



Solid/electrolyte interface phenomena during anodic polarization of Pd_{0.2}M_{0.8} (M = Fe, Co, Ni) alloys in H₂SO₄

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ABSTRACT

Pd_{0.2}Fe_{0.8}, Pd_{0.2}Co_{0.8} and Pd_{0.2}Ni_{0.8} alloys were subjected to electrolysis in H₂SO₄ for production of nanoporous Pd. Surface analyses with different surface sensitivities revealed that Fe and Ni at the surface layer dissolve in H₂SO₄ after the electrolysis of Pd_{0.2}Fe_{0.8} and Pd_{0.2}Ni_{0.8}, respectively, but this dissolution is confined to the surface layer. On the other hand, aggregation of Pd adatoms at the solid/electrolyte interface allowed exposure of internal Co atoms to the electrolyte, and as a result, nanoporosity formed only from Pd_{0.2}Co_{0.8} alloys. These results experimentally suggest that the aggregation of remnant element (Pd in this case) at solid/electrolyte interface is necessary for the formation of nanoporosity by dealloying.

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1. Introduction

Nanoporous metals can be fabricated by the selective dissolution (or dealloying) of binary alloys [1,2]. The less reactive element in the binary alloy spontaneously forms a nanoporous structure after the selective removal of more reactive element. The fabrication of nanoporous Au from Au–Ag alloy and its properties have been surveyed very frequently [1–5]. Other nanoporous metals such as Cu [6], Ni [7,8], Pt [9,10] and Pd [11–13] can also be fabricated from proper initial binary alloys.

Nanoporous Pd can be readily fabricated by the dealloying of Pd–Co alloy in H₂SO₄ under a suitable electrochemical potential [12,13]. Pd–Fe and Pd–Ni are other possible initial binary alloys for nanoporous Pd because standard electrode potentials of Fe and Ni as well as that of Co are sufficiently lower than that of Pd [14]. However, the passivity of Pd–Fe and Pd–Ni inhibits the formation of nanoporosity during the constant-potential electrolysis in H₂SO₄ [12]. Fe, Co and Ni are adjacent elements in the periodic table and their properties are similar; nevertheless, when alloyed with Pd, their dissolution behavior significantly differs.

The passivity of Pd–Fe and Pd–Ni may be attributed to the formation of an oxide film formation or the surface enrichment of nobler element, as observed in Ni–P [15]. Actually, dealloying involves several surface/electrolyte interface phenomena such as the dis-

solution of the sacrificial element and the surface diffusion of the remnant element, which may be responsible for the passivity [2]. In this study, surface analyses with different surface sensitivities were carried to determine the passivation and dealloying mechanisms of Pd_{0.2}M_{0.8} (M = Fe, Co, Ni) alloys in H₂SO₄.

2. Experimental

Commercially available Fe, Co, Ni and Pd (>99.9 mass% purity) were melted together in an arc furnace under an Ar atmosphere to fabricate Pd_{0.2}Fe_{0.8}, Pd_{0.2}Co_{0.8} and Pd_{0.2}Ni_{0.8} alloy ingots. The ingots were subjected to homogenization annealing at 1173 K for 24 h under an Ar flow and were then water quenched. The starting alloys were single-phase solid solutions with no intermetallics [16]. Metallographic technique revealed that the grain sizes of the alloys were 100–500 μm. For reference, pure Fe, Co and Ni ingots were also prepared by arc melting. The surface of the ingots was prepared by cutting, grinding and polishing using a 1 μm diamond paste.

The ingots were then subjected to electrochemical measurements including anodic polarization and electrolysis at a constant potential. A typical three-electrode electrochemical cell was used with a saturated calomel electrode (SCE) as a reference electrode, the polished ingot as a working electrode and a Pt plate as a counter electrode. In this paper, the potentials are expressed relative to the SCE. The ingot surface was sealed with a Teflon film and an area of 3 mm × 3 mm of the ingot surface was exposed to the electrolyte, which was 0.1 mol/L H₂SO₄ degassed by 30 min Ar bubbling. Starting from the open-circuit potential, the potential was positively scanned at a scan rate of 1 mV s⁻¹ during anodic polarization measurements. Electrolysis at a constant potential of +0.6 V vs. SCE was also conducted on the Pd_{0.2}Fe_{0.8}, Pd_{0.2}Co_{0.8} and Pd_{0.2}Ni_{0.8} alloy ingots for 1800 s. All electrochemical experiments were carried out at 298 K.

