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Letter

Synthesis conditions in tailoring morphology of reticular particles in porous nickel powders prepared by template-assisted polyol process

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ABSTRACT

Porous nickel powders having reticular structure were synthesized with polyvinylpyrrolidone (PVP) as a soft template through a polyol process. PVP addition brought structural change of nickel particles from agglomerates to interconnected particle network. Surface morphology of the particles was changed from prickly to smooth structure with increasing reaction temperature and was also dependent on PVP polymerization degree. The reticular structure formed above a certain level of Ni concentration and neck region of the interconnected particles became thicker at higher Ni concentration. The porosity of the powders increased with increasing PVP content and was saturated at a certain amount of PVP, which is required to obtain a maximum porosity of the powders.

1. Introduction

Porous materials have attracted much interest because of their potential applications [1–3]. Especially, porous nickel powders have been widely investigated because they provide a degree of chemical activity such as a catalyst or adsorption surface for molecular storage and engineering. Their excellent properties lead to unique opportunities in multi-functional applications such as electrodes for molten carbonate fuel cell (MCFC), rechargeable lithium batteries, etc. [4]. Recently, high aspect, sub-micron and nanoscale, filamentary nickel powders, known commercially as Nanostrands^{TM}, fabricated by atmospheric pressure chemical vapor deposition process were introduced for many potential applications including filler materials for electrical conductive polymer/metal composites [5].

Generally, nickel powders can be prepared via vapor phase method, spray pyrolysis, chemical solution routes, etc. [6–10]. Among these methods, the chemical solution process is a cost-effective and promising approach for large-scale production and control of structure and morphology of the particles [11,12]. Recently, some polyol processes have been used to prepare metal powders with porous nanostructure [13,14]. However, there have been few works on synthesis conditions in tailoring morphology of particles in porous nickel powders prepared by template-assisted polyol process.

Particles with rough surface are suitable for catalytic applications because of their high surface area and powders with reticular structure are preferable for applications requiring high porosity such as electrodes of MCFC and batteries. The filamentary particles having high aspect ratio are also a good candidate as filler materials for conductive polymer/metal composites because it can render high electrical conductivity by the addition of smaller fraction of the materials than particles having low aspect ratio such as spherical particles. Therefore, it is very important to control the morphology and microstructure such as particle size, pore structure, porosity, and surface morphology of the particles for practical applications.

In this work, we synthesized porous nickel powders having three-dimensional network structure by a polyol process with multi-functional ligand polyvinylpyrrolidone (PVP) as a template and investigated the effects of reaction temperature, nickel concentration, PVP content, and polymerization degree of PVP on morphology and surface structure of the nickel particles and porosity of the powders. We found there are strong effects of the process conditions on the particle morphologies and could synthesize filamentary nickel powders having various surface structures and microstructures of the particles. We also suggested a possible explanation for the effect of PVP template on the reticular structure formation of the nickel particles.

2. Experimental

All chemicals were of analytical grade. Nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) and PVP (average molecular weight, $M_w = 10{,}000$, 55,000, and 1,300,000) were received from Aldrich. 80% hydrazine monohydrate ($N_2H_4{\cdot}H_2O$; A.R.) solution and ethylene glycol were purchased from Junsei chemical. The water used throughout this study was deionized with purification system. The procedure for synthesis of the nickel powders is as follows: ethylene glycol (300 mL) was heated to reaction

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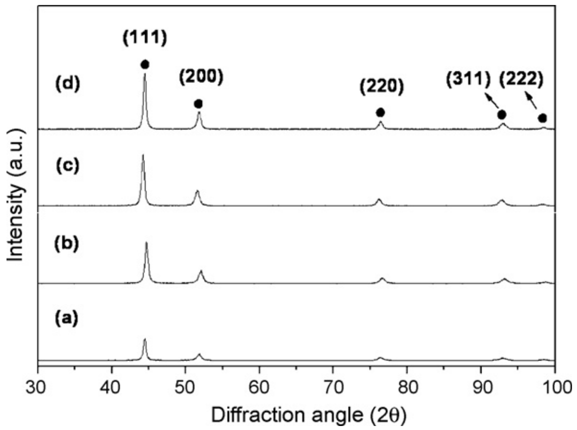

