A nanoporous composite by dealloying rapidly quenched Co$_{75}$Pd$_{20}$Si$_{5}$

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Abstract. In this work we report the fabrication of a nanoporous composite by electrochemical dealloying a rapidly quenched Co$_{75}$Pd$_{20}$Si$_{5}$ alloy in a 0.5M H$_2$SO$_4$ aqueous solution. The melt-spun alloy exhibited a two-phase microstructure with the precipitation of an unknown secondary phase on the FCC solid solution matrix. Upon dealloying, a nanoporous composite was formed, which consisted of nanoligaments of two different length scales, namely, ~5-10 nm and ~100-150 nm. The sample surface was free of cracks and the as-dealloyed ribbons exhibited good mechanical integrity. The secondary phase was found to be more corrosion-resistant than the FCC solid solution phase under the same electrochemical conditions, and after dealloying the framework structure of the phase preserved to reinforce the dealloyed microstructure.

1. Introduction

Nanoporous (NP) metals have unique three dimensional structures comprised of interconnected nanoligaments and nanopores. Electrochemical dealloying has proven very effective to turn alloys into NP metals [1, 2]. In a dealloying process, the less noble constituents are selectively dissolved out from the alloy, leaving behind a spongy residue consisting mainly of noble metals. Extensive solid solution alloys are the widely used precursor materials for dealloying, from which NP structures with pore size ranging from a few to hundreds of nanometers are readily made. The unique nanostructures deliver intriguing material properties, for instance the anomalous surface plasmon resonance [3] and the surface-enhanced Raman scattering (SERS) effect [4, 5]. The unusual optical properties would give rise to their potential applications as sensors in molecular diagnostics. Some NP metals are ideal electrode or substrate materials for electrocatalysis [6-8]. In a nutshell, the exotic nanostructured materials are currently believed to have a wide range of applications in catalysis, absorption, sensing, and nanomechanics [9].

For device applications, the mechanical integrity and the robustness of NP metals are of critical significance. Usually, a dealloyable extensive alloy is enriched in the less noble metal, and volume contraction of the grains may occur when the majority constituent is dissolving out from the alloy. As a consequence, massive cracking is commonly observed in the as-dealloyed samples [4, 5]. Recently, there appeared several accounts on the making of crack-free bulk NP samples. Senior et al. [10] have successfully obtained NP-Au bulk samples of good mechanical integrity by optimizing the precursor binary alloy composition and the dealloying condition control. Sun et al. used multi-step dealloying strategy to make robust bulk NP-Au samples [11]. In the two cases, the precursor materials are single
phase Au-Ag extensive solid solution alloys. Jin et al [12], on the other hand, have realized the fabrication of macroscopically strong NP-Pt by dealloying several two-phase Pt-Ag alloys, in which one solid solution phase appears as a secondary dendrite phase embedded on the matrix solid solution phase. NP structures with good mechanical integrity have attracted much attention in the recent development activities of functional NP metal devices.

Hakamada and Mabuchi [13, 14] have made a comprehensive study on the different dealloying behaviors of Pd-transition metals (Fe, Co, or Ni) solid solution alloys. Co\textsubscript{80}Pd\textsubscript{20} was found to be a favourable precursor to obtain NP-Pd with ultrafine nanopores of a few nanometers. In our previous study on the dealloyed microstructure of rapidly quenched Co\textsubscript{80}Pd\textsubscript{20} alloy, massive surface cracking were found to occur inevitably in the samples. In the present work, we first attempt to make a two-phase microstructure by alloying Co\textsubscript{80}Pd\textsubscript{20} with a glass-forming element Si. It is expected that a small amount of Si addition into the alloy would result in the formation of a more corrosion-resistant secondary phase than the matrix FCC solid solution phase, which plays the role of reinforcement in the dealloyed sample for improved mechanical integrity.

