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# Role of Microwave Irradiation for the Preparation of Nickel Nanoparticles by a Polyol Method

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Ni(OH)<sub>2</sub> was reduced by ethylene glycol, in the presence of polyvinylpyrrolidone (PVP) under microwave (MW) heating in a pulse mode and oil-bath heating. The temperature profile in the two heating methods was controlled to be identical in order to determine whether the role of MW irradiation for the preparation of nickel nanoparticles is only thermal or not. Aggregated spherical nickel nanoparticles with diameters of 5±2 nm were produced under MW heating for 35 min, while larger monodispersed spherical nanoparticles with diameters of 20±4 nm were prepared in oil-bath heating for 35 min. Different size and dispersion pattern of nanoparticles under the two heating methods indicated that MW irradiation affects the nucleation, growth, and aggregation of Ni nanoparticles.

**Key words:** *Metals and alloys; Nanomaterials; Microwave heating; Polyol method; Electron microscopy*

## 1. Introduction

Microwave (MW) dielectric heating has received considerable attention in recent years as a new promising technique for the synthesis of monodisperse metallic nanoparticles in a polyol method.<sup>1-12)</sup> The main advantage of MW irradiation is that it produces a uniform heating of the solution, so that a more homogeneous nucleation is achieved as well as a shorter crystallization time, as compared to conventional oil-bath heating. Further advantages are rapid initial heating, absence of convection processes, and low running cost.

All of previous MW-polyol experiments have been carried out under much faster heating rates than those in an oil-bath. Tu and Liu<sup>2)</sup> studied preparation of Pt, Ir, Rh, Pd, Au, and Ru nanoparticles by a polyol method under MW and oil-bath heating. The temperatures at which the solution changed color and the rate of disappearance of metal precursor and formation of metal clusters in the solution monitored by UV absorption spectra were similar between MW and oil-bath heating. These results indicated that the mechanism of formation for metal particles under MW heating is similar to that which operates with oil-bath heating. Therefore, they concluded that the role of MW irradiation is mainly thermal.

In order to determine whether the role of MW irra-

diation for the preparation of metallic nanoparticles is only thermal or not, particles must be synthesized under the same temperature profile in MW and oil-bath heating. In this work, we prepared Ni nanoparticles under MW and oil-bath heating. The temperature profile of solution under MW heating was controlled to be identical to that in oil-bath heating by using a pulse mode of MW. Nanoparticles obtained by the two heating methods were compared to clarify the role of MW irradiation.

## 2. Experimental

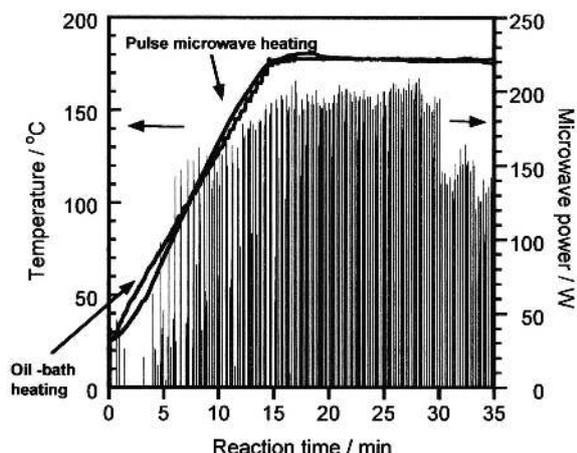
A MW oven was modified by installing a condenser and thermocouple through holes of the ceiling and a magnetic stirrer coated with Teflon at the bottom. A 100 ml glass flask was placed in a MW oven and connected to a condenser. A resolved solution of Ni(OH)<sub>2</sub> (24 mg:0.26 × 10<sup>-3</sup> mol) and H<sub>2</sub>SO<sub>4</sub> (5N 0.5 ml) containing PVP (average molecular weight: 40000, 332 mg:2.98 × 10<sup>-3</sup> mol in term of monomeric units) in ethylene glycol (20 ml) was irradiated by MW in a pulsed mode (Shikoku Keisoku: 200 W). PVP acts as a stabilizer of small Ni metal particles. For comparison, the same solution was heated in a conventional oil-bath (500 W). Products particles were characterized by using transmission electron microscopy (TEM:JEOL JEM-200CX) and UV-visible absorption spectroscopy (Shimadzu UV-2450).

