.

3. Results and discussion

3.1. Characterization of precursor PdAl alloy

Fig. 1 shows the XRD pattern of $Pd_{20}Al_{80}$ at different fabrication stages. Pd peaks and Al peaks were decreased after mechanical alloying (Fig. 1b) and accompanied by line-broadening, which is caused by the increase of internal strain during milling [15]. The XRD pattern shown in Fig. 1c reveal that the prepared PdAl alloy is mainly composed of $PdAl_3$ and less Al phase.

Fig. 2 shows FE-SEM images of $Pd_{20}Al_{80}$ alloy. Basically, the resultant PdAl alloy was shown to consist of two distinct structure, nanocrystalline structure (region A in Fig. 2a) and monolithic grain structure (region B in Fig. 2a). Fig. 2b was the high magnification FE-SEM images of region A, which had a nanocrystalline structure with grain size of ~200 nm. On the contrary, region B was a monolithic grain structure with a few micrometers in size. Fig. 2c is the EDS pattern of region B, which reveal the atomic ratio of Al/Pd is 3:1, identical to the stoichiometric ratio of $PdAl_3$. According to XRD result in Fig. 1, nanocrystalline structure in region A was composed of $PdAl_3$ and Al phases. These heterogeneous structures were caused by the different diffusion coefficient of Al and Pd atoms.

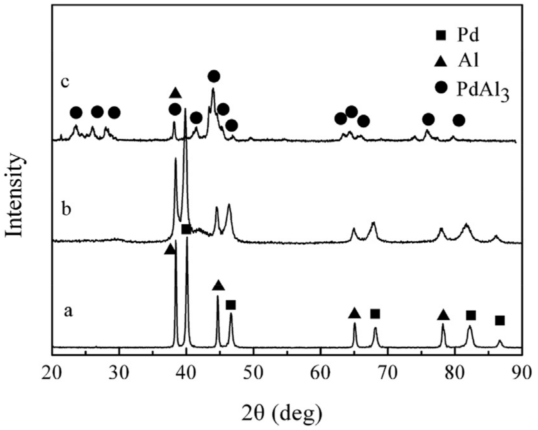

Fig. 1. XRD patterns of $Pd_{20}Al_{80}$ powder and alloy. (a) $Pd_{20}Al_{80}$ mixed powder, (b) mechanical alloying powder, 300r/min, 10 h, (c) SPS sintering compact, 600 °C, 30 min.

3.2. Evolution of nanoporous structure during dealloying process

Microstructures of BHNPP materials after dealloyed in 0.1 M HCl for different time are shown in Fig. 3. From the images, both bimodal porous structure (Fig. 3a, c, e) and monolithic porous structure (Fig. 3b, d, f) can be observed. These different nanoporous structures were formed in the regions where the microstructure was heterogeneous. The bimodal porous structure (region A in Fig. 3g) was originated from nanocrystalline structure (region A in Fig. 2a), which was caused by different dealloying behaviors of Al and $PdAl_3$ phases. From some study, porous materials with multimodal pore size have many advantages in some specify applications, such as micro fluidic-based sensors and the applications with gas flow [16,17]. Besides, the monolithic porous structure (region B in Fig. 3g) was obtained by dealloying of monolithic grain structure (region B in Fig. 2a). Also, the ligament size of BHNPP after dealloyed for different time is increase as the increasing of dealloying time. Fig. 4 shows FE-SEM images of BHNPP after dealloyed in different concentration of HCl solutions. Both bimodal porous structure and monolithic porous structure also can be observed. Significant coarsening of ligament occurs as the increased of concentration of dealloying solutions. Additionally, ligament size of BHNPP after dealloyed in the mixed solution of 0.1 M HCl and 0.9 M NaCl solution is larger than that in 0.1 M HCl solution (Fig. 4e, f).

Ligament size of BHNPP materials as a function of dealloying time and the concentration of dealloying solutions are shown in Fig. 5. The ligament size of BHNPP after dealloyed for different time exhibited a slightly increase as the increasing of dealloying time (Fig. 5a). As a contrast, the ligament size distinctly increases as the increased of concentration of dealloying solutions. Length scales of ligaments-channels in nanoporous metals could be tuned by simply changing the dealloying solutions [18,19]. In this work, it is obvious that the ligament size increases with the increased of concentration (0.1 M–1 M) of HCl solution.

The species and concentration of solutions were strongly influence the surface diffusion of more noble elements along alloy/