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Fabrication of nanoporous bi-metallic Ag–Pd alloys with open pores

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ABSTRACT

Nanoporous bi-metallic Ag–Pd alloys were synthesized by dealloying of amorphous Ag–Pd–Cu–Si alloys in acid solutions. Less noble Cu and Si elements were removed from the amorphous precursors by free dealloying process. The ligament with the characteristic width of less than 100 nm is composed of Ag grains with the solid soluted Pd, and the average grain size is about 50 nm. The present work shows that the wide composition range and microstructure homogeneity of amorphous alloys makes them potential to obtain nanoporous alloys with tunable composition by simple dealloying process.

1. Introduction

Nanoporous (NP) noble metals fabricated by dealloying process have received intensive interest as free-standing nanomaterials due to their potential for various chemical applications [1–4]. The high price and difficulty in getting homogeneous NP structure with tunable composition is the main bottleneck which restricts the applications of NP noble metals and alloys. Among the noble metals silver is economically more attractive combined with unique physical and chemical properties. The fabrication of NP Ag foil was mainly based on Ag–Al, Ag–Cu, Ag–Mg and Ag–Zn polycrystalline alloys and the ligament is Ag grains with trace alloying elements [5–12]. In order to get better properties, more homogeneous microstructure and tunable composition is the possible solution. NP bi-metallic alloys such as Pd–Au, Au–Pt, Ag–Pd and Au–Ag have been fabricated by dealloying process. NP Ag–Pd alloys were fabricated by dealloying crystalline Mg–Ag–Pd alloys and they were proved to show better catalytic properties comparing with NP Ag [13–16]. However, the solid solution ability of the precursor restricts the composition of the ligaments. Another way to obtain NP Ag–Pd alloys is hydrothermal synthesis in which process NP Ag is immersed into Pd-containing metallic salt [17]. This is more complex and costly comparing with dealloying process.

Most recently, amorphous Ag-containing alloys such as Ag–Mg–Ca and Ag–Cu–Si were developed as precursors [18,19]. Amorphous alloys have homogeneous composition and microstructure, and are free of grain boundaries and intermetallic compounds [20,21]. The homogeneity makes them inherent precursors for fabrication of NP metals and alloys by dealloying process. The wide composition range of amorphous alloys makes them promising to fabricate NP alloys with tunable composition. The starting alloys are $Ag_{38.75-x}Pd_xCu_{38.75}Si_{22.5}$ ($x=0$–10) based on our previous work in Ref. [19], in which $Ag_{38.75}Cu_{38.75}Si_{22.5}$ foil has been proved to form amorphous structure and is a good precursor for NP Ag. Based on the component coexistence criterion developed for investigation of glass forming abilities [22], Pd is a good substitution element of Ag since they possess similar positions in the periodic table of elements. It is expectable to obtain amorphous $Ag_{38.75-x}Pd_xCu_{38.75}Si_{22.5}$ precursors by rapid-solidification process and fabricate NP Ag–Pd alloys by free dealloying process.

2. Experimental

The alloy ingots were made by mixing pure Ag, Pd, Cu, Si elements in arc melting furnace. The ingots were rapidly solidified on a copper wheel at a linear speed of 94 m s^{-1}. The width of the resulting foils was around 2 mm and the thickness was around 10–15 μm. The etchant for dealloying was the mixture of diluted nitric acid and HF acid. The phases and microstructures of the as-spun and as-dealloyed foils were identified by RigakuD/max2500PC XRD diffractometer, high-resolution JEOL-7500F scanning electron microscope (SEM) and a high-resolution JEM-2100F transmission electron microscope (TEM). The TEM specimens were prepared by ultrasonic vibration of as-dealloyed samples in ethanol.

3. Results and discussion

Five typical quasi-ternary alloys are spun-melted as precursors, i.e. $Ag_{38.25}Pd_{0.5}Cu_{38.75}Si_{22.5}$, $Ag_{37.75}Pd_1Cu_{38.75}Si_{22.5}$, $Ag_{35.75}Pd_3Cu_{38.75}Si_{22.5}$,

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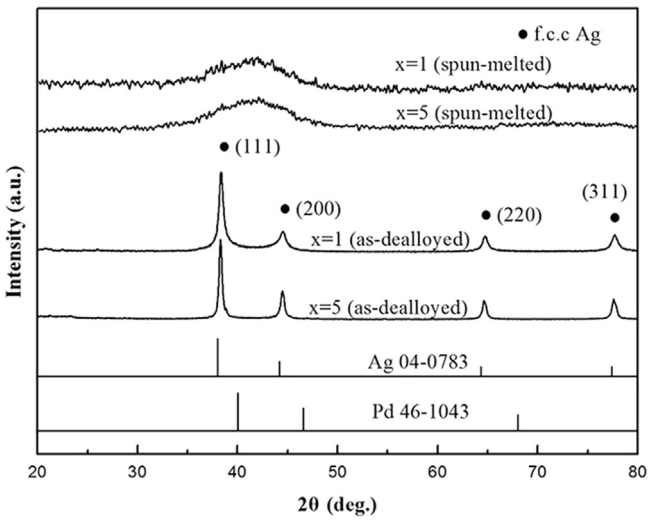

Fig. 1. XRD patterns of rapidly solidified $Ag_{38.75-x}Pd_xCu_{38.75}Si_{22.5}$ precursors and as-dealloyed foils.

