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Effect of surface modification on de-alloying of $Pd_{70}Ag_{30}$ nanoparticles

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Abstract

Heating of surface modified $Pd_{70}Ag_{30}$ alloy nanoparticle pellets in air was conducted and the effect of surface modification on selective oxidation of Pd and surface segregation of Ag on the surface was examined. For unmodified nanoparticles at 250 °C, free Ag was observed because of preferential oxidation of Pd. Modification with stearic acid reduced the degree of oxidation and the amount of free Ag. With polyethylene glycol, the oxidation of Pd was further suppressed. No free Ag was formed on the pellet surface, instead, more segregation of Ag within the alloy nanoparticles to the surface occurred. The effectiveness of these two surfactants gradually diminished at 350 °C.

Keywords: $Pd_{70}Ag_{30}$ nanoparticles; Surface modification; Stearic acid; Polyethylene glycol

1. Introduction

Surface modification is a common material processing technique and is often used in many fields of materials technology [1,2]. For nanomaterials, modification by surfactants may substantially change the surface properties because of the large surface area [3–5]. From thermodynamic point of view, there is a tendency for material systems to reach the minimum surface energy state. If a small amount of surfactant (low surface energy component) is added to a sample material, it will easily spread over the surface to lower the surface energy of that material [5,6].

In alloy nanoparticles, de-alloying may take place during annealing by out-diffusion of one component from the interior [7,8]. Such a process may be induced by the change of mobility of one of the components in the alloy when the other one is preferentially oxidized in air [9,10], or one of the components is attracted to the surface by the atmospheric gas so that significant diffusion takes place [10,11].

Previously, heating of $Pd_{70}Ag_{30}$ nanoparticle pellets in air at 250–450 °C has been studied [12]. It was observed that Pd was preferentially oxidized at 250–300 °C, resulting in formation of free Ag, in addition to the alloy phase. Heating at higher temperatures caused more intensive oxidation of Pd and yielded fewer and smaller free Ag particles. The compositional reconstruction on surface was determined by the competition between selective oxidation of Pd and segregation of Ag [12]. In this paper, the change of driving forces for surface segregation and oxidation in the same $Pd_{70}Ag_{30}$ nanoparticles by surface modification was studied. The behaviors of segregation of Ag and oxidation of Pd in the surface modified alloy were examined and compared with those of unmodified sample.

2. Experimental

The alloy nanoparticles $Pd_{70}Ag_{30}$ were prepared by a chemical precipitation method [13]. $Pd(NO_3)_2$ and $AgNO_3$ were mixed at the atomic ratio of 70:30, and then reduced by formaldehyde in a basic environment. Since the reduction potentials of Pd and Ag are different in the solution, the composition within the as-prepared $Pd_{70}Ag_{30}$ alloy particles is inhomogeneous [14,15]. The average size of the particles was 8 nm [13–15]. The alloy particles were then surface modified with 1 wt% of stearic acid (SA) with a chemical formula $CH_3(CH_2)_{16}COOH$ (Merck Co.) and polyethylene glycol (PEG) with a formula $H(OCH_2CH_2)_nOH$ (Showa Chemical Co.) and a molecular weight near 200 g/mol. The modified samples are named $Pd_{70}Ag_{30}$-s and $Pd_{70}Ag_{30}$-p, respectively.

The nanoparticles were then pressed as pellets and heated in air at 250–350 °C for 1 h. The heating rate was 10 °C/min. The phase structure of the nanoparticles after heating was examined by X-ray diffraction (XRD, Rigaku) with a Cu Kα source. The surface morphology of the pellets was examined by field emission scanning electron microscopy (FESEM, JEOL JSM-6500F). Electron spectroscopy for chemical analysis (ESCA, Physical Electronics PHI 1600) equipped with a dual (Al/Mg) anode X-ray source and a spherical capacitor analyzer was used to study the surface composition of the alloy nanoparticles.

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X-ray absorption near edge spectrum (XANES) was measured on the BL15B Tender X-ray beamline at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The L3-edges of Pd and Ag were obtained in a fluorescence mode to determine the surface-enriched component in the alloy pellets.

