Effect of Reaction Conditions on the Preparation of Nano-sized Ni Powders inside a Nonionic Polymer

Tea Wan Kim[1, a], Dong-Hyun Kim[1, b], Hong Chae Park[1, c], and Seog-Young Yoon[1, d]

[1]School of Materials Science and Engineering, Pusan National University,
San 30, Jangjeon-Dong, Gumjeong-Ku, Busan, 609-735, Korea
[a]ktw27410@nate.com, [b]ding7412@hanmail.net,
[c]hcpark1@pusan.ac.kr, [d]syy3@pusan.ac.kr

Abstract

Monodispersed and nano-sized Ni powders were synthesized from aqueous nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$) inside nonionic polymer network by using wet chemical reduction process. The sucrose was used as a nonionic polymer network source. The effect of reaction conditions such as the amount of sucrose and a various reaction temperature, nickel sulfate hexahydrate molarity. The influence of a nonionic polymer network on the particle size of the prepared Ni powders was characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and particle size analysis (PSA). The results showed that the obtained Ni powders were strong by dependent of the reaction conditions. In particular, the Ni powders prepared inside a nonionic polymer network had smooth spherical shape and narrow particle size distribution.

Keywords : Nano-sized Ni powder, polymer network, wet chemical reduction, sucroses

1. Introduction

Increasing demands on fine metal powder materials have been brought forward in recent years from the viewpoints of chemical and physical interests, but their size, shape, and composition should require to be judiciously controlled to meet extensive applications in various fields, especially in the technology of advanced materials.[1] Many methods such as ball milling, electrodeposition, thermal plasma, polyol process, chemical vapor deposition, chemical reduction in aqueous solution and microwave-hydrothermal method have been applied to prepare fine metal powders.[2] However, most of these methods are not suitable for the massive production of fine metal powders due to the technical difficulties and the expensive equipments involved. One of the possible preparation methods is the chemical reduction of metal cations from the solution of metal salts with the strong reduction agent.

Recently, some groups [3] have become interested in the production of resin-stabilized metal nano particles based on the anchoring of suitable precursors, such as metal ions or complexes, to properly designed functional resins. Mild chemical reduction of these precursors inside the swollen polymer network produces metal atoms, which later agglomerate into metal nano particles. Consequently, the growth of the metal nano particles during reduction could become limited by steric restrictions imposed by the three dimensional polymer network, a possibility that would permit precise control of the metal nano particle size.

In this work the preparation of Ni powder by the principles of wet chemical reduction synthesis with and without sucrose as a polymer network matrix. In addition, the influences of the amount of sucrose and various of reaction temperature and diversity of the molarity on the morphology and particle size for the synthesized Ni powders will be investigated.

2. Experimental and Results

The starting materials were used nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$; Junsei Chemical Co.), sodium hydroxide (NaOH; Kanto Chemical Co., Ltd 97%) and commercial sucrose as a reactant, pH control agent and nonionic polymer network, respectively. Hydrazine hydrate ($N_2H_4 \cdot H_2O$; Junsei Chemical Co., Ltd 80%) was used as a reducing agent. An appropriate amount of nickel sulfate hexahydrate (0.36~1.24M) and NaOH (2.4M) were dissolved directly in distilled water with sucrose (0~0.05M). The resulting mixture was heated to (50~80℃) for 1h, and then hydrazine hydrate (molar ratio of $N_2H_4 \cdot H_2O/NiSO_4 \cdot 6H_2O = 7$) slowly dropped in mixtures. After washing and filtration, as-prepared products were dried at 50℃ for 24 h in a vacuum dry oven.

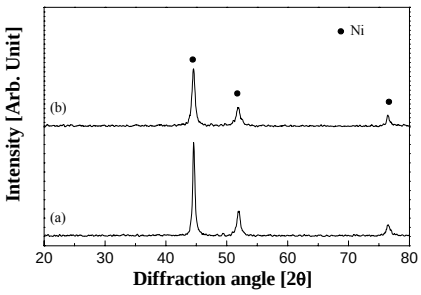

Fig. 1. XRD patterns of the samples prepared by wet chemical reduction without (a) and with (b) sucrose.

