Conference Paper

Synthesis in Supercritical Ammonia and Characterization of Nanostructured Nickel Oxinitride

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Abstract

Supercritical fluids have shown an increasing interest as reactive media (tunable properties from liquid to gas) to synthesize nanostructured materials by thermal decomposition of inorganic precursors at relatively low pressure and temperature. The particle formation process (nucleation and growth) is made by high supersaturation in the supercritical fluid. So, the adjustment of synthesis process parameters results in a precise control of particle shape, size (between 10 nm and 10 μm), and chemical composition. We present the technique of thermal, chemical-heat, and structural strength treatment of materials to produce nanostructured nickel oxinitride in supercritical ammonia (solvent and reactant) from the thermal decomposition of nickel hexafluroroacetylacetonate (280°C, 18 MPa). A preliminary study concerning magnetic properties of the material was done and a correlation between particle size and magnetic behavior was pointed out.

Keywords: supercritical fluids, decomposition, nucleation, growth, nickel, particle size, magnetic

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Received: 9 September 2016
Accepted: 19 September 2016
Published: 12 October 2016

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Selection and Peer-review under the responsibility of the ASRTU Conference Committee.

1. Introduction

Nowadays, one of the main challenges in materials science concerns the synthesis of nanomaterials, since they exhibit interesting properties that can be different of those of bulk materials. Consequently, numerous processes of nanomaterial synthesis have been investigated aiming to control their size, morphology, structure, and chemical composition.

In laboratory thermal and chemical-heat treatment of materials, structural strength of materials is based on the thermal decomposition of metal precursor and allows to control directly the particle size and morphology with the process parameters: pressure, temperature, residence time, and precursor concentration [1, 2].

After a brief description of the experimental set-up and operating conditions, one example of obtained nanostructured materials is described in terms of chemical composition, crystal structure, morphology, and mean particle size. In the second part, a primary study of the material magnetic properties is presented.

Residence time (s)	Concentration (g/g)	Size distribution (nm)
15	0.002	4.40 ± 2.50

Table 1: Experimental conditions of nickel precursor decomposition in supercritical ammonia (T = 280°C, P =18 MPa, concentration is given in gram per gram of solvent).

2. Methods

Solvent used for experiments is a mixture of anhydrous ammonia (T_C = 132.4°C and P_C = 11.29 MPa) and methanol in the molar proportion 70% NH_3 / 30% methanol. Continuous flow experimental set-up is a tubular reactor (diameter of 1.6 mm, length of metricconverterProductID4.31 m4.31 m) with a flow rate of 11/h [3]. Pressure was about 18 MPa and temperature was 280°C in order to perform thermal decomposition of nickel precursor (nickel (II) hexafluroroacetylacetonate, Ni $(hfac)_2$). Optimal decomposition temperature was determined by in situ UV-visible spectroscopy. Experimental data are reported in Table 1.

Physico-chemical characterization of materials was carried out by chemical analysis, thermogravimetric analysis (TGA) coupled with mass spectroscopy, conventional X-ray powder diffraction (XRD: CuKα radiation), and structural rectification [4]. Powder morphology was observed by scanning electron microscopy (SEM, JEOL 840), and transmission electron microscopy in dark field (TEM, JEOL 2000FX). Size distributions were determined by manual counting.

Chemical analysis and structural rectification were used to determine the chemical composition and structure of the synthetized material. These characterizations show that a nickel oxinitride was synthesized with the $Ni_3NO_{0.18}$composition corresponding to the $P6_322$ space group with a hexagonal unit cell (a = 4.6233 and c = 4.3084).

Experimental and theoretical XRD patterns of $Ni_3NO_{0.18}$ are presented in Figure 1.

The structure rectification shows that oxygen atoms are inserted inside the nickel nitride structure (Ni_3N) in position 2d with a proportion of 18%. Unit cell of nickel oxinitride is presented in Figure 2.

Powders are composed of shapeless aggregates, constituted by crystallized nanoparticles. Aggregates were observed by SEM and nanoparticles by TEM in dark field (Fig. 3). To summarize this part, homogeneous powders constituted of aggregated nanoparticles were obtained.

3. Results

Magnetic measurements were performed with a SQUID at 0°C. Two samples with studied: initial sample (4.4 nm); annealed sample (250 nm).

