

STUDY OF THE STRUCTURE AND MAGNETIC PROPERTIES OF NANODISPersed NICKEL PARTICLES OBTAINED BY INTERPHASE SYNTHESIS

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Abstract

The peculiarities of metal nickel nanoparticles preparation with narrow size distribution and controlled size using interphase reduction technique of nickel (II) oleate by sodium borohydrate without special added protective agent were described. As-prepared Ni nanoparticles were concentrated in polar phase mainly as black colloidal dispersions. The size, composition and morphology of the colloid's dispersive phase were determined by TEM, XRD and IRS. The dispersed phase has been formed by crystalline spherical nickel (fcc) nanoparticles. In polar phase (aqueous, ethanol) particles could grow up to 20–30 nm and have rather narrow size distribution in the range of 2–8 nm. Size distribution histograms showed the average size of 4.6 nm. The stability of nickel colloidal dispersions was achieved by the surfactants formed *in situ* and determined nanoparticles nucleation conditions. Magnetization versus temperature was measured using a ponderomotive method in the interval from 100 to 800 K. The results showed Ni nanoparticles with a ferromagnetic behavior and saturation magnetization of 20.3 emu/g (in contrast to 54 emu/g for bulk Ni), that may be related to a partial surface particles oxidation.

Keywords: Ni nanoparticles, TEM, Interphase synthesis, Magnetism, Reduction

1. INTRODUCTION

Nanocrystalline metal Ni particles with magnetic properties continue to attract great interest across diverse areas of science and technical applications including magnetic fluids and recording media [1,2], catalysts [3-5], aimed drug delivery [6-8] etc. due to their unique physicochemical properties attributed to the quantum size effect. Since transition metal nanoparticles are easily oxidized only several chemical and physical methods have been used for effective Ni nanoparticles preparation: microemulsion technique [7,9], aqueous and nonaqueous reduction [2,3,6], sonochemical and precursors' thermal decompositions [4,5,10], polymeric ion-exchange technique and electrolytic reduction [6].

However such particles prepared by these methods normally cannot be isolated, the coalescence and agglomeration process can be observed [3]. A suitable soluble polymer (e.g., polyvinylpyrrolidone) usually was added as a protective agent. In the case of its absence, the resultant particles were in the micrometer size range even the precursor concentration was quite low ($\sim 10^{-3}$ M). But it was difficult to remove completely the soluble polymer on the particle surface by simple washing. Thus, it might be an interesting challenge to prepare stable colloidal nickel dispersions without special addition of soluble polymers. Another challenge for nanoparticle preparation is to obtain particles with uniform size.

In present work, we describe the preparation and study of metal nickel nanoparticles with narrow size distribution and controlled size using interphase reduction technique of nickel (II) oleate by sodium borohydrate as a reductant in hexane–water system in the absence other protective agents. During the interphase synthesis both phase should not be intermixed [11,12] in contrast to microemulsion and two-phase ones [13]. Their interaction may occur at different phases: aqueous, organic, at the interface both on the source of water and non-polar organic phase.

2. EXPERIMENTAL SECTION

2.1 Reagents and chemicals

Nickel acetate tetrahydrate, oleic acid, sodium borohydride and *n*-hexane had the analytical reagent grade. All of them were used without further purification. The distilled water was used throughout these experiments.

2.2 Interphase synthesis

In this experimental work nickel (II) oleate was used as a precursor of nickel nanoparticles. This choice was determined by the fact that oleic acid has unusual surfactant properties, which in the majority cases influence the particles size and their shape. Nickel (II) oleate was synthesized by the successive method according to our previous work [11].

In typical experiments on preparation of Ni nanoparticles, an appropriate amount of nickel oleate was dissolved directly in hexane to form $10^{-2} - 5 \times 10^{-2}$ M solution. A ten-twenty fold excess of sodium borohydride aqueous solution was prepared. At temperature of 20 °C, nickel nanoparticles were formed in a capped three-necked flask with two-level stirring, which enable to mix aqueous and organic phases separately. . The reduction reaction could be expressed as:



2.3 Instruments and characterizations

The nickel particle sizes were obtained by transmission electron microscopy (TEM) using a Model LEO-906 field emission transmission electron microscope with a resolution of 0.1 nm at accelerating voltage of 100 kV. The samples for TEM were prepared by placing a drop of the colloidal dispersion onto a carbon-covered copper grid and drying it in the air at room temperature.

