Hydrothermal-reduction Synthesis of Ni Nanoparticles by Superrapid Heating Using a Micromixer

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Single-phase, high-crystalline, and single-crystalline Ni nanoparticles under 20 nm were continuously prepared through hydrothermal reduction by superrapid heating of $Ni(HCOO)_2$ solution using a micromixer in a homogeneous mixture field of H_2O and H_2 at 673 K and 30 MPa over 0.5 s.

Ni nanoparticles have great potential in several technological applications such as internal electrodes in multilayer ceramic capacitors and as material with high hydrogen storage capacity because of lower cost compared with noble metals.[1] There are a number of studies of the synthesis of Ni nanoparticles.[2] However, these methods often require multistep treatment, complex preparation of starting solutions, large amounts of organic solvents, and relatively expensive surfactants for obtaining single-phase, high-crystalline, and single-crystalline Ni nanoparticles.

Supercritical water (SCW) has several specific features such as drastic changes of dielectric constant and ionic product by manipulating temperature and pressure while maintaining a single phase without any organics, acids, or bases, and also formation of homogeneous mixtures with organics and gases.[3] Because of these features, SCW has high controllability of redox and crystallization reactions, which are major reactions for the synthesis of the Ni nanoparticles[4] and could lead to environmentally benign innovative chemical processes. Until now, a few studies of Ni nanoparticle synthesis in SCW have been reported.[5] In these studies, a continuous synthesis method[6] was applied for heating a starting solution to reaction temperature. However, the products did not meet the above-mentioned characteristics because homogeneous nucleation could not be achieved due to mainly the slow heating rate of starting solution.

In this study, we introduce a newly constructed micromixer for continuous synthesis through superrapid heating of a starting solution and try to directly synthesize single-phase, high-crystalline, and single-crystalline Ni nanoparticles in SCW and H_2.

A starting solution was prepared by dissolving precise amounts of $Ni(HCOO)_2 \cdot 2H_2O$ (Purity >92%, Wako Pure Chemicals) in distilled and deionized water (Resistivity >0.18 MΩ m). HCOOH solution was prepared by dissolving HCOOH (Purity >99%, Wako Pure Chemicals) in water. Concentrations of $Ni(HCOO)_2$ and HCOOH (C_{HCOOH}) were 0.1 and 0.0–2.5 mol kg^{-1}, respectively. HCOOH was used to produce H_2 as a reductant produced by hydrothermal decomposition.[7] These solutions were continuously purged with Ar during each experiment to remove dissolved O_2.

Continuous synthesis was performed using a newly constructed micromixer. A schematic diagram of the experimental apparatus, a newly constructed micromixer, and a conventional mixer are shown in Figures 1a, 1b, and 1c, respectively. The starting solution (fed from the left branch at 20 g min^{-1}, 298 K) was mixed with a preheated HCOOH solution (fed from the upper branch at 80 g min^{-1}, 702 K) in the micromixer, which was mainly composed of a microtube (0.18 mm i.d.) and a union tee (2.3 mm i.d.). Velocities of the starting solution before the mixing in the newly constructed micromixer and the conventional mixer are 13 and 0.08 m s^{-1}, respectively. Reynolds number (*Re*) of the solution in the reactor after the mixing was 2.1×10^4, and the *Re* values were the same for both mixers. By this construction, the starting solution was fed to a mixing point without preheating before mixing because of the high velocity, and it was rapidly heated to the reaction temperature of 673 K after the mixing due to the high *Re*. System pressure was controlled at 30 MPa by a back-pressure regulator. The residence time, τ, was calculated using the total flow rate, the reactor volume, and water density at 673 K and was varied from 0.5 to 2.0 s by changing the reactor length. Products were recovered as a slurry solution, removed using a membrane filter, and dried at 333 K in an electric oven for 24 h. In the case using the conventional mixer, the products could not be recovered because of the plugging in the left branch tube.

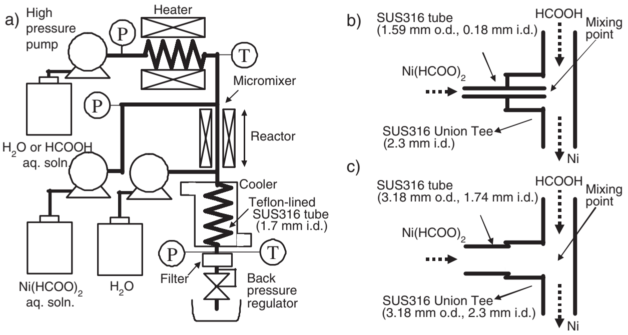

Figure 1. (a) Schematic diagram of apparatus. (b) Newly constructed micromixer. (c) Conventional mixer.

The crystal structures were analyzed by XRD. The crystallite sizes, D_{XRD}, were calculated from FWHM by the Scherrer equation. Morphological observation was performed by TEM. The particle size distribution and the average particle size, D_{TEM}, with the standard deviation (SD) were determined on the basis of a TEM image. The magnetic properties at room temperature was measured with VSM for the determination of the saturation magnetization, M_S, and the coercivity, H_C. Concentration of remaining nickel ion in the recovered solution was measured by ICP-AES to evaluate conversion of nickel ion into solid product, *X*.