Fig. 1 shows temperature profiles of the Ni(OH)<sub>2</sub>-PVP-H<sub>2</sub>SO<sub>4</sub>-ethylene glycol solution for different heating time in an oil-bath and with a pulsed mode of MW irradiation. The MW pulses were

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**Figure 1.** Dependence of temperature on the reaction time for  $\text{Ni}(\text{OH})_2$ -PVP- $\text{H}_2\text{SO}_4$ -ethylene glycol solution heated by pulse MW and in an oil bath. MW pulses used are also shown.

controlled by a microcomputer in order to obtain the same slow initial heating rate to that in the oil bath. In both heating, solution temperature increases from 25 °C to 175 °C after 15 min. Then, the solution was kept at 175 °C for 20 min.

### 3. Results and Discussion

In order to examine morphologies of Ni nanoparticles obtained by pulse MW and oil-bath heating, TEM photographs and diffraction patterns are measured. We attempted to remove PVP by centrifugation. In this case, the product solution was diluted with water and centrifuged at 13,000 rpm for 1 hour. Although this technique was useful for the separation of Au nanoparticles from PVP,<sup>8)</sup> it has little effect in the case of Ni nanoparticles. Heavy covering of PVP over Ni nanoparticles prevented from observation of clear TEM photographs. However, it was

possible to measure particle size by a careful observation of TEM photographs.

Figs. 2 and 3 show TEM photographs of nickel nanoparticles prepared by microwave and oil-bath heating for 25 and 35 min, respectively. The following six diffraction rings due to metal nickel (cubic form) were observed in TEM diffraction pattern of all particles shown in Figs. 2 and 3: (111), (200), (220), (311), (222), and (400). It was thus concluded that nanoparticles obtained were composed of pure nickel crystal. These Ni nanoparticles must be produced through the following reactions:

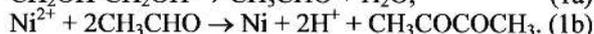
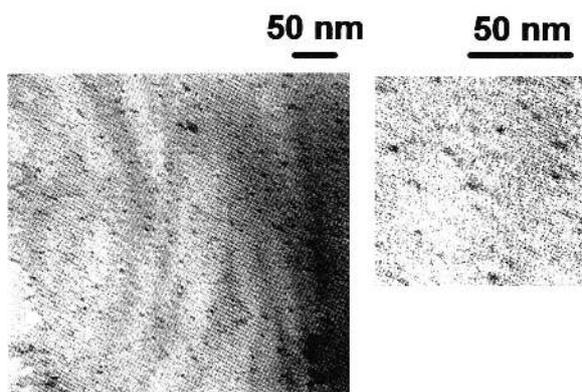


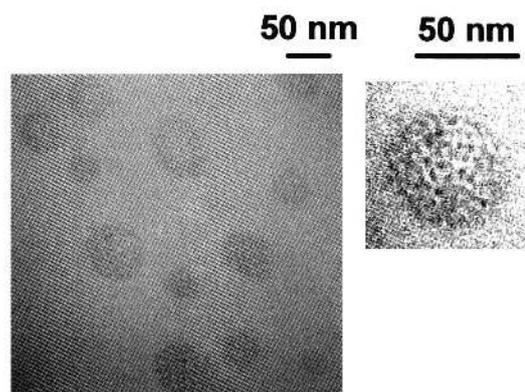
Fig. 2(a) indicates that spherical nanoparticles with diameters of  $5 \pm 2$  nm are produced under MW heating for 25 min. Further MW heating for 10 min leads to aggregation of these particles [Fig. 2(b)], though no growth of primary particle is observed. The size of aggregated secondary particles is 30-80 nm. Larger spherical nanoparticles with diameters of  $7 \pm 3$  nm are produced in oil-bath heating for 25 min [Fig. 3(a)]. Further heating for 10 min leads to a larger particle size of  $20 \pm 4$  nm [Fig. 3(b)]. On the basis of the above findings, aggregation of small nanoparticles occurs under MW heating, while growth of larger nanoparticles takes place under oil-bath heating.

