



Phase, size and shape controlled formation of aerosol generated nickel and nickel oxide nanoparticles



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ABSTRACT

Ferromagnetic Ni nanoparticles were formed by a levitation-jet aerosol synthesis under different gas environments and metal precursor feed rates. At a constant background gas inlet temperature, it was found that a higher Ni loading resulted in enhanced particle growth through coalescence. The partial atmosphere favors surface condensation of evaporated Ni atoms over coalescence as the surface area reduction mechanism in the nanoparticles. A flow of 2.5% air in the background gas mixture was enough to oxidize 75% of the initial Ni load, inducing a drastic destabilization of particle size and shape distribution. Regardless of the background inert gas composition, necked nanoparticles were observed in samples prepared with a 1 g/h Ni feed rate, whereas discrete nanoparticles resulted from a higher feed rate of ca. 4 g/h, confirming the key role of Ni loading on the rate of coalescence. The highest saturation magnetization ($51.75 \text{ A m}^2 \text{ kg}^{-1}$ measured at 300 K) and the lowest coercivity (0.008 T) were obtained under an Ar flow. Zero-field cooled and field-cooled magnetization curves measured under an applied field of 10^{-2} T revealed that the blocking processes of nanoparticles are dominated by their particle size distributions, with some features attributable to interparticle interactions.

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1. Introduction

The interest in nickel nanoparticles research mainly comes from their use in catalysis [1–3], although other applications such as energy storage [4] ferrofluids [5], electroanalysis [6], and more recently biology and medicine [7–10], have also been important. Compared to the other ferromagnetic transition metals, a significantly lower number of reports dealing with the synthesis and physicochemical characterization of Ni nanoparticles have been published. Microwave-assisted synthesis, combustion, pulsed laser ablation, vacuum evaporation or chemical precipitation are, among others, some of the methods reported for preparing Ni nanoparticles [11–15]. Within these methods, some make use of surfactants for different purposes, such as preparing core–shell structures [16], controlling size and shape distributions [17] or surface functionalization [18]. Despite these achievements, one of the weak points of these methods is the relatively low saturation magnetization (σ_s) of the final nanoparticles when compared to that of the bulk nickel [19–28]. This feature is central for some novel applications like

magnetically recoverable Ni catalysts for hydrogenation reactions [29], which aims to reduce the costs of metal-based catalysts and eliminate the leaching effect associated with post-reaction filtration procedures by using magnetic filtration. Apart from a high saturation magnetization, both a low coercivity and remanence are also convenient in order to minimize the applied field needed to demagnetize the system and prevent particle agglomeration upon removal of the field.

Saturation magnetization, as an intrinsic magnetic property, is structure insensitive and only depends on the magnitude of the atomic magnetic moments and the number of atoms per unit volume. The most common reason for the reported low σ_s values in metallic (Ni, Fe, Co) nanoparticles is the occurrence of uncontrolled oxidation processes during synthesis, typically leading to the presence of antiferromagnetic oxides, such as NiO, CoO or $\alpha\text{-Fe}_2\text{O}_3$. In the case of Ni, this is a major drawback stemming from its kinetically favoured oxidation [30], which seems to be inherently associated with many deposition methods [6]. In wet-chemical preparations, this issue has been addressed through the incorporation of surfactants or coating agents in the reaction medium at some point [31], but this route is mainly suited for applications in liquid media and often entails a certain performance reduction of the as-synthesized nanoparticles. Furthermore, complete

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removal of surfactants is not always possible and involves additional processing steps [6]. There is then a clear need for a cost-efficient and scalable technique suitable for producing Ni nanoparticles of controllable size and shape while keeping their σ_s as close as possible to the bulk material.

Levitation-jet aerosol synthesis under an inert gas flow allows for simultaneous manipulation of the shape and composition of nanoparticles without the need of further surfactants or capping agents, minimizing the amount of precursors used and generally allowing for a large-scale production of high-purity nanopowders. An important advantage of this technique is that the metal precursor load is melted into a droplet and levitated by the action of a high-frequency (HF) field in an inert gas flow, precluding any contact with surfaces and hence minimizing nanoparticle formation over them. This method is particularly attractive for synthesising stable metallic nanoparticles due to the close control that can be exerted over oxidation processes by adequately manipulating the relevant experimental conditions. Moreover, the reagents involved are kept to a minimum, hence reducing both the chances of side reactions and the necessity of further post-processing stages.

In the present work we report on the successful application of the levitation-jet aerosol synthesis under an inert gas flow for preparing ferromagnetic Ni nanoparticles of various shapes and sizes. The influence of some crucial experimental parameters on the final structural and magnetic properties of the nanoparticles is demonstrated. The latter comprise the composition and flow of the inert gas mixture, as well as the Ni precursor feed rate into the system.

2. Materials and methods

A series of samples were prepared at room temperature by a crucibleless levitation-jet aerosol method in the presence of a gaseous mixture with variable composition. The set of synthetic conditions are summarized in Table 1. A metal droplet levitated inside a thin quartz tube (HF electromagnetic field levitation) and blown up by a gas stream is heated up to melting and vaporization by the action of the field. The laminar gas stream consisted of either Ar (99.987 at.%), He (99.99 at.%), He/air or Ar/air mixtures each supplied at the flow rates indicated in Table 1. The case of an Ar/He mixture is not considered here as it has been previously studied elsewhere [32]. The formation of aerosol nanoparticles takes place in a region around the droplet, where atoms from the evaporated precursors condense and eventually form clusters. In order to sustain the nanoparticle production, the Ni droplet is fed at a constant rate with the metal precursor (Ni, 99.9 at.%) in the form of a 0.2 mm diameter wire.