Table 1. Summary of experiments on the synthesis of nickel nanoparticles using a micromixer

Run no	τ /s	C_{HCOOH} /mol g^{-1}	X /%	Product	D_{TEM} (SD)/nm	D_{XRD} /nm	M_{s} /emu g^{-1}	H_{C} /Oe
1	2.0	0.00	99.6	NiO	18.2 (8.3)	9.2 (2 0 0)	1.2	—
2	2.0	0.63	98.9	NiO	23.5 (9.2)	10.5 (2 0 0)	1.7	—
3	2.0	1.25	94.2	NiO	20.1 (9.5)	14.2 (2 0 0)	1.0	—
4	0.5	2.50	76.2	Ni	15.8 (4.3)	23.5 (1 1 1)	45.5	85.6
5	2.0	2.50	82.6	Ni	18.3 (5.8)	22.9 (1 1 1)	50.0	96.7

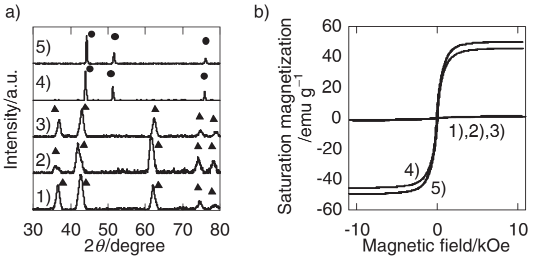

Figure 2. (a) XRD patterns of the products. Circle and triangle denote Ni and NiO, respectively. (b) Magnetization loops of the products. (1) $\tau = 2.00$, $C_{\mathrm{HCOOH}} = 0.00$. (2) $\tau = 2.00$, $C_{\mathrm{HCOOH}} = 0.63$. (3) $\tau = 2.00$, $C_{\mathrm{HCOOH}} = 1.25$. (4) $\tau = 0.50$, $C_{\mathrm{HCOOH}} = 2.50$. (5) $\tau = 2.00$, $C_{\mathrm{HCOOH}} = 2.50$.

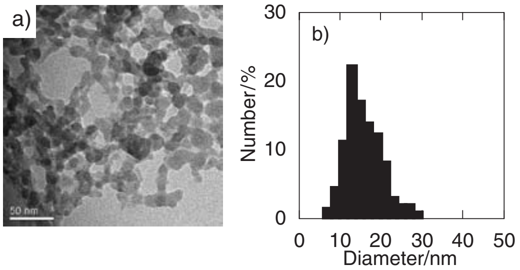

Figure 3. (a) Typical TEM image of the product ($\tau = 0.50$, $C_{\mathrm{HCOOH}} = 2.50$). (b) Particle size distribution of the product from TEM ($\tau = 0.50$, $C_{\mathrm{HCOOH}} = 2.50$).

Experimental conditions and results are summarized in Table 1. The XRD patterns of the products (Runs 1–5) are shown in Figure 2a. The VSM results of the products (Runs 1–5) are shown in Figure 2b. Typical TEM image and particle size distribution of the product (Run 4) are shown in Figures 3a and 3b, respectively. At lower C_{HCOOH}, NiO (JCPDS, No. 04-0835) was produced. At high C_{HCOOH}, 2.50 mol kg^{-1}, Ni (JCPDS, No. 04-0850) was produced as single phase because a sufficient amount of H_2 was supplied for the Ni^{2+} reduction and high degree of supersaturation was formed for the Ni crystallization. X in the case of NiO products (Runs 1–3) was over 94%, and X in the case of Ni products (Runs 4 and 5) was under 83%. The result suggests that the Ni products are not produced by way of NiO but directly synthesized from the starting solution by hydrothermal reduction. Hysteresis loops in Figure 2b (Runs 4 and 5) and a chain structure in Figure 3a are strongly related to the ferromagnetic nature of the Ni products. D_{TEM} values of the Ni products were below 20 nm and these were high-crystalline, and single-phase particles as shown in Figures 2a and 3. D_{TEM} of the products slightly increased from 15.8 to 18.3 nm with increasing τ due to the increase in X. D_{XRD} values of the products were around 23 nm. The result suggests that each nanoparticle in TEM image is a single crystal around 20 nm. M_{s} and H_{C} of the products slightly changed from 45.5 to 50.0 emu g^{-1} and from 85.6 to 96.7 Oe with increasing D_{TEM}. M_{s} and H_{C} for bulk Ni crystals (2–3 μm particles) were reported to be 55 emu g^{-1} and 100 Oe, respectively.[8] H_{C} depends on the size of magnetic particles. However, M_{s} usually does not show any size dependency but depends on the impurity effect.[8] In the present study, C, H, or O was assumed to be the possible impurity of produced Ni nanoparticle because longer residence time showed higher M_{s} value.

In conclusion, continuous hydrothermal-reduction synthesis of single-phase, high-crystalline, and single-crystalline Ni nanoparticles was achieved by superrapid heating using a micromixer in supercritical water and hydrogen homogeneous reaction field.

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