3. Results and discussion

Fig. 1 shows the FESEM micrographs of the three pellet samples after heating at 250 °C. As seen in Fig. 1(a), many white particles on the surface are observed for the unmodified sample. As reported previously, these white particles are all pure Ag [12]. For $Pd_{70}Ag_{30}$-s, fewer and smaller particles of Ag are present in Fig. 1(b). On the contrary, the surface is smoother and is basically free of such individual particles for $Pd_{70}Ag_{30}$-p in Fig. 1(c).

Fig. 2 displays the XRD patterns of the three nanoparticle pellets after heating in air. For the unmodified nanoparticles heated at 250 °C, formation of palladium oxide and free Ag is observed, which results in a peak shift of the alloy phase. From the peak positions, the composition calculated by Vigard's law is approximately Pd:Ag = 44:56 [12]. The sharp peaks of Ag imply the extraction of Ag from the alloy due to the oxidation of Pd. Large crystallites of Ag are formed, which is consistent with the SEM observation, Fig. 1(a). This phenomenon has been discussed previously [12], and is similar to that in the Au–Cu alloy system where preferential oxidation of Cu results in a de-alloying phenomenon [10]. Compared to the strong and sharp Ag peaks in the pattern for unmodified $Pd_{70}Ag_{30}$ at 250 °C, the peaks for free Ag in $Pd_{70}Ag_{30}$-s are weaker and the size of Ag is smaller, implying relatively less oxidation of Pd, less de-alloying, and less sintering of Ag to form free Ag crystallites in this sample. On the other hand, much lower PdO is formed in the $Pd_{70}Ag_{30}$-p pellet, probably because active surface segregation of Ag inhibits the oxidation of Pd and prevents de-alloying. No split of the peaks in the pattern of $Pd_{70}Ag_{30}$-p suggests that the alloy nanoparticles remain as solid solution but with a gradient structure of Pd core/Ag shell. Therefore, the two surfactants have different effects on surface segregation of Ag and oxidation of Pd in the alloy nanoparticles.

When the unmodified $Pd_{70}Ag_{30}$ was heated from room temperature to 350 °C, the composition has different reconstruction due to more intensive oxidation of Pd. The oxidation of Pd becomes more dominant than the surface segregation of Ag. No or very little free Ag is observed, and because of depletion of Pd in the alloy particles, the peak positions of the alloy phase are shifted closer to those of Ag. For the modified samples heated at this temperature, most of the surfactants have desorbed or decomposed [15]. Therefore, the difference in XRD patterns