X-ray powder diffraction (XRD) patterns were recorded on a HZG 4A X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 0.1542$ nm) in the angle range $2\theta = 30-90^\circ$. To prepare samples for X-ray analysis the colloidal Ni dispersions were settled on a permanent magnet, then obtained precipitates were separated and washed by distilled water and finally were dried in a desiccator with P_4O_{10} at room temperature.

FT-IR spectroscopy-identification was measured using a model Spectrum One (Perkin-Elmer) spectrometer in the vibration range $4000-400$ cm^{-1} . The samples for IR-analyses were prepared by drying the formed interphase product and removal of excess surfactant from metal particles in hot hexane at 60 °C.

Magnetization of powdered nickel particles obtained from its colloidal dispersions versus temperature was measured using a ponderomotive method in the interval from 100 to 800 K. This method make it possible to investigate the temperature dependence of magnetization and magnetic susceptibility even for small quantity of substances.

The concentration of Ni^0 in as-prepared colloidal dispersions was determined by the colorimetric analysis of nickel complex compound with dymethylhlioxime at the wavelength of $\lambda = 465$ nm.

3. RESULTS AND DISCUSSION

In the result of the interphase reduction of nickel oleate (dissolved in hexane) by sodium borohydride (dissolved in water) the black colloidal dispersion in water in 5–15 min after the intermixing was formed. In several experiments the formation of partially colored in black gel-like product on the interphase boundary was observed. The organic phase did not undergo the meaningful visible changes.

The influence of the reagent ratio on the reaction products state and their localization phase is shown in **Table 1**. It is clearly seen that using of 5–20-fold reducing agent excess leads to the formation of black

aqueous nickel colloidal dispersion. Subsequent increase of NaBH_4 concentration brings to the obtaining of gel-like product in aqueous phase.

Table 1 The influence of the reagent ratio on the interphase reaction products. Concentration of $[\text{Ni}(\text{Oleate})_2] = 10^{-2}$ M and was constant, room temperature.

Sam-ple	Molar ratio $[\text{Ni}(\text{Oleate})_2]/[\text{NaBH}_4]$	Phase of localization and product state	Ni^0 concentration in colloidal dispersion, M	Reaction time, h	Efficiency, %
1	1 : 5	aqueous phase, colloidal dispersion	$1,7 \cdot 10^{-3}$	6	17
2	1 : 10	aqueous phase, colloidal dispersion	$4,1 \cdot 10^{-3}$	3	41
3	1 : 20	aqueous phase, colloidal dispersion	$8,5 \cdot 10^{-3}$	1,5	85
4	1 : 30	aqueous phase, gel-like phase	$5,1 \cdot 10^{-3}$	0,75	51

In the case of using constant reagent ratio (1:20) and increasing the molar concentration of nickel (II) oleate from 10^{-2} M up to 5×10^{-2} M the interphase products are formed both in aqueous and organic phases. Our previous experiments on the investigation the effect of both precursor and reductant concentrations on the average size of nickel particles have been successfully carried out [11]. Thus, for typical experiments we have used 5×10^{-2} M solution of nickel (II) oleate in *n*-hexan and 5×10^{-1} M aqueous solution of NaBH_4 .

A typical TEM micrograph and the size distribution for the nickel nanoparticles are shown in **Fig. 1**. The particles of spherical shape essentially are very fine and discrete. According to the histogram of the size distribution, their diameter vary within 2–8 nm, the average size of nickel particles is 4.6 nm ($\delta=0.09$). The absence of a protective agent did not result in particle agglomeration. This revealed that nanosized nickel particles could be obtained in aqueous or hexane phases, even in the absence of additional protective polymer. It can be suggested that oleic acid or sodium oleate might form a protective layer around the particle surface via the interaction of carboxylic COO^- groups with nickel atoms, preventing the particle aggregation or agglomeration. More detailed TEM-investigations have shown that nickel nanoparticles could grow up to 20–30 nm at appropriate conditions and have rather narrow size distribution.