Fig. 1 shows the XRD patterns for metallic Ni powders prepared by wet chemical reduction without sucrose (a) and with sucrose (b). As shown in Fig. 1, the diffraction patterns represents a typical Ni powders with orientations such as (111), (200), and (220) in both samples, indicating that Ni has a face-centered cubic structure. However, the XRD peaks of the samples synthesized with sucrose were broader than those of the samples prepared without sucrose. Such XRD peak broadening, in general, originates from the diminution of particle size [4]. This result implied that the particles size could be reduced by adding of sucrose as a polymer network.

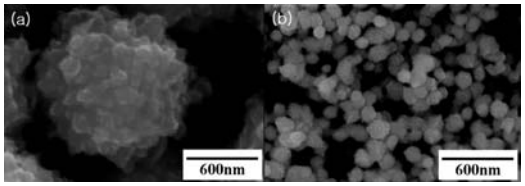

Fig. 2. SEM micrographs of the Ni powders prepared by wet chemical reduction without (a) and with (b) sucrose.

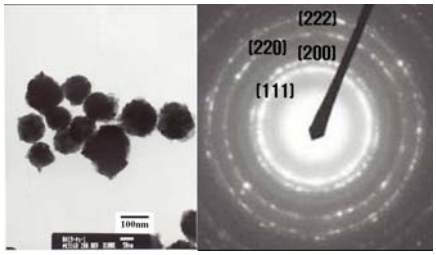

Fig. 3. TEM micrographs (a) and selected Area Diffraction (SAED) (b) of the Ni powders.

Fig. 2 shows the SEM images of Ni powders prepared without sucrose (a) and with sucrose (b). In the case of without sucrose, the larger Ni particles, which would be formed by the coalescence of primary particles, were agglomerated in irregular shape. On the contrary, the Ni powders obtained by adding of sucrose were spherical in shape and not agglomerated. This would be due to the homogeneous metal distribution inside the swollen polymer network [3]. Fig. 3 (a) shows TEM image of the Ni powders synthesized by adding sucrose, the Ni powders were nearly spherical in shape and seemed to be nano-sized, typically in the range < 100 nm with not being agglomerated. The selected area electron diffraction (SAED) patterns shows in Fig. 3. (b) The characteristic rings in poly crystalline diffraction pattern could be indexed to the {111}, {200}, {220}, {222} allowed inflecting plans expected from fcc Ni.

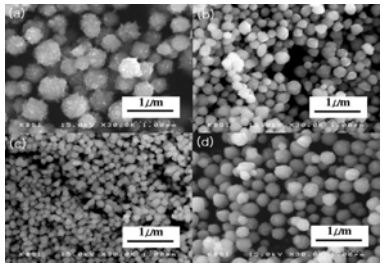

Fig. 4. SEM micrographs of the Ni powders prepared at different sucrose contents: (a) 0, (b) 0.005, (c) 0.025, and (d)0.05M.

To investigate the effect of sucrose on the morphology and particle size of resulting powders, the reduction reaction were performed at 60°C for 1h at various amounts of sucrose in the water solution. Fig. 4 shows the SEM images of the Ni powders synthesized by the addition of 0, 0.005, 0.025, and 0.05 M of sucrose. As the sucrose increased, the particle size of Ni powders steeply decreased and reached the minimum value of approximately 100 nm at the sucrose content of 0.025 M. The particle size increased again with a further increase of sucrose content. This is believed to be due to the pore size of the swollen polymer network.

3. Summary

The spherical nano-sized Ni powders have been prepared by the chemical reduction method of aqueous $NiSO_4$ using the hydrazine inside the swollen polymer network. The Ni powders prepared by adding of sucrose as a polymer network were nearly spherical in shape and seemed to be nano-sized, typically in the range of 100 nm with not being agglomerated. As the sucrose content increased, the particle size of Ni powders steeply decreased and reached the minimum value, however, the particle size increased again with a further increase of sucrose content.

4. References

1. K. Yu, D. J. Kim, H. S. Chung, H. Liang: Mater. Let. Vol. 57 (2003), p. 3992.
2. K. Yurij, F. Asuncion, R. T. Cristina, C. Juan, P. Pilar, P. Ruslan, G. Aharon: Chem. Mater. Vol. 11 (1999), p. 1331.
3. A. Biffis, A. A. D'Archivio, K. Jerabek, G. Schumid, B. Corain: Adv. Mater. Vol. 12 (2000), p. 1909.
4. M. Disersns, J. Patscheider, F. Lévy: Sulf. Coat. Technol. Vol. 108-109 (1998), p. 241.