Nickel Nanoparticles Synthesized in Near Critical Water

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Summary
Nickel nanoparticles have been synthesized in aqueous solution using a continuous flow reactor in order to investigate this route of synthesis and the possibility of control over particle size. The synthesis parameter space (T, P, concentration) has been explored and the process allows continuous synthesis of nanoparticles in the 20 nanometer range.

1. Introduction

We report on synthesis of nickel nanoparticles using a continuous flow supercritical system that allows quick exploration of synthesis parameter space (temperature, pressure, concentration). The particles have been characterised using Powder X-Ray Diffraction (PXRD). The synthesis system has large chemical flexibility, and unlike batch systems there is no operating down time. Nickel nanoparticles have been synthesised using nickel salts in near supercritical water. The synthesis times are short (seconds) since the extremely hot supercritical solvent is mixed with the cold reactant. Besides giving control of temperature and pressure, this also leads to instantaneous crystallisation, where crystal nucleation far exceeds crystal growth. In "conventional" synthesis methods there are process steps, where the mass or heat is poorly controlled. The removal of such process may lead to narrow particle size distributions in the supercritical method.

The interest in nanoscale metal powders is fuelled 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 catalysis and information storage. In the case of cobalt nanoparticles various chemical routes allow control of particles sizes from 2 - 30 nm [1, 2]. The synthesis of nickel metal particles has also been carried out in a number of ways including vapour deposition and solvothermal methods. However, such methods suffer from a limited scalability or the need for surfactants to be removed in a later step. Furthermore, long synthesis times have a tendency to broaden the size distributions.

2. Experimental

The present supercritical synthesis system is inspired by the work of several authors [3, 4, 5] and it is sketched in Figure 1. The essential features are, that all pumps are kept "cold", and that the synthesis is continuous, which allows scaling and control over synthesis parameters. The only expensive material required is for the pipes and the reactor block, which are made out of the corrosive resistant alloy Inconel625. 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 relative to the reactant string can be maintained all the way to the reactor block, which is temperature controlled by resistance heaters drilled into the block. Once outside the furnace effective cooling of the reaction mixture is performed. All "cold" components are made of standard Steel 316, which can handle up to 1500 bar and 150^{o}C.