Crystal structure and phase composition of samples were determined by X-ray diffraction in a DRON-3M diffractometer using Cu K α radiation. Powder Diffraction File (PCPDFWIN ver. 2.02) database was used as the input for Crystallographica Search-Match and PowderCell for Windows programs to perform the XRD phase

Table 1
Gas flow and Ni feeding rate used during the synthesis of the samples.

Sample	S1	S2	S3	S4	S5
Gas mixture flow (l/h)					
He	500	500	0	0	500
Ar	0	0	340	340	0
Air	0	0	0	9	75
Ni feed rate (g/h)	1	3.8	1	1	0.66

Table 2

Main properties of the Ni nanoparticles prepared under different conditions. $\langle d \rangle$ is the average particle size obtained from TEM images, $\langle d_x \rangle$ the crystallite^a size from XRD diffractograms, V_{XRD} the at.% Ni calculated from XRD diffractograms, σ_s the saturation magnetization, V_{MAG} the at.% Ni calculated from magnetometry measurements (see [36]) σ_r the remanent magnetization, H_c the coercive field and S the specific surface area.

Sample	$\langle d \rangle$ (nm)	$\langle d_x \rangle$ (nm)	V_{XRD} (at.% Ni)	V_{MAG} (at.% Ni)	σ_s (Am ² kg ⁻¹)	σ_r (Am ² kg ⁻¹)	$\mu_0 H_c$ (10 ⁻² T)	S (m ² /g)
S1	23.2	18.1	82.8	79.55	45.27	10.68	1.7	18.44
S2	41.1	16.9	83.9	85.97	48.40	13.71	2.4	29.79
S3	87	40.4	99.9	93.24	51.75	4.29	0.8	7.921
S4	56	28.7	21.5	23.22	14.69	3.63	2.2	14.33
S5	11.2	15.1	<5	0.46	0.40	0.05	0.1	72.16

^a The term *crystallite* corresponds here to the size of coherently scattering domains.

analysis. Rietveld analysis of the profiles allowed for determining the Ni/NiO ratio in the nanoparticle powders. Particle size and morphology were studied by transmission electron microscopy (TEM) using a JEOL JEM 1200EX II electron microscope operated at 120 kV. Magnetization measurements at 300 K were made in a 7 T Quantum Design hybrid VSM-SQUID magnetometer, where the samples were mounted into polypropylene sample holders. IUPAC recommendations on reporting and interpreting magnetic properties were followed [33]. A SORBI-M META device was used to obtain the specific surface area (BET) of the nanoparticles from 4-point measurements of nitrogen physisorption.

3. Results

Table 2 summarizes the main parameters extracted from the structural and magnetic characterization. Room temperature XRD diffractograms (Fig. 1) indicate that Ni is present in samples S1 to S4, while NiO appears only in samples (S4 and S5) prepared in the presence of a variable amount of air. No other phases or impurities were detected. A peak broadening effect is observed for samples S1 and S5, those with a smaller crystallite size (d_x) (Table 2).

As seen in TEM images, sample S1 forms a fractal-like arrangement of spheroidal nanoparticles (Fig. 2a; under He and slow Ni feeding), some of which have partially coalesced (Fig. 2b). This particular arrangement is absent in sample S2 (Fig. 2c; He and fast Ni feeding), where the predominant morphology has now changed to hexagonal (Fig. 2d), even more pronounced than that reported for other Ni nanoparticle systems [34]. A higher Ni feed rate increases the average particle size and broadens the size distribution (Fig. 3a and b), furthermore it notably increases the specific surface area (S) compared to sample S1, producing a small increase in the metallic Ni content per sample (Table 2).

The changes introduced by switching to an Ar atmosphere are quite remarkable; the average particle size in sample S3 is bigger than those obtained with a He atmosphere and the size distribu-

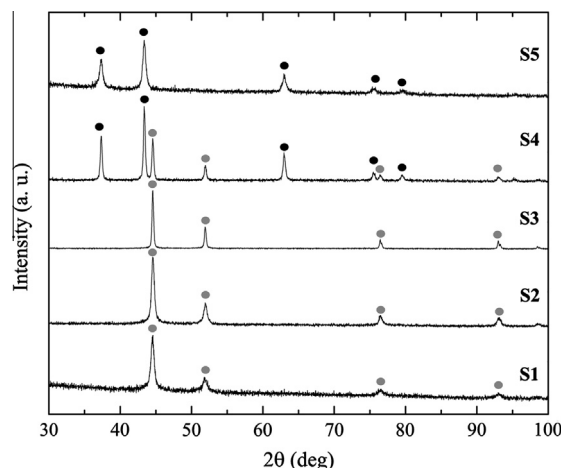


Fig. 1. Room temperature XRD patterns of samples series S1 to S5 indicating the typical peaks of Ni (gray dots, JCPDS card No. 04-0850) and NiO (black dots, JCPDS card No. 73-1519).

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