Annealed sample was obtained by thermal treatment of the initial sample under ammonia atmosphere (1 MPa) during 3 hours at 250°C in order to increase crystal size without changing the structure. Thermal treatment modified sample particle size: starting with particles aggregated with an elementary size of 4.4 nm in average,

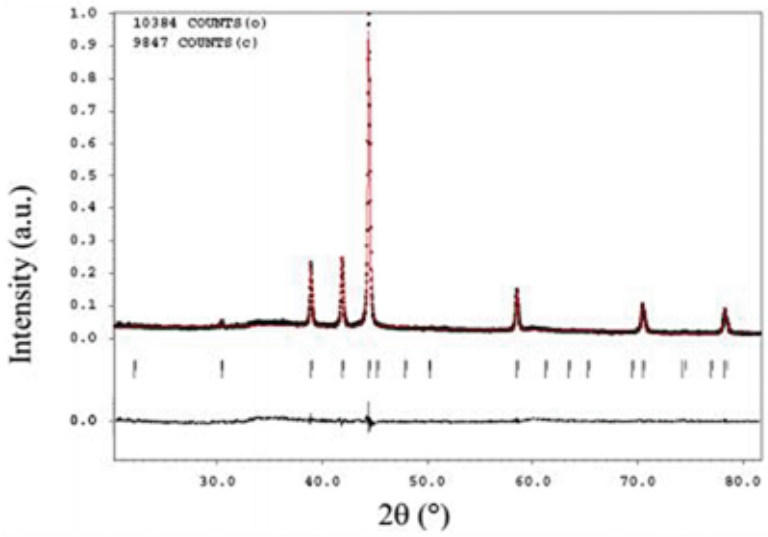

Figure 1: Experimental (black) and theoretical (red) XRD patterns of $Ni_3NO_{0.18}$.

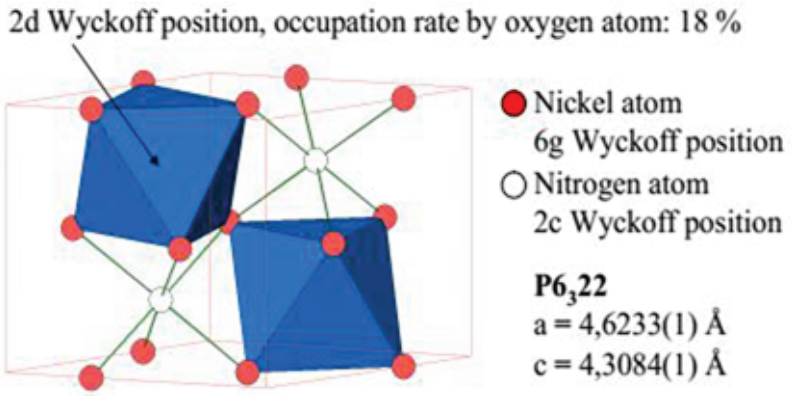

Figure 2: Unit cell of nickel oxinitride $Ni_3NO_{0.18}$ determined with structural refinement.

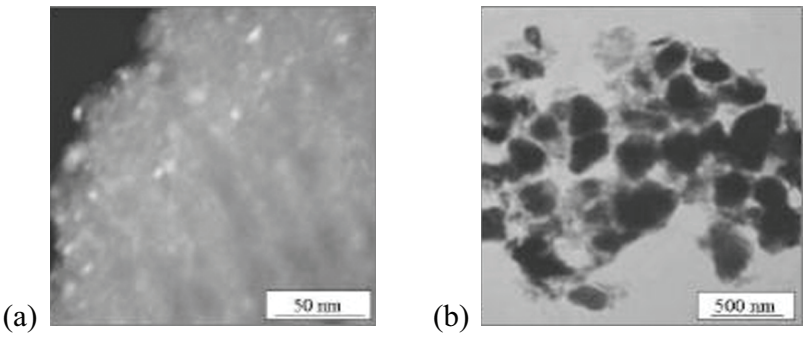

Figure 3: TEM pictures of studied sample: (a) initial sample: aggregates constituted of 4.4 nm nanoparticles in size (dark field); (b) annealed sample: isolated monodispersed crystals with a size of 250 nm (clear field).

isolated monodispersed crystals with a size distribution of 250 nm were obtained. TEM pictures of these samples were presented in Figure 3. We can notify that material structure did not change during the thermal treatment (the same unit cell parameters). The main characteristics of these samples and their magnetic properties are reported in Table 2 and Figure 5.