After the constant-potential electrolysis, the samples were washed by pure water (18.2 MΩ cm⁻¹) several times. Surface elemental analyses were carried out by two methods. One was energy-dispersive X-ray spectroscopy (EDXS; EMAX ENERGY, Horiba, Ltd.) equipped with a scanning electron microscope (SEM; S-4300

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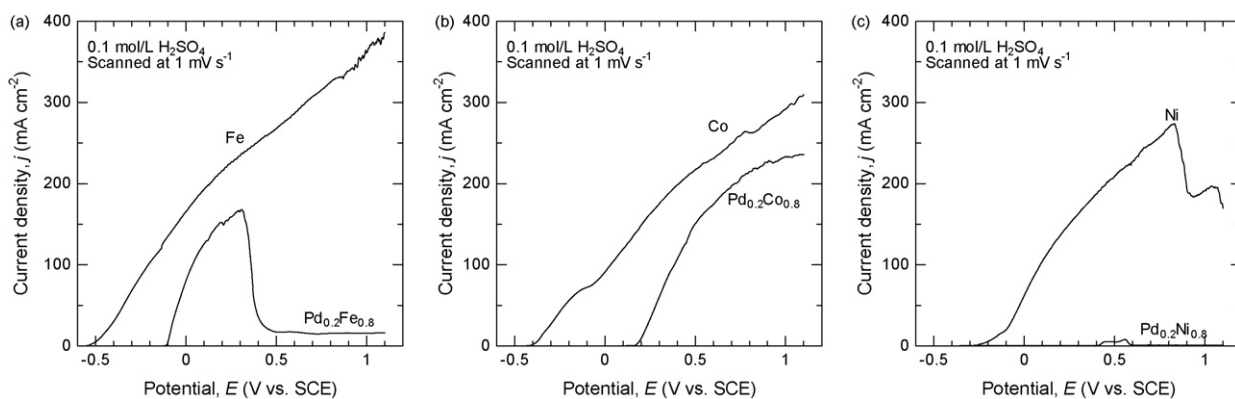


Fig. 1. Anodic polarization curves for (a) pure Fe and $\text{Pd}_{0.2}\text{Fe}_{0.8}$, (b) pure Co and $\text{Pd}_{0.2}\text{Co}_{0.8}$ and (c) pure Ni and $\text{Pd}_{0.2}\text{Ni}_{0.8}$.

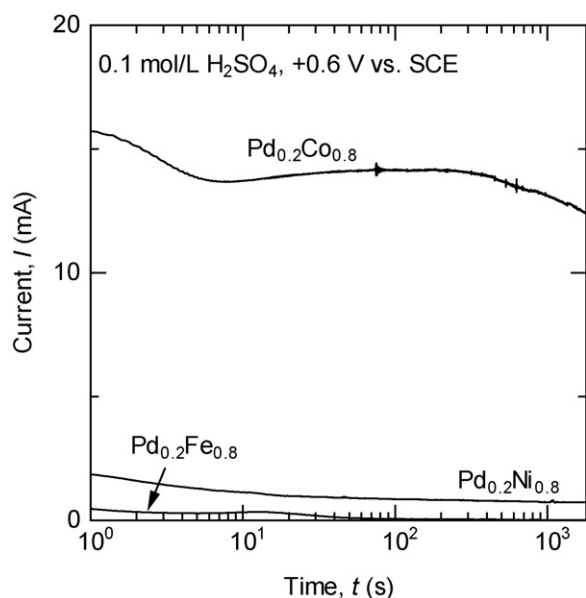


Fig. 2. Time variation in current during constant-potential electrolysis of $\text{Pd}_{0.2}\text{Fe}_{0.8}$, $\text{Pd}_{0.2}\text{Co}_{0.8}$ and $\text{Pd}_{0.2}\text{Ni}_{0.8}$.

by Hitachi High-Technologies Corp.) and the other was X-ray photoelectron spectroscopy (XPS; Thermo Electron, Sigma Probe) using $\text{Al K}\alpha$ radiation ($h\nu = 1486.6$ eV). No significant sample charging was observed, but binding energy in XPS was calibrated using the C 1s peak (285.0 eV).