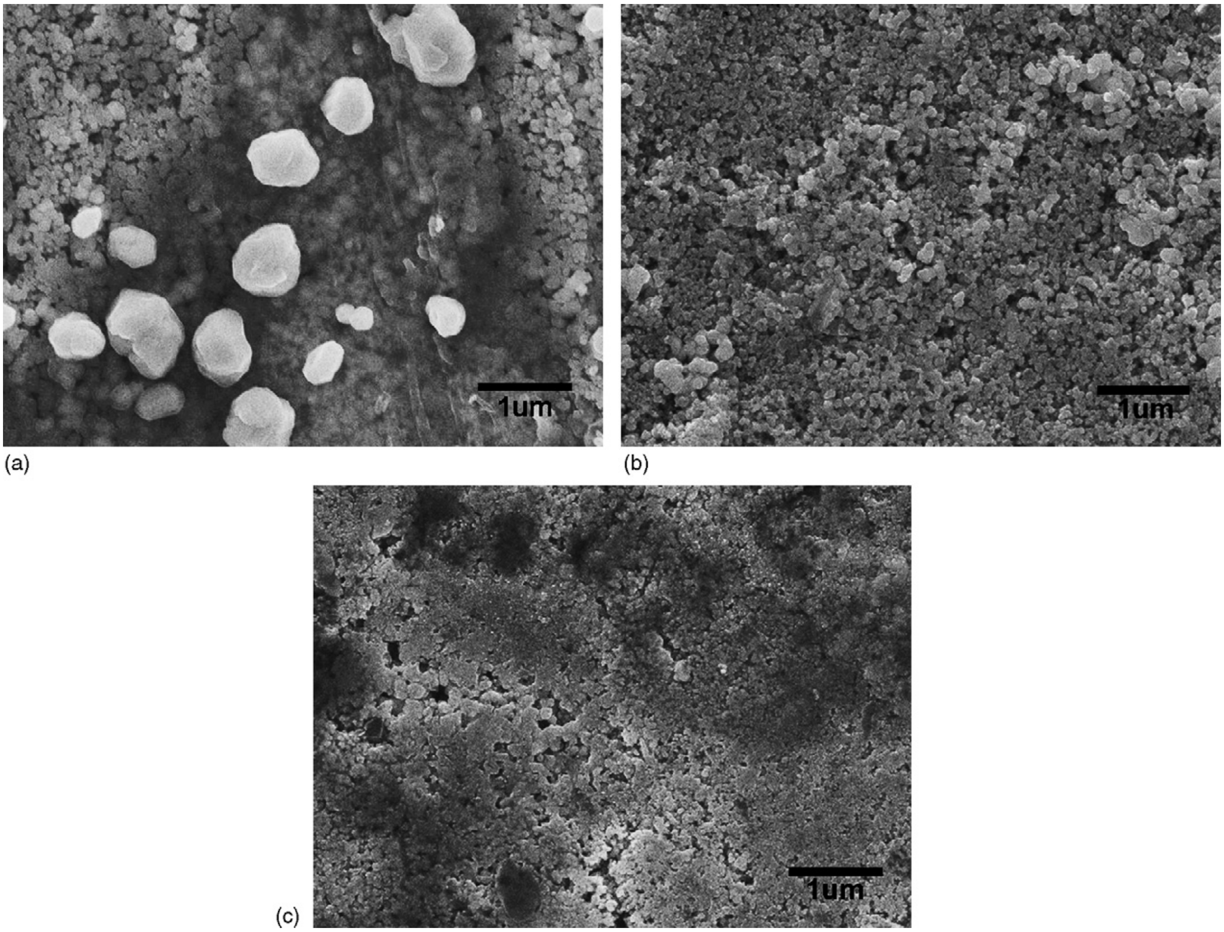

Fig. 1. SEM micrographs of three $Pd_{70}Ag_{30}$ nanoparticle pellets after heating in air at 250 °C: (a) $Pd_{70}Ag_{30}$, (b) $Pd_{70}Ag_{30}$-s, and (c) $Pd_{70}Ag_{30}$-p.

