Surfactant-free synthesis of nickel nanoparticles in near-critical water

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ABSTRACT

Nickel nanoparticles have been produced by combining two well-tested methods: (i) the continuous flow supercritical reactor and (ii) the reduction of a nickel salt with hydrazine. The normal precipitation of a nickel–hydrazine complex, which would complicate pumping and mixing of the precursor, was controlled by the addition of ammonia to the precursor solution, and production of nickel nanoparticles with average sizes from 40 to 60 nm were demonstrated. The method therefore provides some size control and enables the production of nickel nanoparticles without the use of surfactants. The pure nickel nanoparticles can be easily isolated using a magnet.

1. Introduction

The interest in nanoscale metal powders is motivated by the improved characteristics of the pure metals and alloys. On a macroscopic scale, they may exhibit significantly improved hardness and strength, and other uses include microelectronics, catalysis, and magnetism [1,2]. When the literature concerning synthesis of fine nickel particles is reviewed, it falls roughly in two categories: (i) either no surfactants are used, resulting in broad size distributions and relatively large particles (hundreds of nanometres) [3–5] or (ii) sol–gel processes and surfactants are used, resulting in small particles with narrow size distributions [6–8]. In the latter case, the particles are however coated in a layer of surfactant, which is undesirable for some applications and sol–gel is typically a batch process, which may complicate large-scale synthesis.

Here, we report on the synthesis of nickel nanoparticles using a continuous flow supercritical system that allows quick exploration of synthesis parameter space (temperature, pressure, and concentration). Synthesis of nanoparticles in supercritical fluids has in recent years been the topic of many studies [9]. Supercritical fluids exhibit highly tuneable properties and often the solubility of a particular compound can be changed drastically by small changes in supercritical pressure or temperature. Reduction of nickel in near-critical water has been demonstrated by Adschiri et al. [10] using gaseous hydrogen as the reducing agent. This produced nickel particles, but with a rather large size (600 nm) and a broad size-distribution. In the present case, the nickel nanoparticles were synthesised by hydrothermal reduction of nickel salts with hydrazine. By mixing a stream of cold reactant with a superheated solvent stream, mixing and heating occurs in seconds. Besides giving control of temperature and pressure, this rapid increase in temperature also leads to instantaneous crystallisation. The process improves on "conventional" solvothermal synthesis methods, where the mass or heat is poorly controlled. The supercritical synthesis system used here [11,12] is inspired by the work of several authors [13–15]. In the present setup, the solvent is first pressurised and then pumped into a tube furnace using standard air-driven liquid pumps. After reaching the desired temperature and pressure, the solvent meets one or more reactant solution(s) in the reactor block, and reaction then takes place immediately upon mixing as well as during the back flow through the furnace. The superheating of the solvent string can be maintained all the way to the mixing point, which is temperature controlled by resistance heaters. Once outside the furnace rapid cooling of the reaction mixture is performed and the pressure is lowered by means of a proportional relief valve.

Nickel and cobalt can be produced by the reduction of nickel and cobalt ions using hydrazine, as demonstrated by Li [16], who synthesised nickel fine powder by heating a solution of an inorganic nickel salt and hydrazine in an autoclave. It was of interest to explore if this synthesis route could be adapted to a continuous flow system and the possibility of achieving control over particle size and size distribution. Use of a continuous flow reactor is inherently preferable for industrial production compared with batch processes. As described by Li [16], a precipitate

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of pink hydrazine–nickel complex is formed upon mixing solutions of hydrazine and nickel ions. Hydrothermal treatment of the precipitate produces nickel particles, but from the reported transmission electron microscopic (TEM) images of the particles it is impossible to provide reliable size estimates (probably between 50 and 200 nm) [16]. A suspension is not ideal for synthesis in the present apparatus, but it was found that the precipitation of the complex could be delayed for almost an hour by the addition of ammonia.

2. Experimental method

In total, 5.60 g of $NiSO_4 \cdot 6H_2O$ (0.0213 mol) was dissolved in 360 mL distilled water. Around 120 mL 2 M ammonia solution (0.24 mol) was slowly added while stirring to give a deep blue solution. Immediately before the synthesis, 6.0 mL of hydrazine hydrate (98%, 0.123 mol) was added, resulting in a Ni^{2+} concentration of 0.044 M. The precursor solution and the preheated distilled water were both pumped continuously at a rate of 10 mL/min. The two liquids were mixed in the T-piece and the residence time in the hot reactor tube after mixing was kept constant at 1 min. The pressure was kept constant at 30.0 MPa after initial tests showed no effect of pressure on the synthesis product. The synthesis temperature was varied from 150 to 350 °C. As there was no gelling or surfactants in the reaction mixture, the nickel particles could be easily isolated from the reaction mixture using a neodymium magnet through the wall of a beaker while decanting the aqueous phase. Using the conditions listed above, 1.5 g of nickel nanoparticles is produced in 1 h.