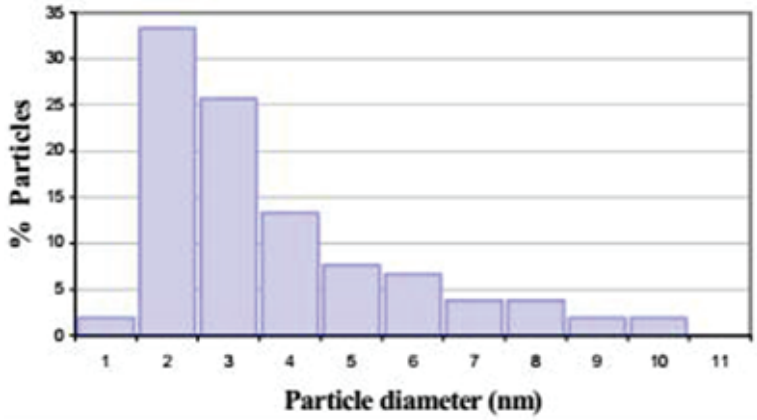

Figure 4: Histogram of studied sample.

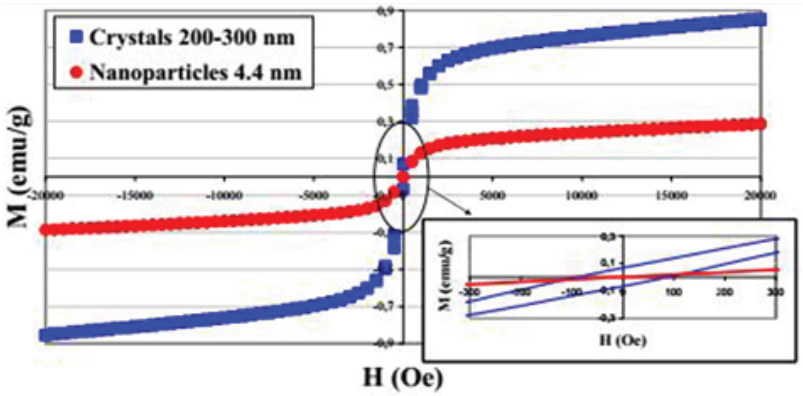

Figure 5: Magnetization evolution versus applied magnetic field at 0°C. Influence of the particle size on magnetic properties.

4. Conclusion

We have synthesized nanoparticles of nickel oxinitride by thermal decomposition of nickel hexafluroroacetylacetonate in supercritical ammonia, used here as solvent and reactant. Nickel oxinitride crystallized in the $P6_322$ space group with a hexagonal unit cell (a = 4.6233Å and c = 4.3084Å) with the chemical composition $Ni_3NO_{0.18}$.

Sample	Particle size (nm)	Unit cell Parameters (Å)	Magnetic behavior at 0°C		
			σ_s(emu/g)	R	H_c(Oe)
Initial	4.4 ± 2.5	a = 4.587	0.29	0.012	18
		c = 4.334			
Annealed	250 ± 50	a = 4.586	0.85	0.080	87
		c = 4.331			

Table 2: Morphological, structural, and magnetic properties. σ_s – saturation magnetization, R – remanent ratio (ratio = magnetization at 0 Oe/magnetization 20000 Oe), H_c – coercive field).

This preliminary study of magnetic properties of $Ni_3NO_{0.18}$ has shown that this material presents a ferromagnetic behavior. Moreover, these magnetic properties are influenced by the particle size and the transition of the ferromagnetic state to the superparamagnetic one is put in evidence.

References

[1] V. Pessey, R. Garriga, F. Weill, B. Chevalier, J. Etourneau, and F. Cansell, Control of particle growth by chemical transformation in supercritical CO2/ethanol mixtures, *Journal of Materials Chemistry*, **12**, no. 4, 958–965, (2002).

[2] V. Pessev, Elaboration de poudres inorganiques nanostructurees en milieux fluides supercritiques, in *Physico chemistry*, 1, Bordeaux, 2000.

[3] F. Cansell, C. Aymonier, and A. Loppinet-Serani, Review on materials science and supercritical fluids, *Current Opinion in Solid State and Materials Science*, **7**, no. 4-5, 331–340, (2003).

[4] V. Petricek and M. Dusek, (2000)., Physical Institute, .

[5] NS. Gajbhiye, RS. Ningthoujam, and J. Phys, *J. Phys. Stat. Sol. A*, **189**, 691–695, (2002).

[6] L. Neel, *Theorie du trainage magnetique des ferromagnetiques en grains fins avec applications aux terres cuites*, **5**, Theorie du trainage magnetique des ferromagnetiques en grains fins avec applications aux terres cuites, Ann. Geophys, 1949.