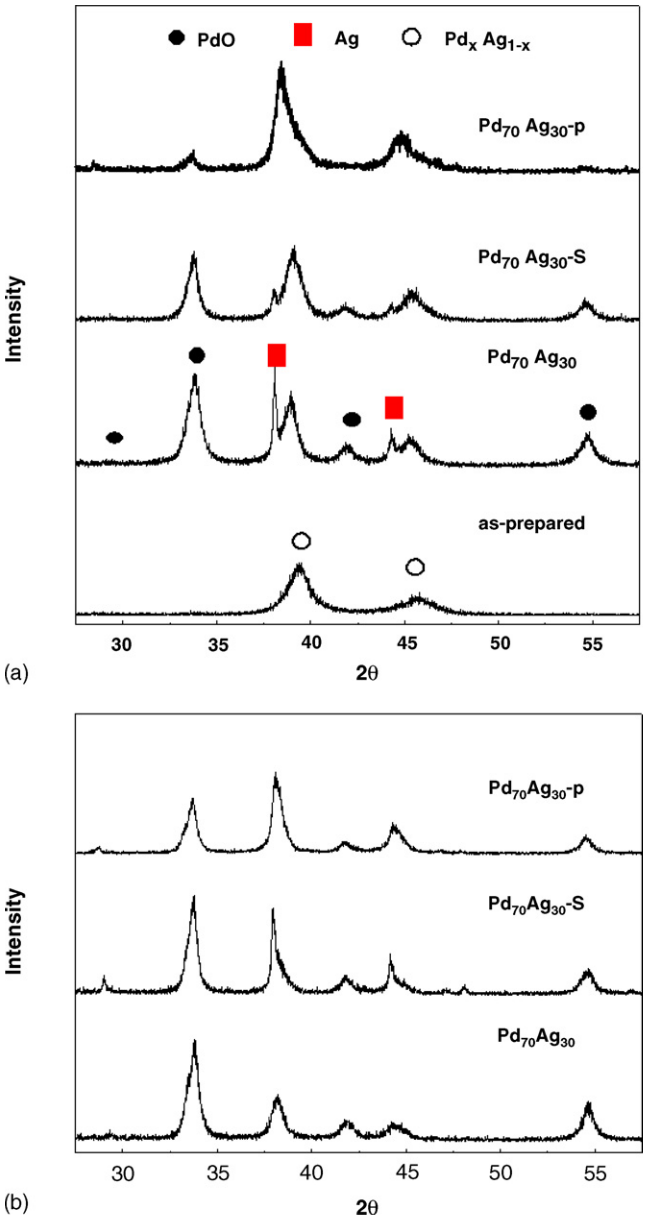

Fig. 2. XRD patterns of three $Pd_{70}Ag_{30}$ nanoparticle pellets after heating in air at different temperatures: (a) 250 °C and (b) 350 °C.

between modified and unmodified nanoparticles has become limited and smaller, and the peak positions of the alloy phase are all about the same except that there is relatively less PdO and more alloy phase in the $Pd_{70}Ag_{30}$-p sample. It is noted that the asymmetric peaks for the alloy phase in $Pd_{70}Ag_{30}$-s may be composed of two sets of peak, one from sharp free Ag and the other from broader alloy phase. This suggests that the PEG treatment is more persistent than the SA one.

Fig. 3 shows the surface compositions by ESCA analysis for various $Pd_{70}Ag_{30}$ samples, as prepared and after heating at 250 °C. For the as-prepared sample, the surface is Pd-rich because of the lower reduction potential of Pd in chemical precipitation [14,15]. The split of Pd peaks indicates that the surface Pd is partially oxidized at room temperature since oxygen is adsorbed by Pd. After heating to 250 °C, the surface Ag concentration is increased in all samples. For unmodified $Pd_{70}Ag_{30}$, the content of Ag (excluding the oxygen content) increases from 20.6 to 28.8 at%, and only oxide state of Pd is observed on the surface, due to oxidation of Pd at 250 °C. For $Pd_{70}Ag_{30}$-s, the increase of Ag is smaller (26.5 at%), and only Pd in oxide state is observed as well. For $Pd_{70}Ag_{30}$-p, however, the surface Ag has increased to 52.3 at%. In the meantime, both metallic and oxide states of Pd are present, with the metallic state more dominant. Therefore, surface modification by PEG has enabled more surface segregation of Ag and indirectly suppressed oxidation of Pd. Since no free Ag crystallites are observed from the SEM micrograph, the enrichment of Ag could occur near the surface within the alloy nanoparticles or yield a continuous layer on the very top surface of the pellet.

