

Desorption of Surfactant and Sintering of Surface Modified Pd_xNi_{1-x} Nanoparticles

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ABSTRACT

The desorption of surfactant and sintering of surface modified Pd_xNi_{1-x} nanoparticles are studied. The surface energy of the nanoparticles depends on the composition and is related to the desorption temperature of surfactant from the nanoparticle surface. For the alloys with higher Ni content, the surface energy is higher and the desorption temperature of surfactant is also higher. With the same composition, the desorption temperature of stearic acid (SA) is always higher than that of polyethylene glycol (PEG) because SA has a higher thermal resistance. After surface modification, the surface energy of the nanoparticles is changed. During heating, the more stable nanoparticles have less sintering and grain growth. Surface modification not only changes the surface energy of the nanoparticles but also prevents the nanoparticles from sintering. SA has better thermal resistance than PEG and shows better suppressing of sintering of the nanoparticles.

Keywords : PdNi, desorption, TPD, surface modification, sintering

1. INTRODUCTION

Nanostructure materials are very attractive because of their large surface area and surface energy [1]. By controlling the surface area or surface energy, the properties of nanomaterials can be manipulated. 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 grain growth during sintering [2], or to increase the dispersibility because of changing of the surface energy [3]. Therefore, surface modification is often used to change the surface energy and in the mean time to control the properties of nanomaterials [4-10].

In this study, a series of the Pd_xNi_{1-x} alloy nanoparticles were prepared. Because Ni and Pd have different surface energy, the surface energies of particles with different compositions are different. The nanoparticles are modified with two surfactants, stearic acid (SA) with a chemical formula CH₃(CH₂)₁₆COOH and polyethylene glycol (PEG) with a formula H(OCH₂CH₂)_nOH. The desorption temperature of the surfactants were

measured and related to the properties of the materials, such as surface compositions and sintering behavior [12-15].

2. EXPERIMENTAL PROCEDURE

A series of Pd_xNi_{1-x} nanoparticles were prepared by a chemical precipitation method. Solutions of palladium nitrate and nickel nitrate were mixed at desired stoichiometries 80:20, 70:30, 30:70 and 20:80, and then reduced by sodium borohydride in an alkaline environment. The average particle size 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 particle surface. The samples modified by SA or PEG are named as Pd_xNi_{1-x}-s and Pd_xNi_{1-x}-p, respectively.

The phase structure and composition of the nanoparticles were examined by X-ray diffraction (XRD). The weight variation of surfactants during heating was analyzed by thermogravimetric/differential thermal analyzer (TG/DTA). Temperature programmed desorption (TPD) was used to examine the desorption temperature of SA or PEG from the Pd_xNi_{1-x} nanoparticles of different compositions. The heating rate was 0.5K/s. The surface morphologies before and 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.

3. RESULTS AND DISCUSSION

The XRD patterns of four Pd_xNi_{1-x} nanoparticles are shown in Fig. 1. The Pd-Ni nanoparticles all form alloys and the particle sizes are all about 10 nm.

The thermal stabilities of the surfactants used in this experiment, SA and PEG, were analyzed by TG. The curves of weight variation during heating are shown in Fig. 2. The decomposition temperature of PEG is lower than that of SA. It starts to decompose at about 100°C, and the slope becomes more rapid at above 170 °C. PEG has almost decomposed at above 270 °C, with less than 1.1 % of residue. SA has a higher decomposition temperature, being at about 140 °C. Above 300 °C, there is still 10 % of residue. As their molecular weights imply, the molecular weight of PEG (200 g/mole) is less than that of SA (284 g/mole), SA is expected to have a higher thermal stability