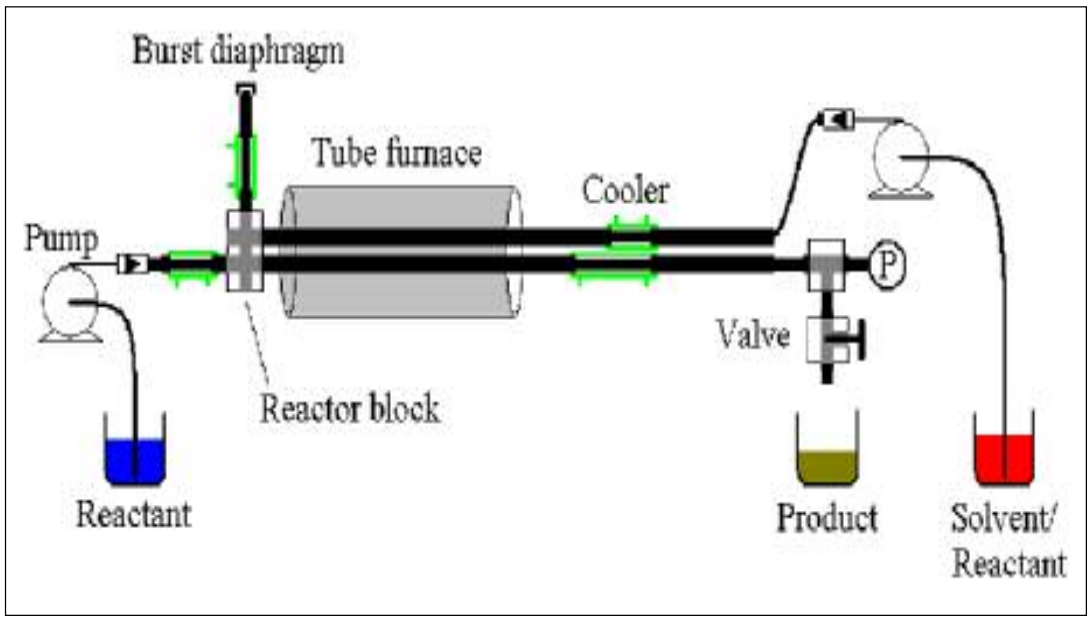

Figure 1: Sketch of the synthesis apparatus

Nickel and cobalt can be produced by the reduction of nickel and cobalt ions using hydrazine, as demonstrated by Li *et al.* [6], who synthesized nickel fine powder by heating a solution of an inorganic nickel salt and hydrazine in an autoclave. It is of interest to explore if this synthesis route can be adapted to a continuous flow system and maybe even achieve the control over particle size and size distribution. As described by Li *et al*. [6] a precipitate of pink hydrazine-nickel complex is formed upon mixing solutions of hydrazine and nickel ions, followed by a hydrothermal treatment. 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. The experimental procedure was: 5.6 g of $NiSO_4.7H_2O$ was dissolved in 360 mL distilled water. 120 mL 2 M ammonia solution was slowly poured into the solution while stirring to give a deep blue solution. Immediately before the synthesis 6 mL of hydrazine hydrate was added. Synthesis time was kept constant at 1 minute and the pressure kept at 300 bars after initial tests had demonstrated no effect of the pressure on the synthesis product. The synthesis temperature was varied from 150 °C to 350 °C. The products were investigated using powder X-ray diffraction and size was estimated from fitting a Pseudo-Voigt function to the (100) peak. The instrumental broadening was obtained from a LaB_6 standard sample. As a reference point the synthesis of Li *et al.* [6] was reproduced. Here a suspension of the nickel-hydrazine complex was treated in an autoclave for three hours at 200 °C, and this gave a pure nickel powder with an estimated size of 25 nm.

3. Results and discussion

Treating the ammonia stabilized nickel-hydrazine complex in the present apparatus, the only synthesis parameter found to have a clear effect on the size of the particles, was the temperature. As illustrated in figure 2, particle size increase with temperature, from 24 nm at 150 °C to 31 nm at 350 °C. In the syntheses of titanium dioxide a distinct reduction in size with decreasing concentration of reactants was observed [7]. This effect could not be seen in the synthesis of nickel.

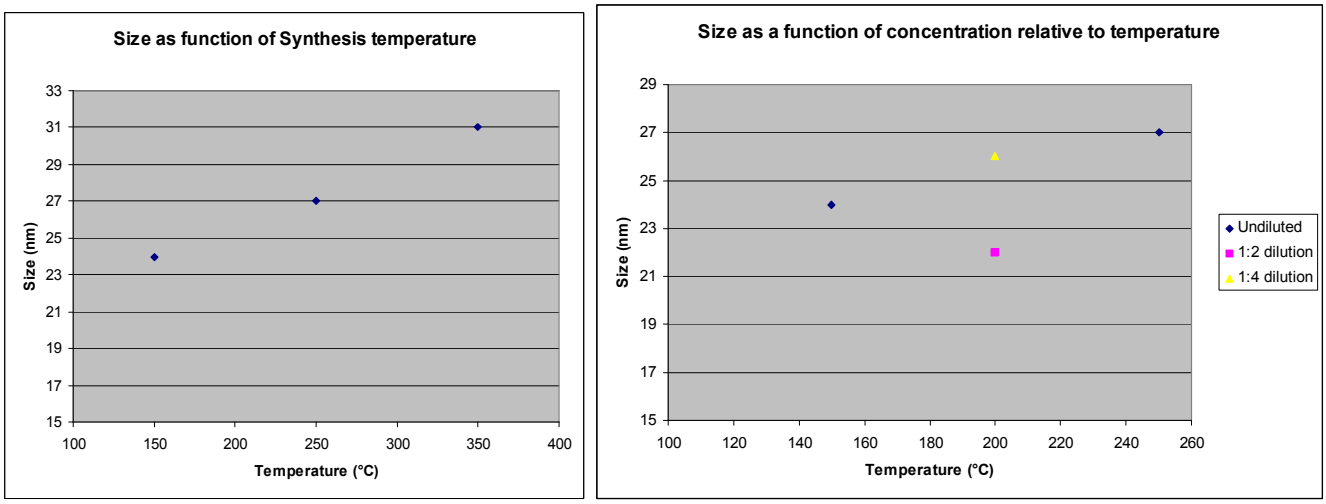

Figure 2: A clear effect of temperature is seen, while the concentration has little effect

4. Conclusion

It has been demonstrated that pure nickel nanoparticles can be produced in seconds using a supercritical synthesis system. The small particle size is obtained because crystallisation is instantaneous when the hot solvent meets the cold reactant. The system described here is comparatively cheap, and pressure, temperature, flow rate and reactant concentrations can be changed continuously. Thus, the synthesis parameter space can quickly be mapped for a new reaction making optimization straightforward. Work is in progress to investigate the size distribution of the Ni powders by transmission electron microscopy and small angle X-ray scattering.

References

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