

Compositional Inhomogeneity of Pd₇₀Ag₃₀ Alloy Nanoparticles

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Abstract

The compositional inhomogeneity of Pd₇₀Ag₃₀ nanoparticles is studied. The composition of the as-prepared Pd₇₀Ag₃₀ nanoparticles by chemical reduction across the diameter is inhomogeneous due to different reduction potentials of Pd and Ag. During the heat treatment, Ag will migrate to the surface because of its lower surface energy. Surface modification can change the surface energy and composition during the oxidation and sintering processes. Surface modification of Pd₇₀Ag₃₀ nanoparticles by polyethylene glycol will decrease the surface energy of Ag and assist the diffusion of Ag from the core to the surface. This makes the nanoparticles easier to sinter together. Surface modification by stearic acid has the opposite effect and results in less sintering of the nanoparticles.

Keywords : Pd₇₀Ag₃₀, nanoparticle, surface modification, stearic acid, polyethylene glycol

1. Introduction

Previously, it was observed that the composition of as-prepared binary Pd-Ag nanoparticles by chemical reduction was not homogeneous [1]. Since the reduction potential of Ag is higher than that of Pd (0.34V vs 0.07V in alkaline solution), Ag will precipitate first and act as the nucleus for growth of the nanoparticles. During heat treatment, however, Ag may move to the surface since it has a lower surface energy ($\gamma_{Ag} = 930 \text{ erg/cm}^2$ and $\gamma_{Pd} = 1500 \text{ erg/cm}^2$). Therefore, the surface composition of Pd-Ag nanoparticles can be affected by the heating condition and is shifted from the nominal stoichiometry.

Surface modification is one of the methods to control the surface properties of nanomaterials [2-4]. It includes changing or meliorating dispersion of nanoparticles, decreasing or increasing chemical activity of particle surfaces, coating of a layer of second phase material, etc. One of the most common surface modification methods is to cover a layer of surfactant on the nanoparticle surface to prevent the particles from agglomeration and to increase the dispersion because of changing the surface energy of the

particles [5].

In this study, the compositional inhomogeneity of Pd₇₀Ag₃₀ nanoparticles with and without surface modification is examined. Two chemicals are used to modify the nanoparticles, one is stearic acid that has a chemical formula $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ and the other is polyethylene glycol (PEG) that has a formula $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ and a molecular weight near 200 g/mol.

2. Experimental

Nanocrystalline Pd₇₀Ag₃₀ powder was prepared by a chemical precipitation method, as described previously [6]. The average particle size of Pd₇₀Ag₃₀ was about 10 nm. Solutions of SA and PEG were prepared and 1 wt % SA or PEG was added to the nanoparticles to form a thin layer on the surface. The modified samples are named Pd₇₀Ag₃₀-sa and Pd₇₀Ag₃₀-p, respectively.

The phase structure and composition of the nanoparticles were examined by X-ray diffraction (XRD). The weight variation during heating was analyzed by thermogravimetric/differential thermal analyzer (TG/DTA). The nanoparticles were pressed as a pellet and tested by thermomechanical analyzer (TMA) to monitor the dimensional change during heating. The surface morphologies after heating were examined by scanning electron microscopy (SEM), and the size and weight of the pellets before and after heat treatment were also measured. The L3 edge jump of Ag at 3351 eV in X-ray absorption near edge spectrum (XANES) and electron spectroscopy for chemical analysis (ESCA) were used to study the surface compositions of the binary nanoparticles under different modifications and heatings.