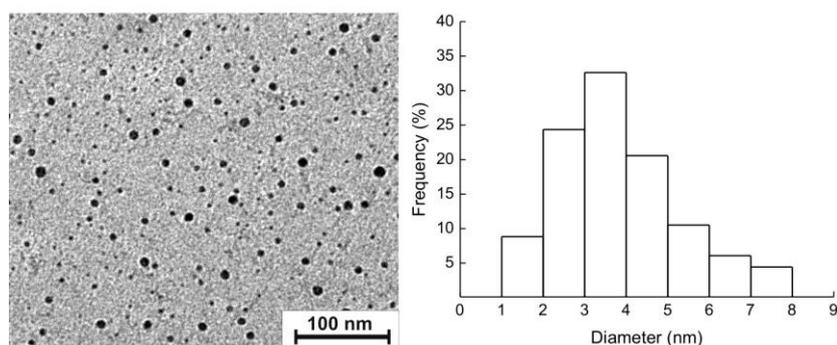


Fig. 1 TEM image and histogram of size distribution of as-prepared Ni nanoparticles. $[\text{Ni}(\text{Oleate})_2]=0.05$ M

Fig. 2 indicates the XRD pattern of as-prepared nickel nanoparticles. One main characteristic pick for the [011] crystallographic plane of face-centered cubic (fcc) Ni at $2\theta=44.5^\circ$ was observed. In addition, small halo centered near $2\theta=80^\circ$ are fixed. The small diffraction peak at $2\theta=76.8^\circ$ are can be attributed to the [220] planes of fcc Ni [11,14]. All diffraction peaks are clearly broadened, which reflect the nanosized nature of sample. It is well known that Ni nanoparticles are easily oxidized in air and aqueous phase to oxides or hydroxides. However, the XRD pattern shows that no oxide phases are detected. This fact may be the result of the protection property of surfactants that are formed *in situ*.

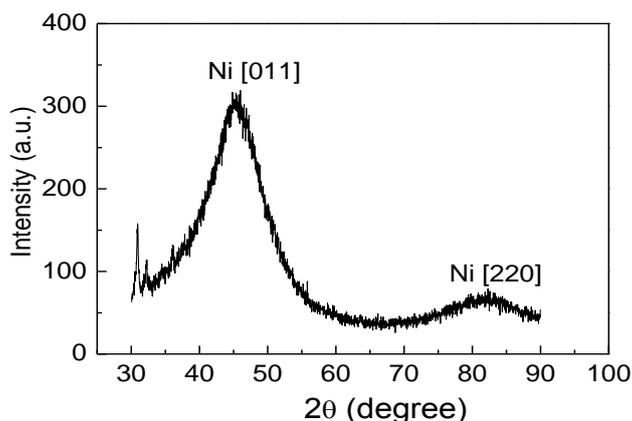


Fig. 2 Powder XRD pattern of Ni nanoparticles. $[\text{Ni}(\text{Oleate})_2]=0.05 \text{ M}$, $[\text{NaBH}_4]=0.5 \text{ M}$, $20 \text{ }^\circ\text{C}$

In accordance with the IR-spectroscopy results [11] the stability of prepared nickel colloidal dispersions was provided by a surfactant mixture including sodium oleate, sodium stearate and oleic acid. These substances were produced as a consequence of the interphase synthesis. The surfactant molecules might be absorbed on the particles formed therein, act as a protective agents limiting the growth and oxidation of nanoparticles.