Fig. 1. X-ray diffraction patterns of nickel powders prepared at different reaction temperatures with 0.1 M PVP (M_w = 55,000): (a) 100 °C, (b) 135 °C, (c) 165 °C, and (d) 190 °C.

temperature (100–190 °C) and maintained for 10 min at the temperature. Hydrazine monohydrate (60 mL) adjusted to 50 vol.% was added slowly to the ethylene glycol and maintained for 10 min. Nickel chloride hexahydrate solution (150 mL) having molar concentration of 0.05–1.0 M and PVP solution (300 mL) having molar concentration of 0–0.5 M were mixed and added to the solution under magnetic stirring. Following reaction for 2 h, the solution with precipitates was centrifuged and rinsed with ethanol more than five times repeatedly. The residual ethanol was removed in vacuum oven maintained at 60 °C. X-ray diffraction (XRD) analysis of the samples was conducted using a Rigaku diffractometer with Ni-filtered Cu-K_α radiation. The morphology and microstructure of Ni particles were characterized by field emission scanning electron microscopy (FESEM; JEOL JSM-5400). The porosity of the powders was measured by mercury intrusion porosimeter (AutoPore IV 9510, Micromeritics).

3. Results and discussion

Fig. 1 shows XRD patterns of the Ni powders prepared at different reaction temperatures with Ni and PVP (M_w = 55,000) concentrations of 0.1 M. The XRD results represent a typical pattern of nickel crystal without any other peak from nickel oxides or precursor compounds and the peak intensity increased with increasing reaction temperature. This seems to be due to the effect of reaction temperature on the extent of crystallinity and grain size of the synthesized powders.

Fig. 2 shows SEM microstructures of the Ni powders and Fig. 2e and f are the magnified images of the particles synthesized at 100 °C and 190 °C showing the surface morphology of the particles, respectively. The nickel particles obtained at 100 °C had irregular particle shape with the prickly surface morphology. Nickel powders obtained at 190 °C, however, showed spherical particles with smooth particle surface.

The effect of Ni concentration on the morphology and pore structure of the porous nickel powders was also investigated. Figs. 3 and 2f show the shape change of the nickel particles synthesized with different Ni concentrations at 190 °C. The particles in the 0.05 M Ni sample did not form fully three-dimensional network, but interconnected structure mostly having one-dimensionally assembled particles (Fig. 3a). This means 0.05 M is not enough Ni concentration to generate three-dimensional reticulation of the particles. When increasing the Ni molar concentration to 0.1 M, the reticular structure started to form with weakly connected neck between the particles (Fig. 2f). With increasing the Ni concentration, the neck region became thicker and the neck of the particles was almost disappeared at the Ni concentration of 1.0 M (Fig. 3c). At high Ni concentration, residual Ni^{2+} ions can move to the neck region following the network formation of Ni particles because normally the neck is energetically favorable site for nucleation and growth of the particles.