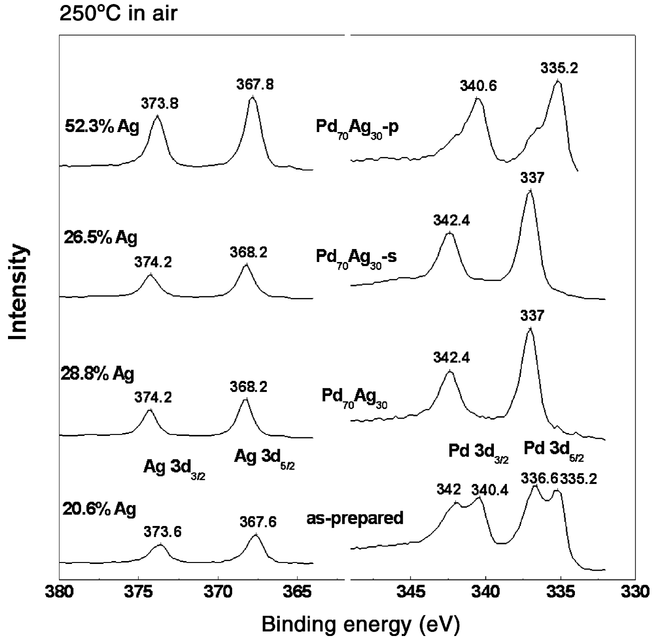

Fig. 3. The Ag ($3d_{3/2}$ and $3d_{5/2}$) and Pd ($3d_{3/2}$ and $3d_{5/2}$) peaks from ESCA analysis for various $Pd_{70}Ag_{30}$ samples before and after heating at 250 °C. The surface composition of Ag (excluding the oxygen content) in each sample is shown on the curve.

In Fig. 4, the L3 edges of Ag at 3351 eV in XANES spectra for the three samples heated to 250 °C are compared. The dramatic jump of the Ag edge for $Pd_{70}Ag_{30}$-p implies the remarkable enrichment of Ag on the pellet surface [16,17]. Note that Ag is easy to partially oxidize on the surface at room temperature. When it was analyzed by XANES at room temperature and ambient pressure, some Ag_xO could be detected in the spectrum, as seen from the Ag edges in Fig. 4. With moderate pre-sputtering under high vacuum in the ESCA analysis, no oxide was detected. In conjunction with the surface compositions analyzed by ESCA, the result of XANES tells that the significant surface enrichment of Ag in $Pd_{70}Ag_{30}$-p is on both the particle and pellet surface. According to these chemical composition analyses and the XRD patterns and SEM micrographs, both surface and bulk oxidations of Pd are inhibited by the modification, especially by PEG.

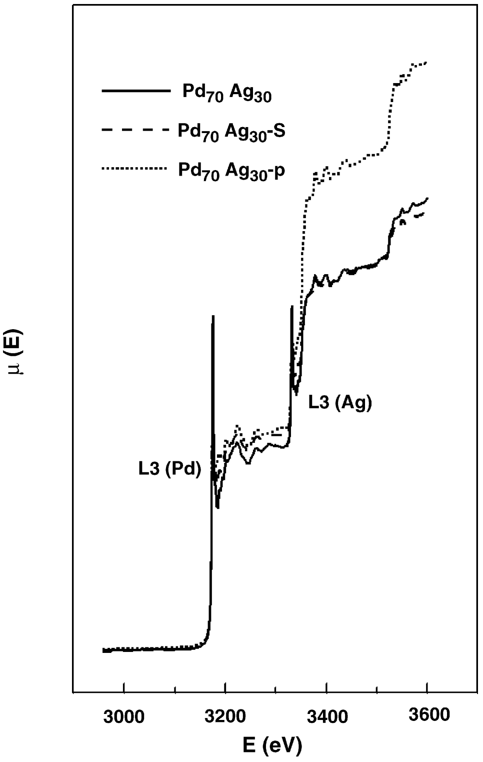

Fig. 4. XANES for the L3 edge of Ag in three $Pd_{70}Ag_{30}$ samples heated to 250 °C in air. The L3 edges for Pd and Ag are at 3173 and 3351eV, respectively.

4. Conclusion

In summary, this work demonstrates that the competition of surface segregation of Ag and oxidation of Pd in $Pd_{70}Ag_{30}$ alloy nanoparticles can be affected by surface modification. At 250 °C, de-alloying of Ag occurs in unmodified $Pd_{70}Ag_{30}$ because of preferential oxidation of Pd. This process is moderately suppressed by modification with SA. For $Pd_{70}Ag_{30}$-p nanoparticles, oxidation of Pd is much more suppressed. Ag is enriched on the nanoparticle surface, but no free Ag is formed on the pellet. The influence of surface modification is reduced when the surfactants are gradually desorbed or decomposed at 350 °C.

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