Figs. 4(a) and 4(b) show UV-visible absorption spectra of reactant and product mixtures prepared by MW and oil-bath heating, respectively. The reactant spectrum is composed of a very weak absorption peak of  $\text{Ni}(\text{OH})_2$  at 400 nm, which gives a green color of solution. The product spectrum under MW heating consists of a strong peak at 210 nm and a weak continuous tail band in the 250-500 nm region. This tail band increases with increasing reaction time from 25 min to 35 min and a very weak surface plasmon band of Ni particles<sup>13)</sup> appears at about 350 nm after 35 min. The absorption spectra in oil-bath heating are similar to those in MW heating. In the spectrum of

(a) 25 min



(b) 35 min



**Figure 2.** TEM photographs of Ni particles obtained by pulse MW heating after 25 and 35 min.

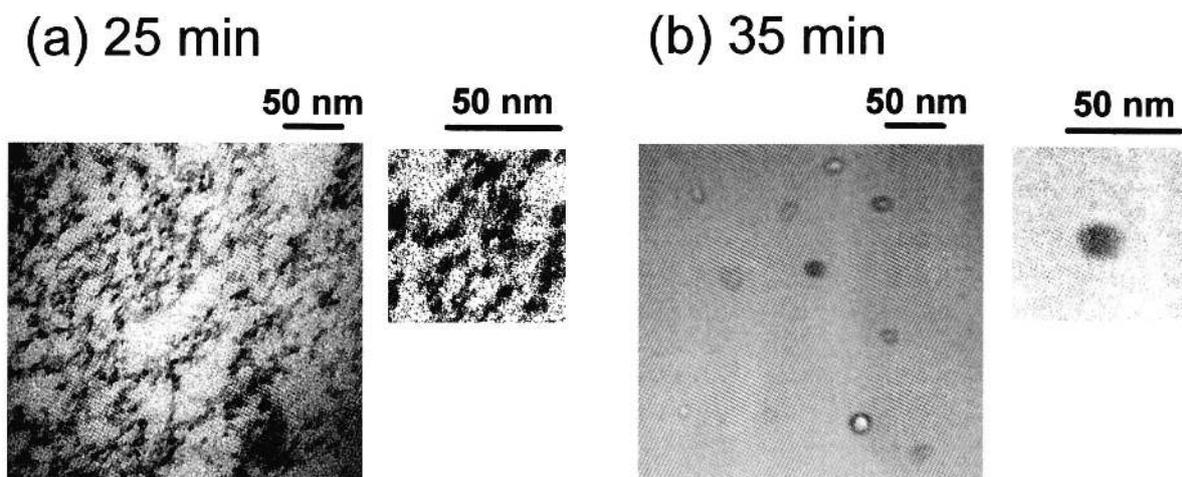


Figure 3. TEM photographs of Ni particles obtained by oil-bath heating after 25 and 35 min.