3. Results and Discussion

The TG curves of Pd₇₀Ag₃₀, Pd₇₀Ag₃₀-sa, and Pd₇₀Ag₃₀-p are plotted in Fig. 1. According to the previous report, the weight gain below 440°C is due to oxidation and the weight loss above 440°C is caused by reduction of Pd [6, 7]. From Fig. 1, the weight gain of Pd₇₀Ag₃₀-p is twice as much as that of Pd₇₀Ag₃₀ and fourfold of that of Pd₇₀Ag₃₀-sa. Initially, oxidation occurs in Pd₇₀Ag₃₀ nanoparticles to

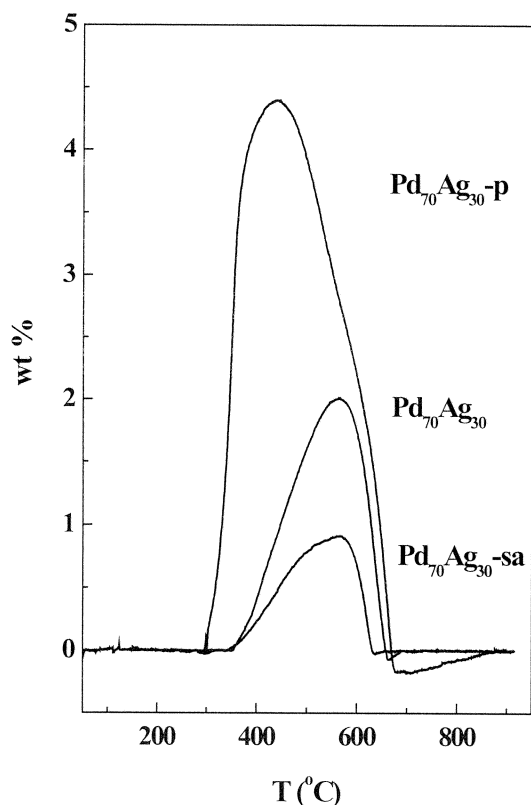


Fig. 1 TG curves for Pd₇₀Ag₃₀ with various surface conditions.

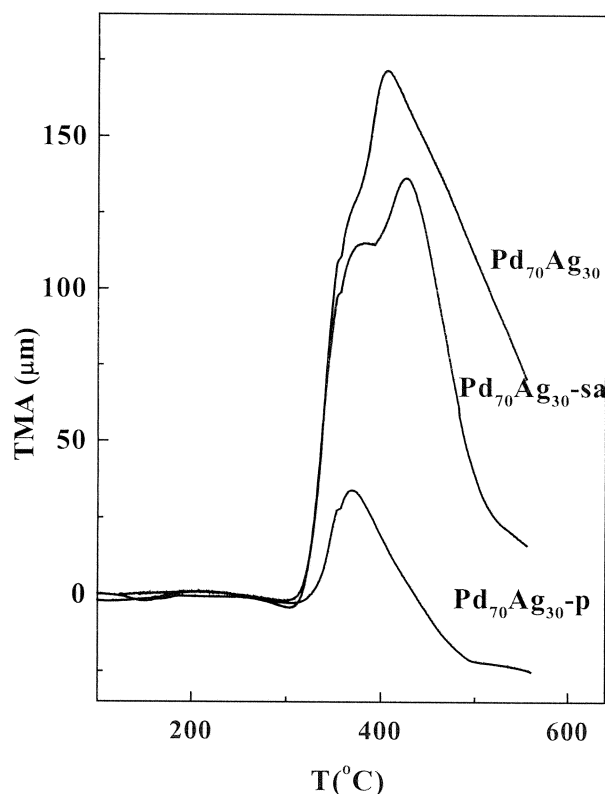


Fig. 2 TMA curves for Pd₇₀Ag₃₀ with various surface conditions.

decrease the surface energy [7]. For Pd₇₀Ag₃₀-sa, as it is covered by SA, oxidation is reduced. SA not only decreases the tendency for oxidation but also prevents the particle surface from exposure to O₂. For Pd₇₀Ag₃₀-p, PEG seems to accelerate the oxidation of Pd. The thermal stability of PEG is lower than that of SA. When it is heated in vacuum, it starts to decompose at lower temperature and will provide oxygen for Pd oxidation. The larger weight gain of Pd₇₀Ag₃₀-p is due to serious oxidation of Pd. Therefore, the surface modification results in various chemical properties of the Pd₇₀Ag₃₀ nanoparticles.