The products were characterised using powder X-ray diffraction and crystallite sizes were estimated from fitting a Voigt function to the (100) peak. Correction for the instrumental profile broadening was performed using the width obtained from Voigt fit of a LaB_6 standard sample [17,18]. The products were also characterised by TEM (data not shown), but as found by Li et al. the images reveal limited quantitative information about the particle size. However, in Fig. 1 a scanning electron microscopic (SEM) image of the product is shown, which confirms the size estimates obtained by PXRD (see below). As a reference point for

the continuous flow synthesis, the synthesis of Li et al. [16] was reproduced both with and without addition of ammonia. A suspension of the nickel–hydrazine complex was treated in an autoclave for 3 h at 150 °C, and this gave a pure nickel powder with a size of 50.9(2.6) nm without NH_3 addition and 44.6(1.6) nm with NH_3 addition.

3. Results and discussion

Treating the ammonia stabilized nickel–hydrazine complex in the present continuous-flow apparatus lead to a clear effect on the size of the particles when the synthesis temperature was varied. As illustrated in Fig. 2, the particle size increased with temperature, from 38.8(1.6) nm at 150 °C to 59.3(4.5) nm at 350 °C.

At temperatures below 150 °C, the product was nickel hydroxide, and a trace of nickel hydroxide is still visible in the 150 °C diffractogram shown in Fig. 3. At temperatures above 350 °C, no product was recovered. This can be explained in two ways. Either as a physical effect, where the nickel particles precipitate in the reactor tube, because they cannot be suspended in the supercritical phase (the critical point of water is 374 °C and 22.1 MPa), or as a chemical effect where hydrazine decomposes at the elevated temperature before the nickel ions are reduced.

A two-fold reduction in the concentration at a constant temperature of 200 °C has virtually no effect on the particle size, whereas a four-fold decrease of concentration leads to a significant increase in particle size. Lower concentrations are normally expected to yield smaller particles, and the result warrants further investigation. As seen in Fig. 3, nickel hydroxide was also produced in the dilution experiments presumably because of the reduced concentration of hydrazine. Other syntheses performed with the same apparatus have all shown a positive correlation between the crystallite size and the concentration of reactant. An example is the syntheses of titanium dioxide in a supercritical isopropanol–water mixture, where a distinct reduction in size was observed with decreasing
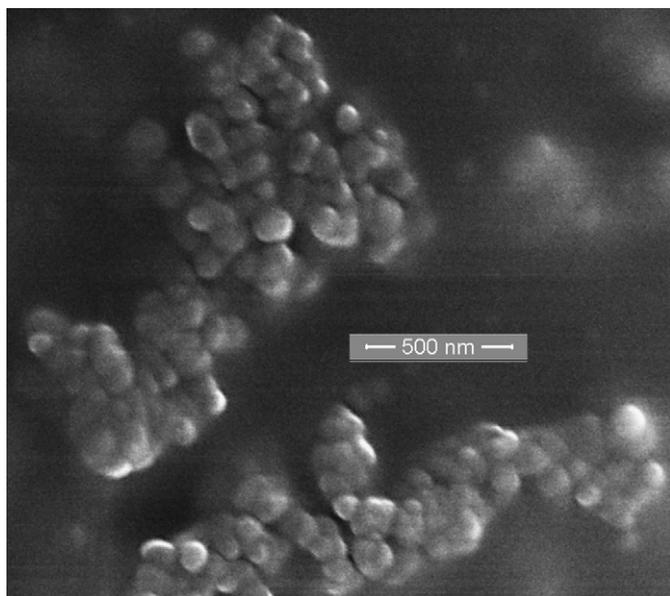