2. Experimental

Alloy ingots of Co\textsubscript{80}Pd\textsubscript{20} and Co\textsubscript{75}Pd\textsubscript{20}Si\textsubscript{5} were prepared by arc melting the mixtures of appropriate amount of Si (purity: 99.999 wt.%), Co (99.99 wt.%), and Pd (99.5 wt.%) under a vacuum level of about 5 × 10\textsuperscript{-4} Pa. Using the master alloys, ribbon samples with a cross section of ~ 0.02 × 1.0 mm were made by single-roller melt-spinning. A HZ-3000 potentiostatic was employed to drive the dealloying of the two kinds of alloys with a platinum counter electrode and a saturated calomel electrode (SCE) reference electrode at room temperature. The dealloying experiments were conducted in a 0.5M H\textsubscript{2}SO\textsubscript{4} aqueous solution. As-dealloyed samples were first soaked in deionized water to remove the electrolyte from the internal pores, and then allowed to air dry for subsequent observation. Phase identification for as-quenched and as-dealloyed samples was conducted via a standard \(\theta\)-2\(\theta\) scan on a Rigaku RINT-ultima IIIsp diffractometer (Cu-K\(\alpha\), \(\lambda = 0.15406\) nm). The scan rate was set to be 0.01°/s in the 2\(\theta\) range of 20-100°. The morphology and composition of alloy phases before and after dealloying were analyzed with a field emission scanning electron microscope (Hitachi S-4800 SEM) equipped with an Oxford energy dispersive X-ray spectrooscope (EDX).

3. Results and discussion

3.1 Component phases and microstructure

The X-ray diffraction patterns of rapidly quenched Co\textsubscript{80}Pd\textsubscript{20} and Co\textsubscript{75}Pd\textsubscript{20}Si\textsubscript{5} alloys are shown in Fig.1. The Co\textsubscript{80}Pd\textsubscript{20} alloy exhibits a single phase FCC structure. In the Co\textsubscript{75}Pd\textsubscript{20}Si\textsubscript{5} alloy, a secondary phase is found to coexist with FCC solid solution phase, while the diffraction peaks cannot be thoroughly indexed by any of the known Pd-Si and Co-Si phases. The typical microstructure of Co\textsubscript{75}Pd\textsubscript{20}Si\textsubscript{5} alloy is shown by the inserted SEM image, in which the unknown phase appears to be grey white. The extensive EDX analysis gave a composition range of ~ Co\textsubscript{39-42}Pd\textsubscript{43-47}Si\textsubscript{14} for the unknown phase. In comparison with the nominal alloy composition, the phase is enriched in Si and Pd, and is depleted in Co. The alloying effect of Si on the phase selection of Co\textsubscript{75}Pd\textsubscript{20}Si\textsubscript{5} may be understood in terms of the enthalpy of mixing between constituent elements. The enthalpies of mixing between Pd, Co and Si at 1:1 atomic ratio are \(\Delta H_{\text{PdSi}} = -38\) kJ/mol and \(\Delta H_{\text{CoSi}} = -21\) kJ/mol, respectively [15]. The strong negative enthalpies of mixing characteristics between Si and Pd and Co metals would favor the formation of intermetallic phase.
3.2 Electrochemical measurement on dealloying behavior

Fig. 2 (a) shows the anodic current-potential behaviors of the two rapidly quenched alloys in 0.5M H_2SO_4. Both alloys exhibit a passivation state at low driving potentials, followed by active dissolution at higher potentials. This electrochemical feature resembles those of dealloyable Au-Ag alloys. It is seen that active dissolution occurs at a relatively lower potential in Co_{75}Pd_{20}Si_{5} at a sweeping rate of 1x10^{-3}V/s. To ensure dealloyability, the current-time behaviors of the single and two-phase alloys were studied at constant driving potentials. The typical results are shown in Fig. 2 (b). At potentials of 0.35V (Co_{80}Pd_{20}) and 0.15V (Co_{75}Pd_{20}Si_{5}), the current densities are found to increase first rapidly to a peak value and then progressively cease to be zero. All the electrochemical measurements suggest that the two alloys are dealloyable.