Fig. 2 shows the TMA curves for the three samples. As the temperature increases, the samples not only gain some weight because of the oxidation of Pd, but also exhibit dimensional expansion or shrinkage from oxidation and sintering. In Fig. 3, the sintering parameters ϕ are displayed for the three samples. The parameter ϕ is defined as $(\rho_s - \rho_g) / (\rho_t - \rho_g)$, where ρ_s , ρ_g , and ρ_t are sinter density, green density, and theoretical density, respectively. It is seen that Pd₇₀Ag₃₀-p sinters better than the other two samples. The expansion from serious oxidation of Pd₇₀Ag₃₀-p is compensated by the shrinkage of sintering, therefore it shows smaller dimensional change. A net shrinkage is observed at above 450°C. The TMA results and sintering parameters of Pd₇₀Ag₃₀ and Pd₇₀Ag₃₀-sa follow the same trends of the TG curves because SA covers and protects the surface from

sintering.

The XRD patterns and SEM micrographs of the nanoparticles sintered in vacuum at 450°C are shown in Figs. 4 and 5, respectively. Although there is grain growth in Pd₇₀Ag₃₀-sa, SA can retard the sintering of Pd₇₀Ag₃₀ nanoparticles and keep the particles in the nanoscale. PEG has the opposite effect for the Pd₇₀Ag₃₀ nanoparticles. It accelerates the oxidation and sintering of the nanoparticles. According to the ESCA and XANES results in Figs. 6 and 7, respectively, the surface composition of Pd₇₀Ag₃₀-p is very much enriched with Ag. There is almost 70 at % of Ag on the particle surface after heating to 450°C. The L3 edge of Ag in the XANES spectrum also shows that it is enriched with Ag on the surface of Pd₇₀Ag₃₀-p nanoparticles because the edge jump of Ag is dramatically increased.

Based on the above results, it is straightforward to understand why Pd₇₀Ag₃₀-p sinters better than the other two samples. The melting point of Ag (962°C) is lower than that of Pd (1552°C), so the particles enriched with Ag will sinter more easily. Since PEG decreases the surface energy of Ag, it helps Ag atoms to migrate from the interior to the particle surface, and therefore results in more sintering of Pd₇₀Ag₃₀-p than the other two nanoparticles. On the contrary, SA on the surface helps to retard the sintering of the nanoparticles in vacuum.

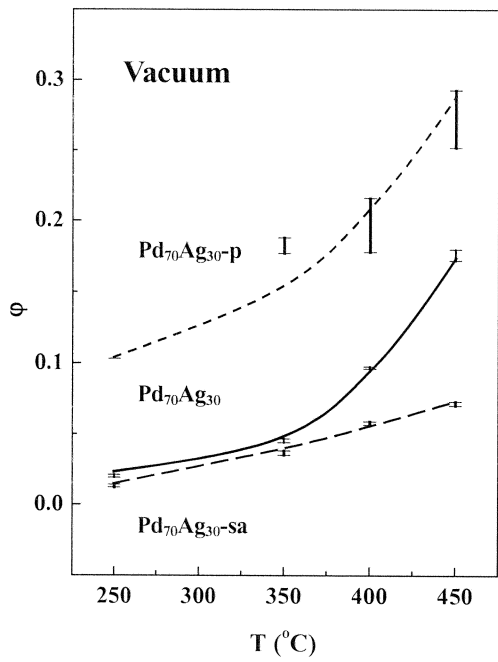


Fig. 3 Sintering curves for Pd₇₀Ag₃₀ with various surface conditions in vacuum.