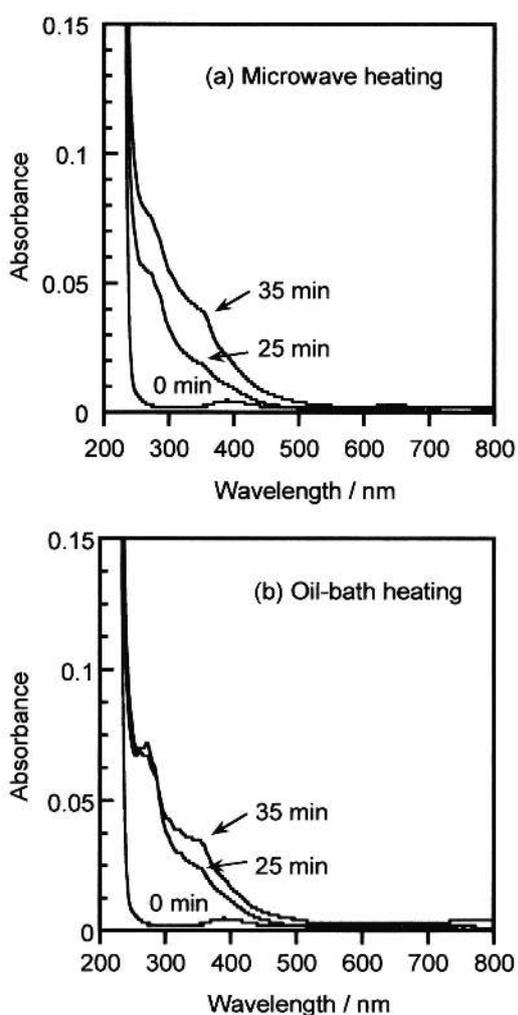


Figure 4. Absorption spectra of the original solution and solutions obtained by pulse MW and oil-bath heating after 25 and 35 min. Sample solutions are diluted by a factor of 50.

oil-bath heating measured after 35 min, a weak plasmon band of Ni particles is observed more clearly. It is generally known plasmon band becomes weak with decreasing particle size and disappears for ultrafine particles.<sup>14)</sup> The weaker intensity of the 350 nm plasmon band in MW heating than that in oil-bath heating is consistent with the fact that smaller particles are produced by MW heating.

TEM photographs and absorption spectra of products indicated that smaller aggregated Ni nanoparticles were prepared by MW heating than those in oil-bath heating, even though temperature profiles under the two heating methods were nearly the same. It was thus concluded that irradiation effects of MW such as MW dielectric heating of  $\text{Ni}^{2+}$  and Ni, superheating, and nonthermal acceleration of chemical reaction,<sup>15,16)</sup> take part in the nucleation, growth, and aggregation of Ni nanoparticles. In order to clarify their relative importance for the nucleation, growth, and aggregation of Ni nanoparticles, further detailed experimental studies are required.

#### 4. Conclusion

Ni nanoparticles were prepared by using MW heating and oil-bath heating under the same temperature profile in order to examine the role of MW irradiation. Spherical nanoparticles with diameters of  $5 \pm 2$  nm were produced under MW heating for 25 min. Further MW heating for 10 min led to aggregation of these particles with diameters of 30–80 nm, though no growth of primary particle is observed. Larger monodispersed spherical nanoparticles with diameters of  $7 \pm 3$  nm were produced in oil-bath heating for 25 min. Further heating for 10 min led to a larger particle size of  $20 \pm 4$  nm. Different size and dispersion pattern were obtained for Ni nanoparticles under MW heating and oil-bath heating. These results gave definite evidence that that irradiation effects of MW

such as MW dielectric heating of  $\text{Ni}^{2+}$  and Ni, superheating, and nonthermal acceleration of chemical reaction, contribute to the nucleation, growth, and aggregation of Ni nanoparticles. Very recently, we have found that the shape of Au nanoparticles prepared under a similar temperature profile is different between MW heating and oil-bath heating.<sup>7)</sup> Although spherical particles were dominantly synthesized by oil-bath heating, polygonal Au nanoplates were prepared under pulse MW irradiation. On the basis of these findings, MW heating is a promising technique for the preparation of different morphology or size of metallic nanoparticles from that obtained by conventional oil-bath heating.

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