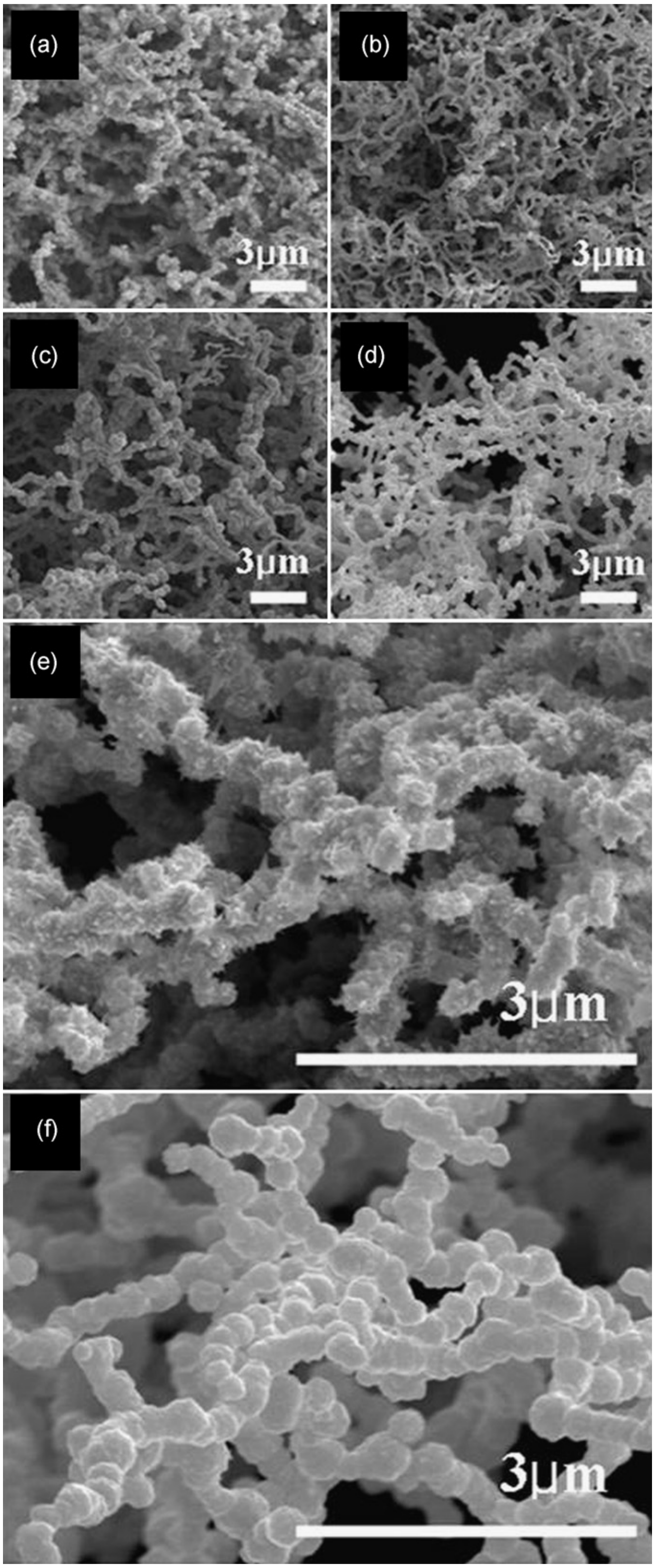

Fig. 2. SEM micrographs of Ni powders prepared at different reaction temperatures with 0.1 M PVP (M_w = 55,000): (a and e) 100 °C, (b) 135 °C, (c) 165 °C, and (d and f) 190 °C.

Effects of polymerization degree of PVP on particle morphology are shown in Figs. 4, 2d, and 2f. The powders were synthesized at 190 °C using Ni concentration of 0.1 M. The powders prepared using PVP with lower polymerization degree (M_w = 10,000 and 55,000) showed smooth particle surface with similar microstruc-