Fig. 1. SEM image of nickel particles obtained from flow synthesis at 350 °C. The product is spheroid particles assembled in larger agglomerates.
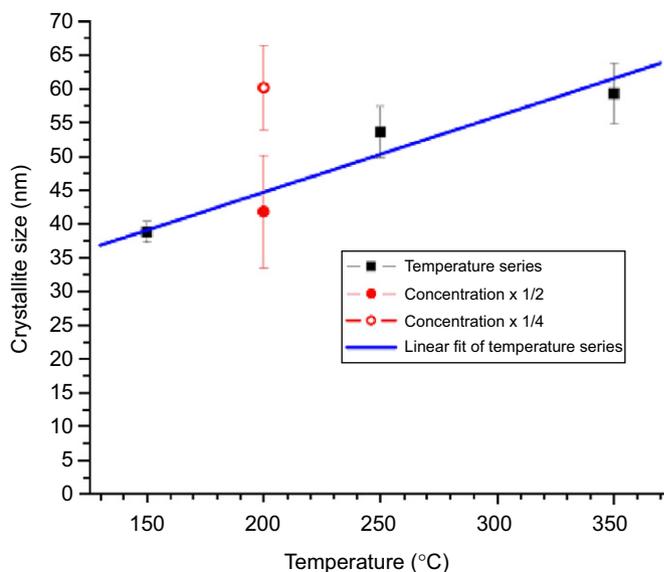

Fig. 2. Crystallite size as a function of temperature and reactant concentration. The size uncertainties were estimated from the peak-width uncertainties of the (100) peak.
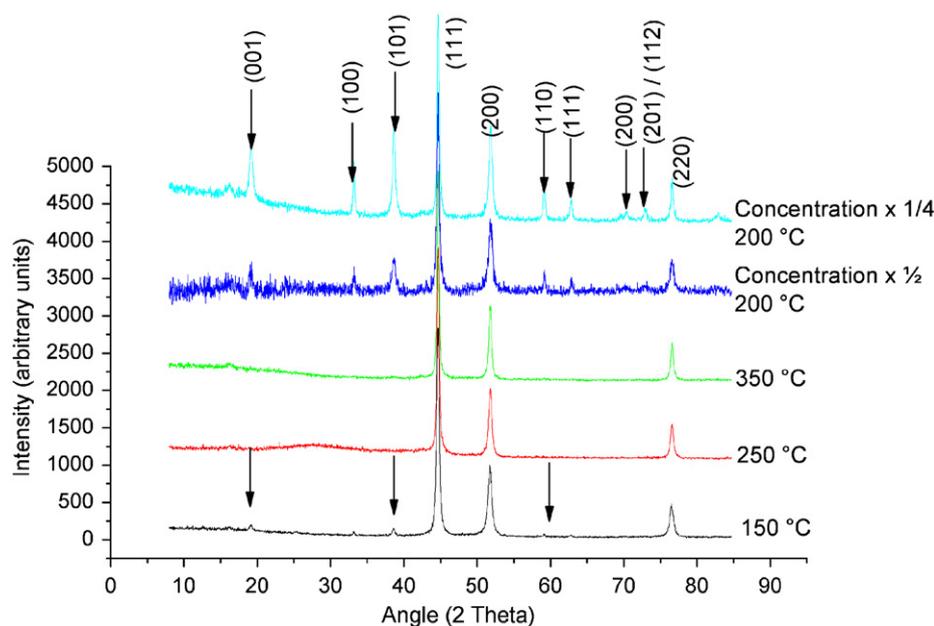
Fig. 3. Powder X-ray diffraction patterns of as-synthesized particles. The arrows mark reflections from nickel hydroxide impurity.

concentration of reactants [11]. However, since the reaction mechanisms vary, comparisons should be made cautiously.

4. Conclusion

The hydrazine reduction route has been successfully adapted to continuous flow synthesis of nickel nanoparticles in near-critical water. Thus, pure nickel nanoparticles can be continuously produced in seconds rather than hours, and the particle size can be controlled between 40 and 60 nm by increasing the reaction temperature from 150 to 350 °C. On the other hand, variation of pressure or reactant concentration does not lead to a clear effect on the particle size. The synthesis system described here is comparatively cheap, and pressure, temperature, flow rate, and reactant concentrations can be changed continuously. In the present bench-top configuration with 6 mm inner diameter of the reactor tubes, approximately 1.5 g of nickel nanoparticles can be synthesised per hour. Since the continuous flow reactor in principle is scalable, continuous production of nickel nanoparticles in kg/day scale should be possible in a scaled-up version of the apparatus. Ongoing studies concentrate on characterisation of the particle size distributions using small angle X-ray scattering and advanced PXRD techniques. A deeper understanding of the crystal nucleation and growth will be sought through in-situ high-energy X-ray scattering studies [19].

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