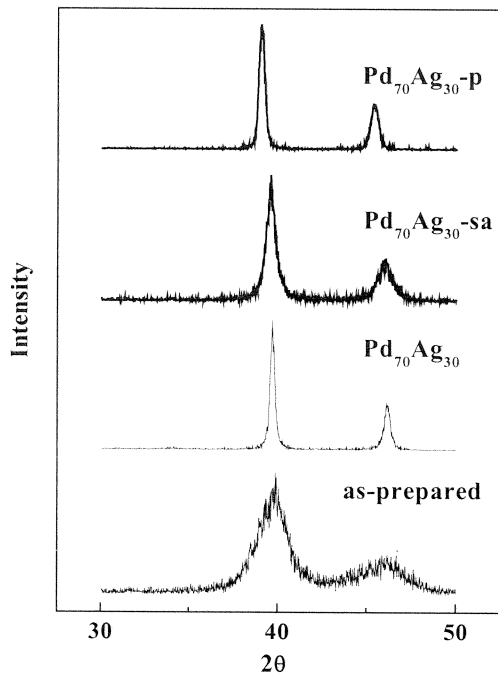
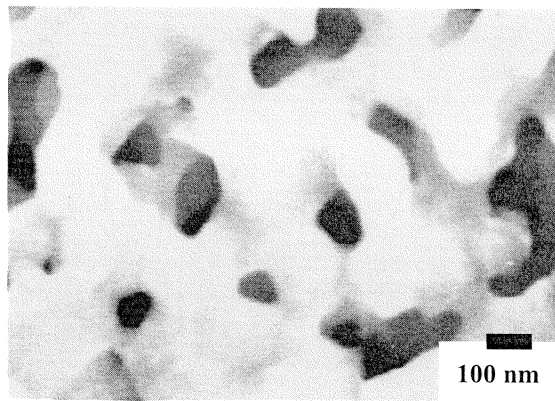
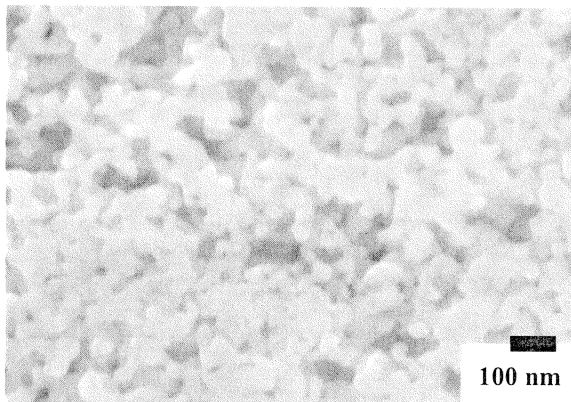


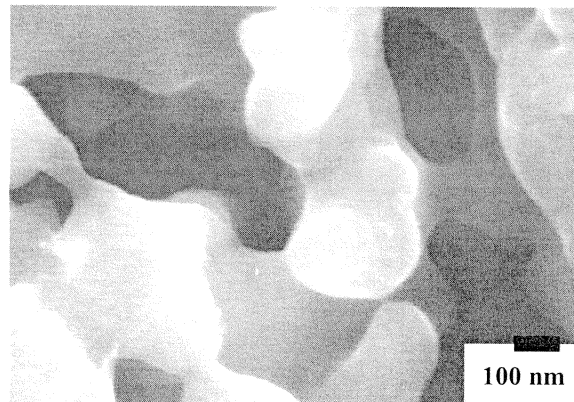
Fig.4 XRD patterns of Pd₇₀Ag₃₀ with various surface conditions sintered at 450°C in vacuum.



(a)



(b)



(c)

Fig.5 SEM morphologies of various Pd₇₀Ag₃₀ samples sintered at 450°C in vacuum. (a) Pd₇₀Ag₃₀, (b) Pd₇₀Ag₃₀-sa, and (c) Pd₇₀Ag₃₀-p.