The obtained colloidal dispersions of Ni nanoparticles are expected to possess the magnetic properties. This has been recognized from the fact that interphase product prepared in our experiments could be recovered from colloidal dispersion by a permanent magnet. In order to further investigate the magnetic properties of resultant Ni particles a typical dispersed sample (mean diameter of Ni nanoparticles 4.6 nm) was exposed for magnetic measurements. Fig. 3 shows a plot of magnetization versus temperature in the interval from 100 to 800 K. No significant magnetization of Ni particles was observed. It could be attributed to the very small size of Ni cores in the aqueous dispersion which were nearly superparamagnetic [14]. When heating pattern of nickel powder to nearly 800 K the individual Ni nanoparticles are sintered into clusters and form aggregates with greater sizes. Thus, cooling of sintered nickel particles corresponds to increase of saturation magnetization (M_s) values up to 20.3 emu/g and indicates a transition of Ni particles from superparamagnetic to ferromagnetic state [6]. The values of the magnetization decrease dramatically when the size of nickel nanoparticles decreases. An analogous explanation for ferromagnetic particles is reported in the literature [1,2]. It is well known that the crystallite size, structure and shape of magnetic materials have effects on magnetic properties. The values of M_s for nanoscale materials is lower than that for bulk ones because the spin disorder on the particle surface considerably reduces the total magnetic moment and is strongly affected by the magnetic anisotropy [14]. Moreover, it was reported that the surface oxidation at grain boundaries of nanoparticles probably causes the decrease of saturation magnetization [8]. The decrease in M_s of nickel nanoparticles may also be attributed to the presence of amorphous, nonmagnetic interface as well as the electron exchange between ligands (protective layer) and surface atoms which could also quench the magnetic moment [9].

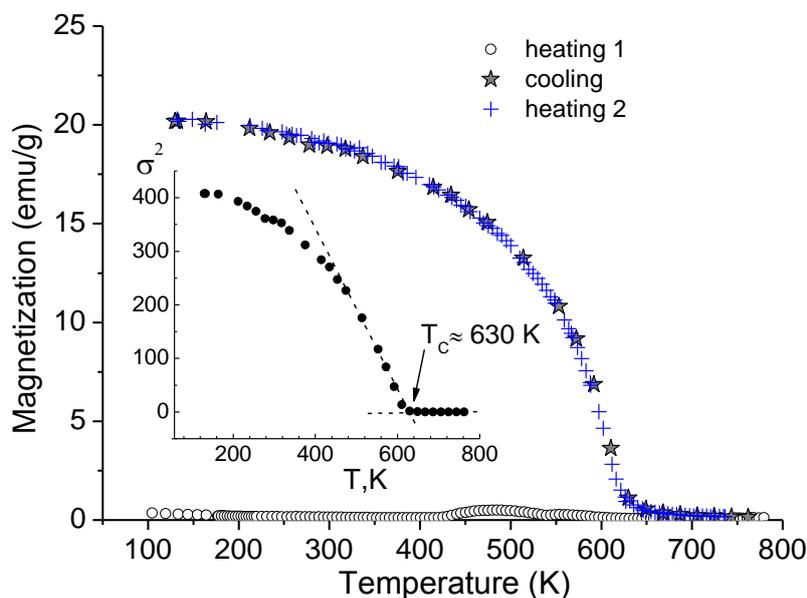


Fig. 3 The plot of magnetization versus temperature for Ni nanoparticles with mean diameter of 4.6 nm

The inset to **Fig. 3** shows the dependence of σ^2 versus temperature (where σ – is the saturation magnetization of as-prepared Ni nanoparticles) and allows to determine Curie temperature (T_C) for nickel that correspond to σ^2 minimum. This value was estimated to be 630 K and is in good agreement with literature data for bulk metal.

4. CONCLUSION

In summary, the facile and efficient rout for producing of nickel nanoparticles by interphase interaction of nickel (II) oleate and sodium borohydride was studied. The reduction reaction was carried out at room temperature using non-toxic precursor. Nickel obtained by such technique was concentrated in an aqueous phase as a black colloidal dispersion. The composition and morphology of the colloid's dispersive phase were investigated by TEM, XRD and IR-spectroscopy. It was shown the dispersive phase of the prepared dispersions represents spherical crystalline metal nickel nanoparticles with average size of 2–8 nm. The stability of nickel colloidal dispersions was achieved by the surfactants formed *in situ* and determined the nanoparticles nucleation conditions. Magnetization versus temperature was measured using a ponderomotive method in the interval from 100 to 800 K. The results showed Ni nanoparticles with a ferromagnetic behavior and saturation magnetization of 20.3 emu/g (in contrast to 54 emu/g for bulk Ni), that may be related to a partial surface particles oxidation.

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