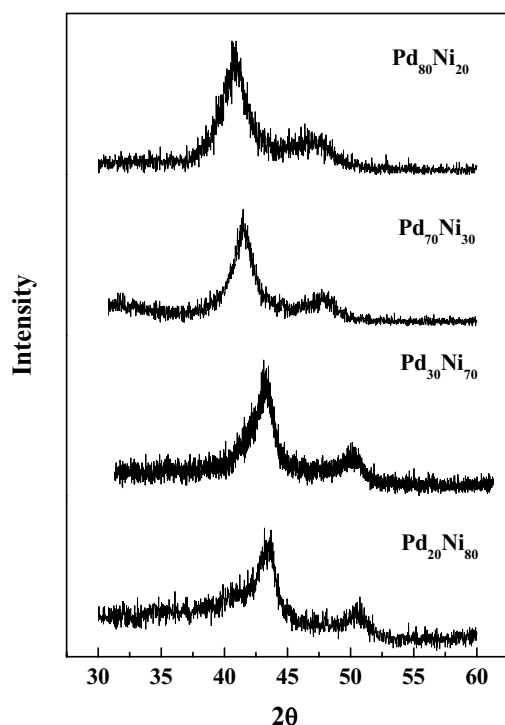


Fig. 1 XRD patterns of Pd_xNi_{1-x} nanoparticles.

than PEG.

The desorption curves of SA from the nanoparticles by the TPD measurement are described in Fig. 3. According to the mass spectrum in NIST handbook for mass 43, the strongest desorption peak, is used to identify the desorption of SA. The peak position in TPD is defined as the desorption temperature of SA ($T_d(\text{SA})$). In the TPD results of Pd₂₀Ni₈₀, the lower temperature peak at 133 °C is the decomposition or evaporation temperature of free SA. Their temperature is consistent with that from the TGA in Fig. 2. The higher temperature peak indicates the desorption of SA from the nanoparticles. As the Ni content increases, the $T_d(\text{SA})$ increases. Because the surface energy of Ni is higher than that of Pd (2.45 J/m² for Ni and 2.05 J/m² for Pd) [11], more Ni means a higher surface energy. There is more interaction between the surfactant and the nanoparticle. During desorption, it takes more energy and therefore higher temperature, for SA to leave from the nanoparticle surface. The influence of surface energy is so important that the $T_d(\text{SA})$ is changed from 240 to 394 °C when the Ni content is increased from 20% to 80%. Therefore, the composition or surface energy is a function of desorption temperature.

For the desorption of PEG, the results are similar. The decomposition temperature of free PEG in Pd₂₀Ni₈₀ is 105 °C.

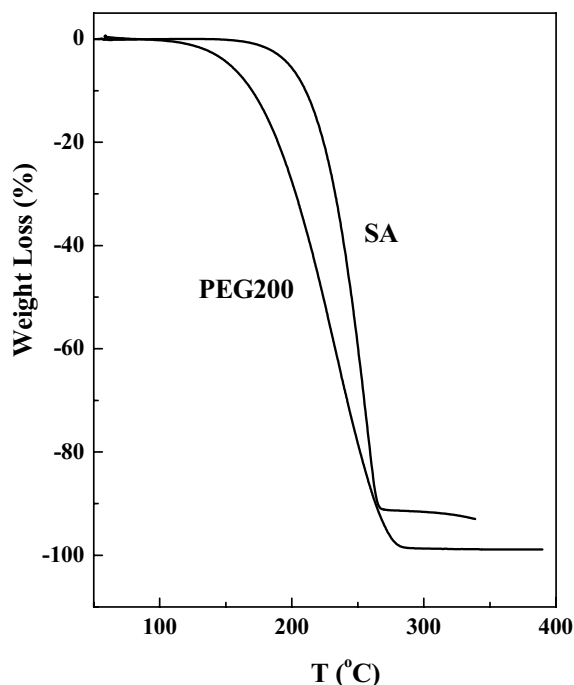


Fig. 2 TG analysis of PEG and SA.

The $T_d(\text{PEG})$ also increases as the Ni content increases, and is changed from 197 to 377 °C as the Ni content increases from 20% to 80%. The comparison of the $T_d(\text{SA})$ and $T_d(\text{PEG})$ for the samples is shown in Fig. 4. The $T_d(\text{PEG})$ is always lower than $T_d(\text{SA})$ for the same composition. This indicates that PEG on the surface has lower thermal resistance than SA. This property could affect the sintering behavior of surface modified nanoparticles.