$Ag_{33.75}Pd_5Cu_{38.75}Si_{22.5}$, and $Ag_{28.75}Pd_{10}Cu_{38.75}Si_{22.5}$. It is detected based on the preliminary XRD that when the content of Pd is no more than 5%, the quasi-ternary Ag–Pd–Cu–Si alloys are amorphous. When the content of Pd is 10%, the precursor is polycrystalline. The 5 precursors were dealloyed and examined. As an example, two representative alloys were selected to show the experimental results, i.e. $Ag_{37.75}Pd_1Cu_{38.75}Si_{22.5}$ and $Ag_{33.75}Pd_5Cu_{38.75}Si_{22.5}$. Fig. 1 shows that the as-spun melting foils possess fully amorphous structure. The mixture of nitric acid and HF acid was chosen to get good removing efficiency for both Si and Cu. The XRD patterns of the samples after etching for 22 min of $Ag_{37.75}Pd_1Cu_{38.75}Si_{22.5}$ and 32 min of $Ag_{33.75}Pd_5Cu_{38.75}Si_{22.5}$ in mixture of 8.7 wt% nitric acid and 2.2 wt% HF acid are also shown in Fig. 1. The as-dealloyed foils show typical Ag crystalline Bragg peaks.

The FEG–SEM images taken from the corresponding foil surfaces are shown in Fig. 2a and b. Tilted views showing the cross-sections are shown in Fig. 2c and d. The weight loss after dealloying of the two foils are 57.4% and 56.8%, respectively. It can be seen that the foils have been dealloyed homogeneously in three-dimensional scale. The EDX spectra of the as-dealloyed samples are shown in Fig. 2e and f. According to the EDX quantitative

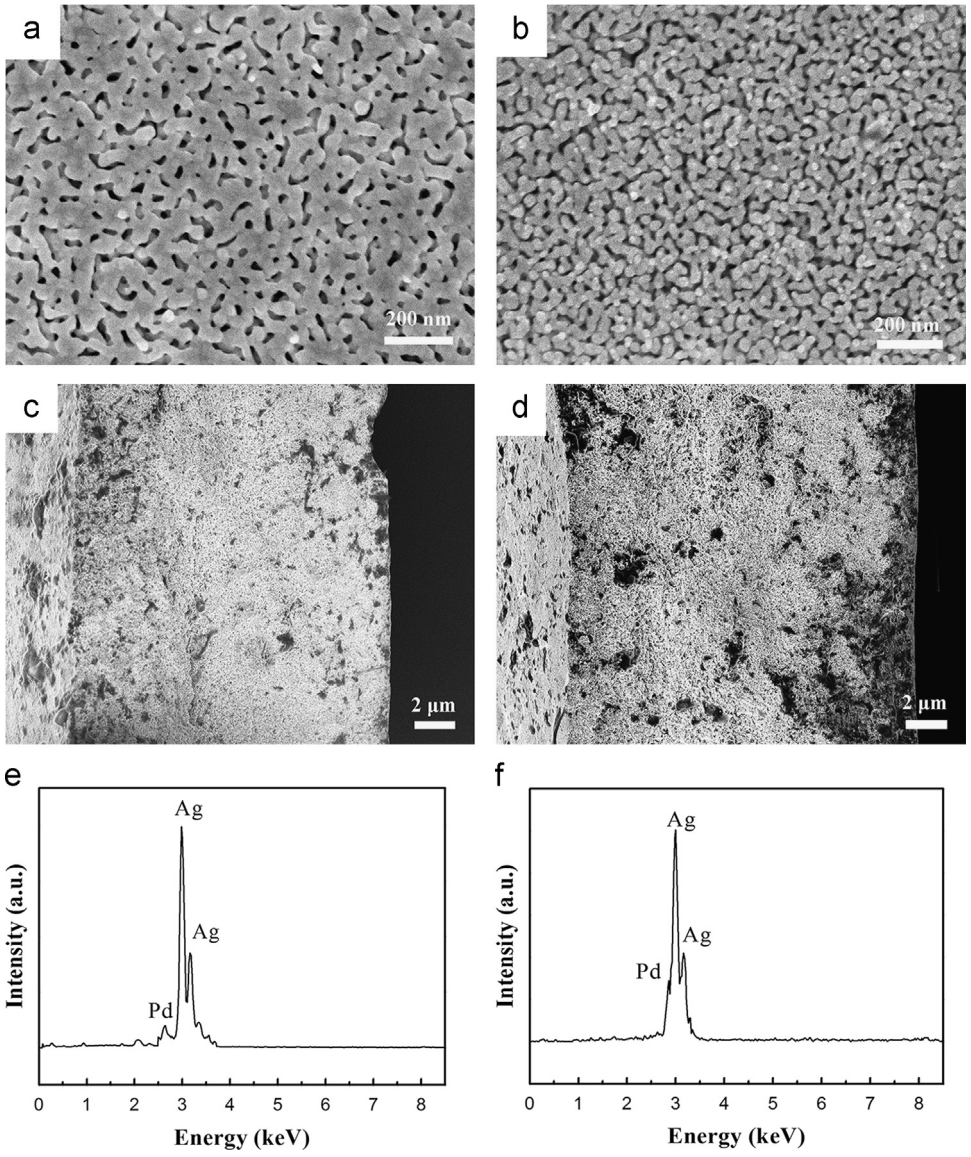

Fig. 2. Microstructures of as-dealloyed foils after immersion in mixture of 8.7 wt% nitric acid and 2.2 wt% HF acid: (a) $Ag_{37.75}Pd_1Cu_{38.75}Si_{22.5}$, (b) $Ag_{33.75}Pd_5Cu_{38.75}Si_{22.5}$. (c) The tilted view of the sample in (a). (d) The tilted view of the sample in (b). (e) and (f) are EDX spectra of dealloyed foils, respectively.