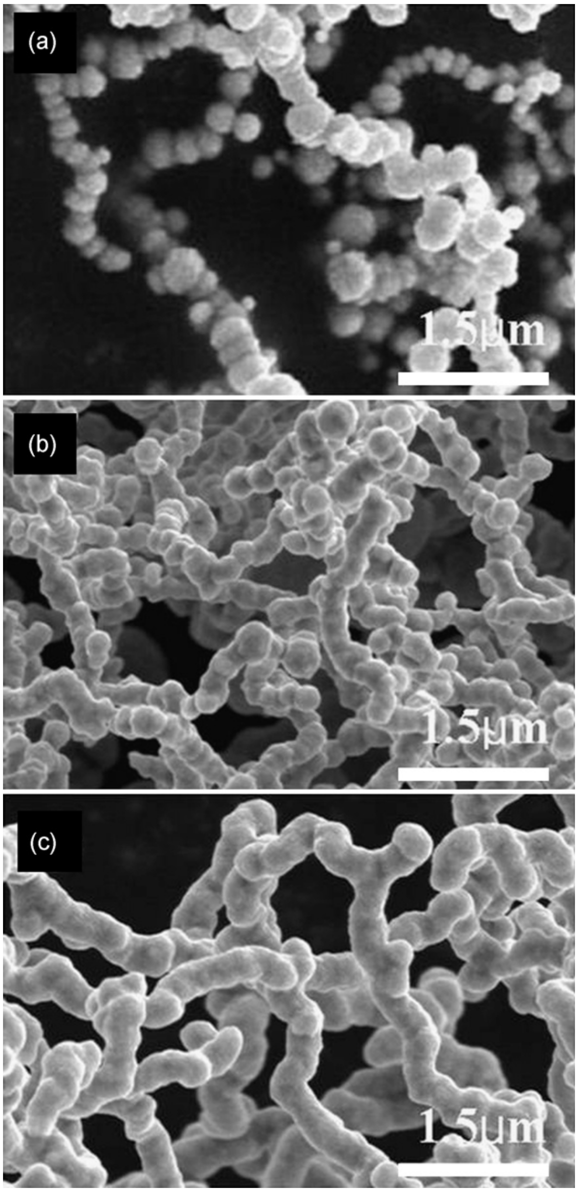

Fig. 3. SEM micrographs of Ni powders prepared with different Ni concentrations with 0.1 M PVP (M_w = 55,000): (a) 0.05 M, (b) 0.5 M, and (c) 1.0 M.

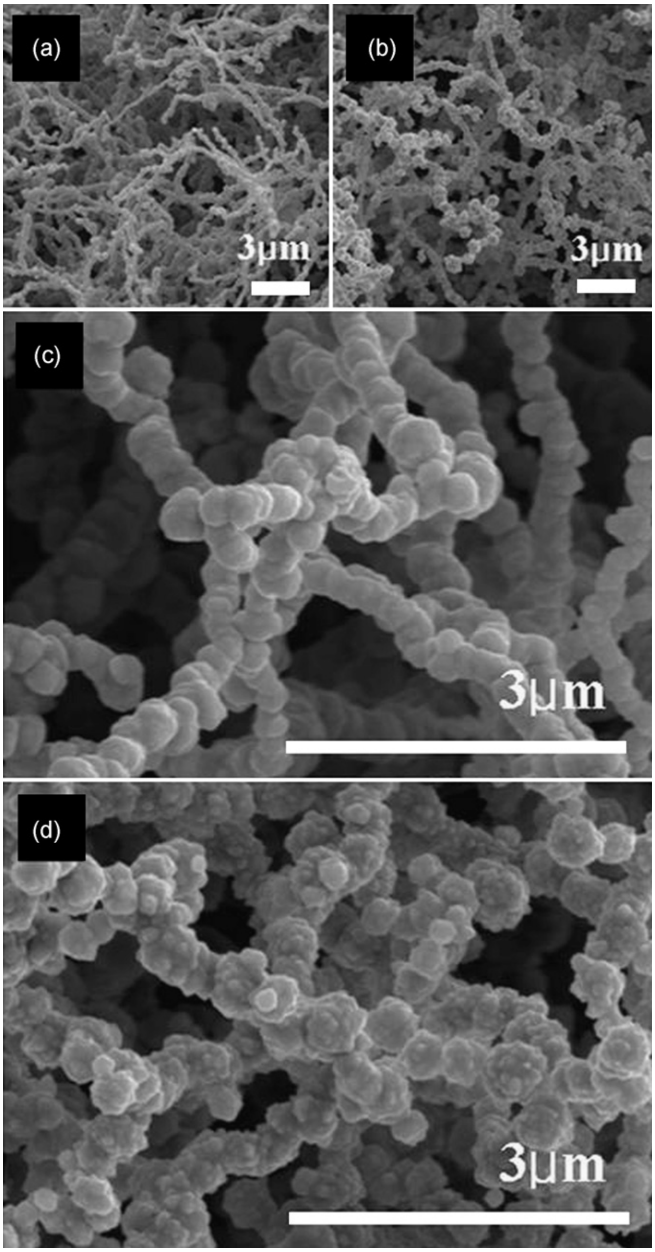

Fig. 4. SEM micrographs of Ni powders prepared with 0.1 M PVP having different polymerization degree: (a and c) M_w = 10,000 and (b and d) M_w = 1,300,000.

tures (Figs. 4c and 2f). The particles synthesized using PVP with higher polymerization degree (M_w = 1,300,000), however, showed rough surface with agglomeration of small particles (Fig. 4d).

Fig. 5 is an SEM microstructure of the Ni powder synthesized without the PVP template showing severe agglomeration of spherical particles. The Ni concentration and reaction temperature were 0.1 M and 190 °C, respectively. The size of the individual particle in Fig. 5 was similar to that in the powder synthesized with PVP shown in Fig. 2f. The powders without PVP, however, did not have any reticular structure of the particles. This indicates the PVP as a soft template strongly affects the formation of three-dimensional network structure.