In Fig. 5, the sintering parameters ϕ is displayed for the three Pd₇₀Ni₃₀ samples. This Pd₇₀Ni₃₀ composition is chosen to study the sintering properties of surface modified nanoparticles. 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. For all three samples, ϕ increases as temperature increases. The as-prepared Pd₇₀Ni₃₀ sample sinters better than the surface modified samples because it has a higher surface energy and the surface is less stable. SA has a greater thermal resistance than PEG. The surface energy of the nanoparticles is lowered more, and the sintering of nanoparticles is more retarded. This result is coincided with those from TPD and TG. In the TG analysis, at the same temperature, there is more residual SA on the nanoparticle surface to protect the nanoparticles from sintering.

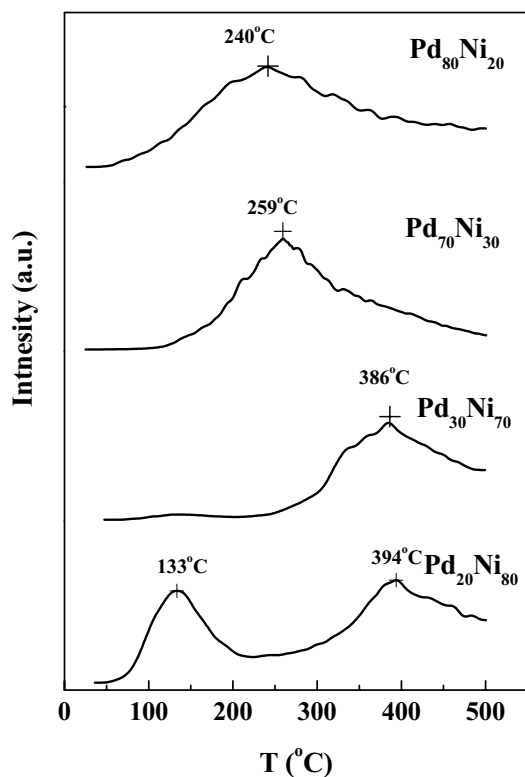


Fig. 3 TPD curves of SA from the $\text{Pd}_x\text{Ni}_{1-x}$ nanoparticles.

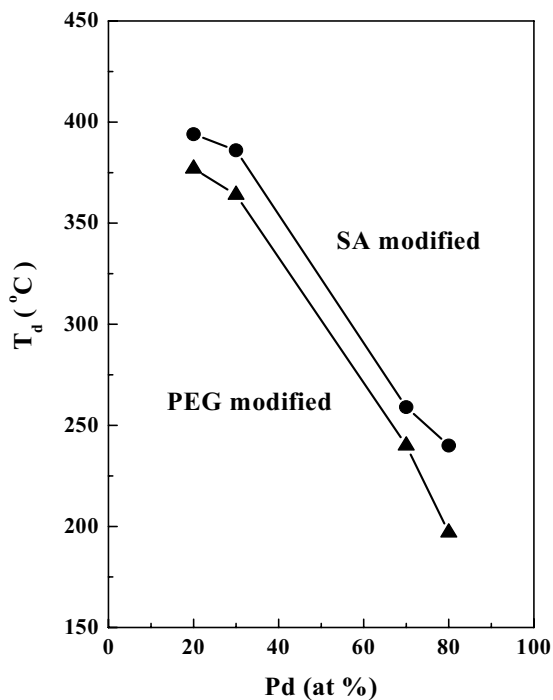


Fig. 4 Desorption temperatures of SA and PEG for the nanoparticles with various contents of Pd.