3.3 Comparison of dealloyed microstructures

Fig. 3 (a) and (b) compare the surface morphologies of as-dealloyed Co_{80}Pd_{20} and Co_{75}Pd_{20}Si_{5} ribbon samples. After dealloying, the Co_{80}Pd_{20} sample exhibited massive cracking over the entire ribbon.
surface, while the as-dealloyed Co$_{75}$Pd$_{20}$Si$_5$ was free of cracks. It should be mentioned that after dealloying the Co$_{80}$Pd$_{20}$ residue exhibited large volume shrinking and the sample became curled, the Co$_{75}$Pd$_{20}$Si$_5$ ribbon, however, almost preserved its original shape and dimensions. The latter sample can be broken by bending. The cross-section views of their dealloyed microstructures are shown in Fig. 3 (c) and (d), respectively. Intergranular cracking in Co$_{80}$Pd$_{20}$ is evidently seen, which can mainly be attributed to the internal tensile stress caused by dissolving-out of Co. In the dealloyed Co$_{75}$Pd$_{20}$Si$_5$ bulk, nanoligaments of two different length scales are formed. The fine nanoligaments are of ~ 5-10 nm size and the coarse ones ~ 100-150 nm. The length scale of the fine nanoligaments is comparable to that obtained in Co$_{80}$Pd$_{20}$. Apart from this, no significant interphase boundary cracking was found in the nanoporous composite.

![Figure 3. SEM images showing (a) significant surface cracking in dealloyed Co$_{80}$Pd$_{20}$ ribbon samples (b) Crack-free surface morphology of dealloyed Co$_{75}$Pd$_{20}$Si$_5$ (c) Intergranular cracking in dealloyed Co$_{80}$Pd$_{20}$ (d) the formation of a two-length scale hierarchical nanocomposite in dealloyed Co$_{75}$Pd$_{20}$Si$_5$. The inserted SEM images in (c) and (d) compare the finest pore sizes obtained in the two dealloyed microstructures. (e) and (f) EDX spectra taken from the secondary phase in the starting and dealloyed Co$_{75}$Pd$_{20}$Si$_5$ samples, respectively. The average compositions of the phase in the two samples are very close.](image)

Fig. 3 (e) and (f) present the EDX spectra taken from the secondary phases existing respectively in the precursor and the dealloyed ribbon samples. The measured composition changes, especially the Si contents in the phase are negligibly small. The compositional evidence indicates that the secondary phase is more corrosion-resistant than the FCC solid solution matrix in the 0.5M H$_2$SO$_4$ aqueous solution under a given potential. It is very likely that selective dissolution mainly occurred in the matrix phase. That is, dealloying was locally confined to the regions separated by the secondary phase framework. The interphase boundary structure between the FCC matrix and the secondary phase appears to be a critical issue to understand the good mechanical integrity of the nanoporous composite.
The crystallographic orientational relationship between the two phases needs to be identified for further discussion. Notwithstanding, the fact that there exists no significant interphase boundary cracking in the sample has delivered an interesting implication. Since the interphase boundary is robust against dealloying, it is possible to realize the continuous network formation of the secondary phase along the FCC matrix grain boundaries by optimizing the precursor alloy composition and the melt-spinning conditions such as quenching temperature and cooling rate. Our recent study on the fabrication of novel nanoporous composite in Co-Pd-Si system is along this line, and the results will be reported elsewhere in the future.

4. Conclusion
By substitutional alloying of 5 at.% Si for Co$_{80}$Pd$_{20}$, a two-phase Co$_{75}$Pd$_{20}$Si$_{5}$ alloy was made by means of melt-spinning. Electrochemical measurement indicated that the Co$_{75}$Pd$_{20}$Si$_{5}$ alloy was dealloyable in 0.5M H$_2$SO$_4$. After dealloying, nanoligaments of two different length scales were formed in the alloy. In comparison with the dealloyed microstructure of Co$_{80}$Pd$_{20}$, the nanoporous composite are free of surface cracking and is of good mechanical integrity. Co-Pd-Si is expected to establish a promising system for the fabrication of various nanoporous structures of good mechanical robustness.

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