3. Results

The anodic polarization curves of pure and alloyed Fe, Co and Ni are shown in Fig. 1. The vertical axes indicate the apparent current density, which was calculated by simply dividing the measured current by the apparent exposed area ($=3 \text{ mm} \times 3 \text{ mm}$). Pure Fe, Co and Ni exhibited monotonic increases in current with increasing potential and no passivity was observed. This suggests that passive surface oxide films of Fe, Co and Ni do not form upon electrolysis in H_2SO_4 . $\text{Pd}_{0.2}\text{Co}_{0.8}$ alloy also exhibited a similar trend in its anodic polarization curve (Fig. 1(b)), although the measured current was smaller than those of pure metals. The monotonic current increase in the anodic polarization curve of $\text{Pd}_{0.2}\text{Co}_{0.8}$ is similar to those for Au–Ag alloys, which produce nanoporous Au upon electrolysis [3]. On the other hand, $\text{Pd}_{0.2}\text{Fe}_{0.8}$ and $\text{Pd}_{0.2}\text{Ni}_{0.8}$ clearly had regions of passivity at high potentials, at which a low constant current was detected. Thus, alloying with Pd significantly affects the anodic polarization behaviors of Fe and Ni in H_2SO_4 .

Fig. 2 shows the variation in current during the constant-potential electrolysis of $\text{Pd}_{0.2}\text{Fe}_{0.8}$, $\text{Pd}_{0.2}\text{Co}_{0.8}$ and $\text{Pd}_{0.2}\text{Ni}_{0.8}$. A large current was detected during the constant-potential (+0.6 V) electrolysis of $\text{Pd}_{0.2}\text{Co}_{0.8}$ in H_2SO_4 , suggesting the considerable dissolution of Co into the electrolyte; however, very little current was observed in the cases of $\text{Pd}_{0.2}\text{Fe}_{0.8}$ and $\text{Pd}_{0.2}\text{Ni}_{0.8}$. Fig. 3(a)–(c) are the SEM microstructures of $\text{Pd}_{0.2}\text{Fe}_{0.8}$, $\text{Pd}_{0.2}\text{Co}_{0.8}$ and $\text{Pd}_{0.2}\text{Ni}_{0.8}$ after the constant-potential electrolysis. $\text{Pd}_{0.2}\text{Co}_{0.8}$ alloy exhibited an open-cell nanoporous structure as shown in Fig. 3(b). The ligament and pore sizes were approximately 20 nm. However,

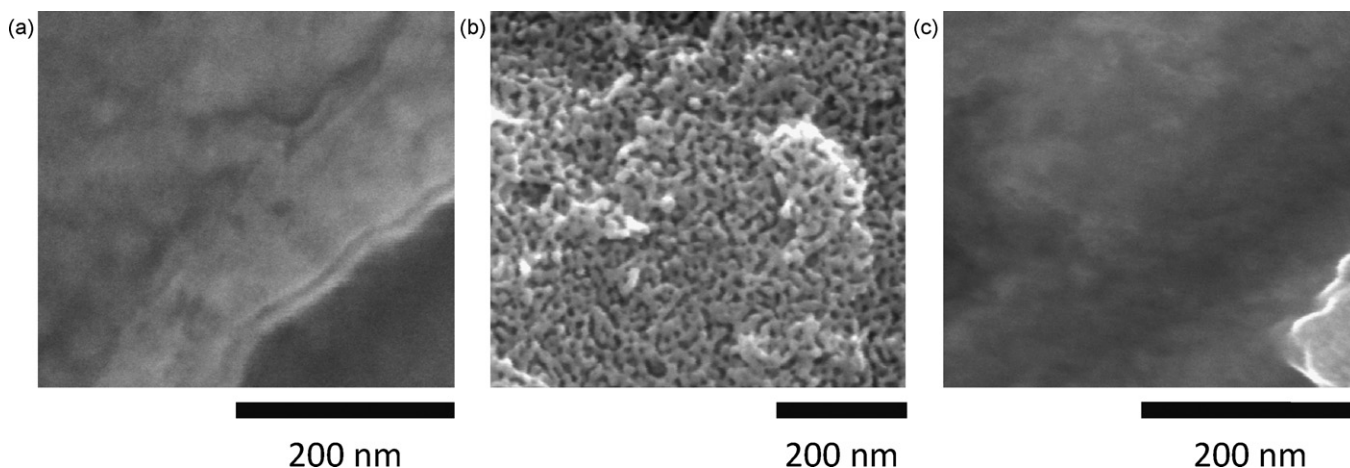


Fig. 3. Scanning electron micrographs for (a) $\text{Pd}_{0.2}\text{Fe}_{0.8}$, (b) $\text{Pd}_{0.2}\text{Co}_{0.8}$ and (c) $\text{Pd}_{0.2}\text{Ni}_{0.8}$ after electrolysis. Electrolysis was conducted at +0.6 V (vs. SCE) in 0.1 mol/L H_2SO_4 for 1800 s at 298 K.

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