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Preparation of Nanosized Nickel Particles by Hydrothermal Method

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The reduction of Ni (OH) $_2$ to ultrafine Ni metal powder under hydrothermal condition with ethylene glycol was investigated. The reduction proceeded gentlly at about 160 °C and did not pollute the environment. The particle size obtained was about 10 nm.

Ultrafine Ni metal powders are attracting more and more attention in recent years in the field of function materials, i.e. catalysts, magnetic materials, conducting inks, and ferrofluids.[1–3] Various preparation methods have been reported. Derry and Whittemore[4] reported at the second International Symposium of Hydrometallurgy in 1973 that Ni powders were obtained in a pressure reduction system from slurries of Ni (OH) $_2$ generated from sulfate solution using H_2 at 170 to 250 °C. Che et al.[5] got submicron particles by hydrogen reduction at temperatures over 300 °C. Hedge et al.[6] had found that nanocrystalline nickel powder could be produced in ethylene glycol using hydrazine as the reducing agent at elevated temperature. Chou and Huang[7] have developed a method by which nanosized nickel colloid was synthesized by using nickel chloride as the precursor, hydrazine as the reducing agent, and palladium as the nucleation agent. All of these methods were very useful and of widespread importance, but some limitations such as the elevated temperature, high cost or low yield should be circumvented for practical utilities. Therefore, developing a synthesis method of ultrafine Ni metal powder with mild condition and low cost is still the most important goal of material scientists. In this paper, we report a novel strategy to synthesize Ni powders under hydrothermal conditions in ethylene glycol. The reduction proceded gently at about 160 °C and no other poisonous reagents were needed. To our knowledge, there are few reports about synthesizing Ni powders based on the hydrothermal method. This method may be a new way to synthesize metal nanoparticles.

A mixture of $NiCl_2 \cdot 6H_2O$ (0.5 g) and NaOH was put into a Telfon-lined autoclave of 30-mL capacity. The mole ratio of the alkali to nickel, [OH]/[Ni], was 4.0. The autoclave was filled with ethylene glycol up to 80% of its capacity, maintained at 160 °C for 12 h, and then cooled to room temperature on standing. The products were filtered and washed with distilled water and absolute ethanol in sequence. Finally the black products were dried at 50 °C. The structure and morphology properties of products were characterized by several techniques. Powder X-ray diffraction (XRD) data were collected using a Rigaku D/MAX 2400 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). A transmission electron microscope (TEM: Hitachi 600, Japan) was used to observe the morphology and degree of agglomeration.

Figure 1 shows the X-ray powder diffraction pattern of the product. It is identified as a pure Ni powders (JCPDS NO. 04-0850). The crystalline structure of Ni powders was further characterized using an X-Ray diffractometer as shown in Figure 1.

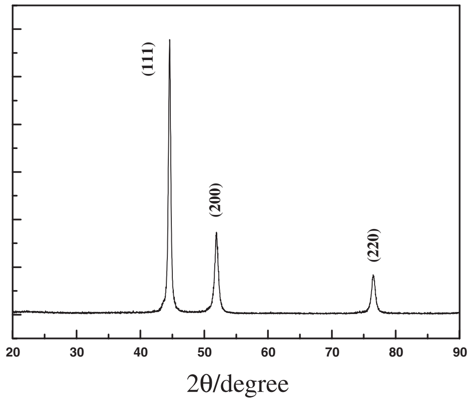


Figure 1. XRD patterns for the sample.

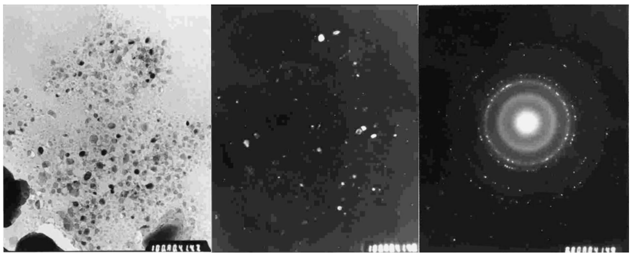
All these diffraction peaks, including not only the peak positions but also their relative intensities, can be perfectly indexed into the crystalline structure of Ni. The result is in accordance with the standard spectrum (JCPDS, NO. 04-0850).

The spherical size of the crystalline was calculated from the major diffraction peak (111) using the well-known Scherrer's formula (Eq 1), by assuming the factors, viz. instrumental

$$D = \frac{0.89\lambda}{B\cos\theta} \tag{1}$$

Where λ is wavelength (1.5418×10^{-10} m), B is the full width at half maximum of the peak, and θ is the Bragg's angle of the XRD peak. The grain size was found to be about 10 nm.

The morphology of the powders was observed by TEM as shown in Figure 2. The Ni powders were dispersed very well and the morphology of which could be obviously observed. It can be seen that Ni crystals are uniformly spherical and their average size is about 10 nm, which is consistent with that estimated from the XRD data. The selected area electron diffraction



(A) (B) (C)

Figure 2. TEM images of Ni powders. (A) Light field; (B) dark field; (C) SAED.

(SAED) results taken from one of Ni powders indicate that the Ni is monocrystalline and match well with the XRD results. The dark field confirmed that the obtained Ni nanocrystals had well-defined crystallinity.

Hegde et al.[7] have prepared Ni nanoparticles in the Ni $(OH)_2$/EG/PVP system in an oil bath at about 200 °C using Pt or Pd catalyst for nucleation and PVP as a stabilizer of small Ni metal particles. They succeeded in preparing nickel nanoparticles having spherical shape. In contrast with their work, Ni powders were prepared with ethylene glycol hydrothermally in our study. The particle size of the Ni nanoparticles prepared in present work was ten times smaller than those reported by Hedge. We also carried the experiment with different mole ratio of the alkali to nickel, [OH]/ [Ni]. It should be emphasized that Ni particles can be formed via the hydrothermal method unless the mole ratio of the alkali to nickel is higher than 4.0. Thus the growth process of Ni particles by the hydrothermal method would be different from that of the conventional method. Hydrothermal method may cause different nucleation and growth of Ni particles with excessive alkali.

In conclusion, this report proposed a simple one-step way to synthesize Ni particles. Well-dispersed Ni powders with size 10–20 nm and spherical shape have been prepared based on the hydrothermal method. No polyol has been used to protect or stabilize the metal powders. A great advantage of the method is that pure Ni powders can be produced without using Pt or Pd catalyst for nucleation. Given the generality of this approach, we hope to extend our synthetic method to prepare other metal nanoparticles.

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