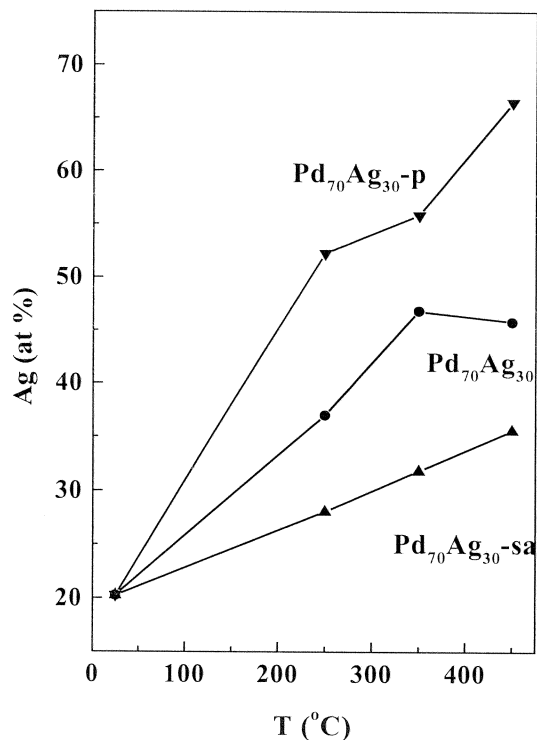


Fig.6 Surface compositions by ESCA analysis for Pd₇₀Ag₃₀ samples heated to different temperatures in vacuum.

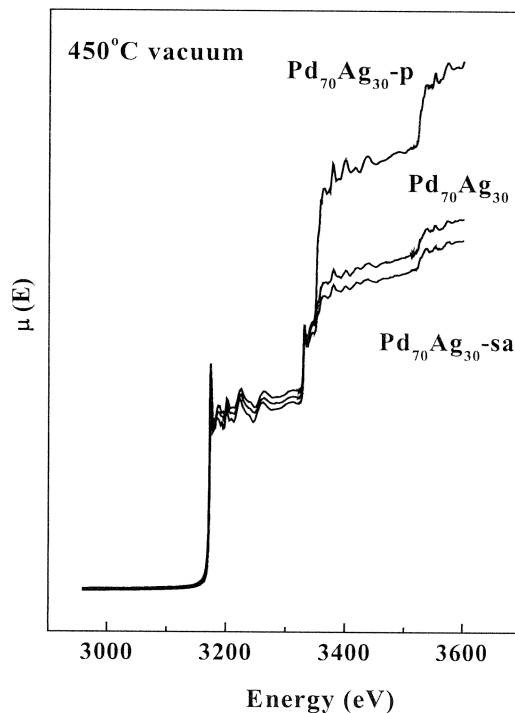


Fig.7 X-ray absorption near edge spectra of Pd₇₀Ag₃₀ samples heated to 450°C in vacuum.

4. Conclusion

Surface modification by surfactants can change the surface energy and thus changing the sintering properties of nanoparticles. The two surfactants used here have totally different effects on the nanoparticles. PEG lowers the surface energy of Ag and makes the particles to sinter more easily. It also accelerates the oxidation of Pd because it is an oxygen source when it decomposes. SA is more stable than PEG and protects the nanoparticles from sintering and oxidation.

5. Acknowledgement

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References

- [1] H. C. Chu, S. R. Sheen, C. T. Yeh, and T. P. Perng, *J. Alloys Comp.*, 322, 198 (2001).
- [2] P. Milani, M. Ferretti, A. Parisini, C. E. Bottani, M. A. Malvezzi, and A. Cavalleri, *Carbon*, 36, 5 (1998).
- [3] A. Meier, I. Uhlendorf, and D. Meissner, *Electrochimica Acta*, 40, 10 (1995).
- [4] L. Yang and P. Alexandridis, *Curr. Opin. Colloid Interface Sci.*, 5, 132 (2000).
- [5] S. F. Lomayeva, E. P. Yelsukov, G. N. Konygin, G. A. Dorofeev, V. I. Povstugar, S. S. Mikhailova, A. V. Zagainov, and A. N. Maratkanova, *Colloid Surf*, 162, 279 (1999).
- [6] C. U. Huang, H. J. Chiang, J. C. Huang, and S. R. Sheen, *NanoStruct. Mater.*, 10, 1393 (1998).
- [7] C. W. Chou, S. J. Chu, H. J. Chiang, C. Y. Huang, C. J. Lee, S. R. Sheen, T. P. Perng, and C. T. Yeh, *J. Phys. Chem., B*, 105, 9113 (2001).