Nickel nanoparticles are known to have a tendency to connect to each other by their magnetic dipole interaction [15]. Therefore, it is not easy to prepare isolated magnetic nanoparticles and the particles can be agglomerated easily (Fig. 5). The surface atoms of metal particles can coordinate with oxygen atoms in PVP, which means PVP can act as a soft template to form one-dimensional nanomaterials such as nanowires and nanorods. Gao

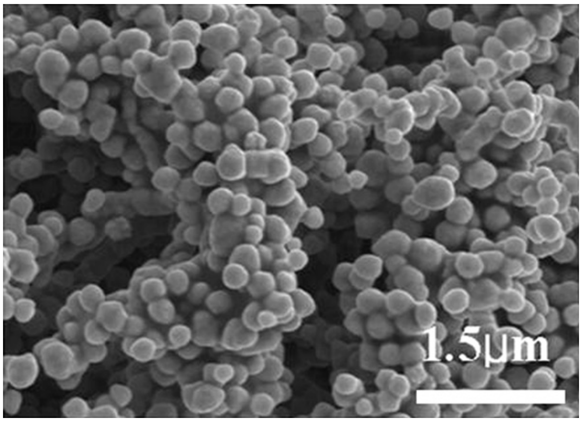

Fig. 5. SEM micrograph of Ni powder prepared without PVP addition.

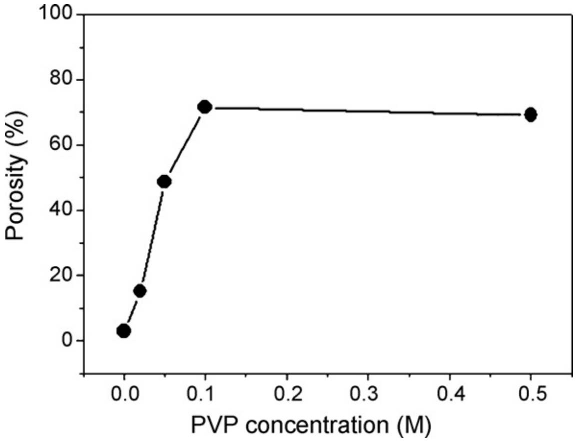

Fig. 6. Porosity of Ni powders prepared with different PVP (M_w = 55,000) concentrations.

et al. reported non-magnetic silver nanowires with linear shape could be synthesized through polyol process in the presence of PVP [16]. Therefore, the difference between the microstructures in Figs. 2f and 5 is thought to be ascribed to the combining effects of the magnetic interaction of nickel particles and preferential nucleation and growth with soft template. Thus, the nickel particles synthesized with PVP did not grow into one-dimensional linear structure, but formed three-dimensional network probably because of the combining effects.

As mentioned above, PVP plays an important role to make the reticular structure of the nickel particles. Therefore, the effect of PVP contents was also investigated. Fig. 6 shows porosity change of the powders prepared with different PVP concentrations (0–0.5 M) using 0.1 M Ni at 190 °C. The powder synthesized without PVP had very little pore volume in good agreement with the SEM results shown in Fig. 5. The porosity increased with adding more PVP and was saturated at 0.1 M. A certain amount of the template material, therefore, is required to obtain a maximum porosity of the powders.

4. Conclusions

The porous Ni powders with reticular structure were synthesized by the polyol process with polyvinylpyrrolidone (PVP) as a soft template. The addition of the PVP template in the process brought structural change of the particles from particle agglomerates to interconnected particle networks. The morphology of the porous Ni powders was strongly dependent on the reaction temperature, Ni concentration, and polymerization degree of PVP. The nickel powder obtained at 100 °C had irregular particle shape with the prickly surface morphology and the powder obtained at 190 °C showed interconnected structure of spherical particles with smooth particle surface. The reticular structure started to form with weakly connected neck at Ni molar concentration of 0.1 M. With increasing the Ni concentration, the neck region became thicker and the neck of the particles was almost disappeared at the Ni concentration of 1.0 M. The particles using PVP with higher polymerization degree (M_w = 1,300,000) showed rougher surface with agglomeration of small particles than those with lower polymerization degree (M_w = 10,000 and 55,000). The porosity increased with increasing PVP content and was saturated at a certain amount of PVP (0.1 M in this study) which is required to obtain a maximum porosity of the powders.

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