The SEM micrographs of the $\text{Pd}_{70}\text{Ni}_{30}$ nanoparticles sintered in vacuum at 450°C are shown in Fig. 6. The unmodified sample is well sintered together. Substantial growth of particles is observed. Sintering of the $\text{Pd}_{70}\text{Ni}_{30}\text{-p}$ sample is somewhat suppressed because of the presence of PEG. The sample $\text{Pd}_{70}\text{Ni}_{30}\text{-s}$ almost remains unsintered. $\text{Pd}_{70}\text{Ni}_{30}\text{-s}$ also has smaller particle size, only 40 nm, followed by 100 nm of $\text{Pd}_{70}\text{Ni}_{30}\text{-p}$ and several hundred nanometers of $\text{Pd}_{70}\text{Ni}_{30}$,

4. CONCLUSION

The surface energy of the modified nanoparticles is a function of desorption temperature of the surfactant from the nanoparticle surface. The desorption temperature increases as the Ni content increases. Surface modification by surfactant can change the surface energy and thus changing the sintering behavior of nanoparticles. SA, which has better thermal resistance and higher desorption temperature than PEG, has a higher ability to retard the nanoparticles from sintering and to suppress grain growth.

5. ACKNOWLEDGEMENT

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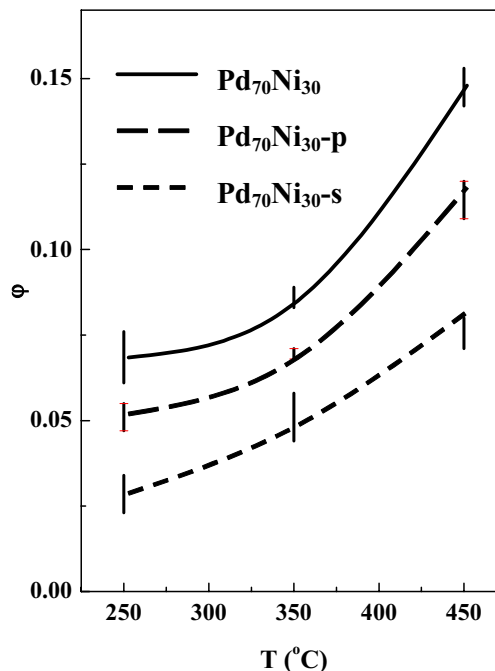
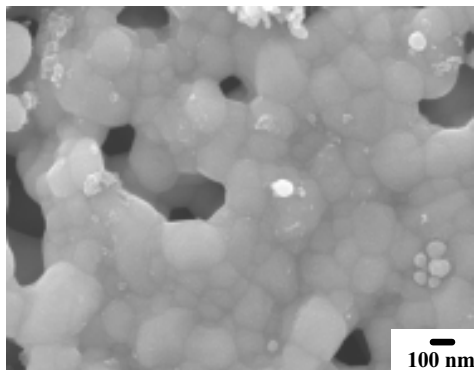
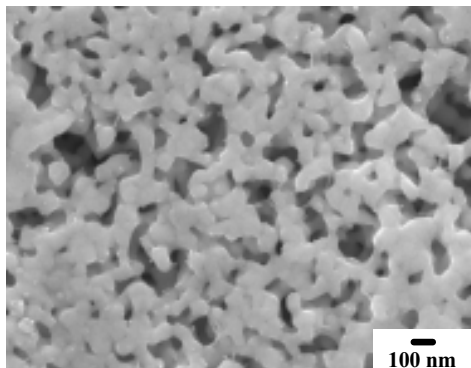


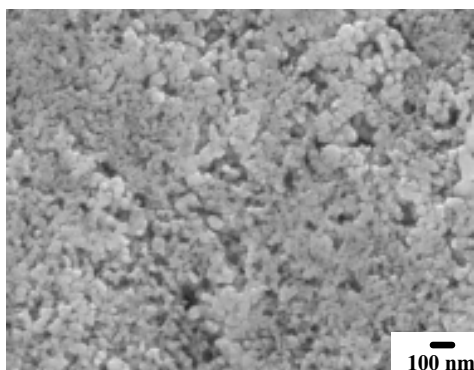
Fig. 5 Sintering curves in vacuum for $\text{Pd}_{70}\text{Ni}_{30}$ with various surface conditions.



(a)



(b)



(c)

Fig. 6 SEM morphologies of various Pd₇₀Ni₃₀ samples sintered at 450°C in vacuum. (a) Pd₇₀Ni₃₀, (b) Pd₇₀Ni₃₀-P, and (c) Pd₇₀Ni₃₀-s.

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