SYNTHESIS IN SUPERCRITICAL AMMONIA AND CHARACTERIZATION OF NANOSTRUCTURED NICKEL OXINITRIDE

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Supercritical fluids have shown an increasing interest as reactive media (tuneable 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 governed by high supersaturation in the supercritical fluid. So the adjustement of synthesis process parameters results in a precise control of particle shape, size (between 10 nm and 10 μm) and chemical composition.
In this communication, we will present the process developed at ICMCB to produce nanostructured nickel oxinitride in supercritical ammonia (solvent and reactant) from the thermal decomposition of nickel hexafluoroacetylacetonate (280°C, 18MPa). A preliminary study concerning magnetic properties of the material was done and pointed out a correlation between particle size and magnetic behaviour.

INTRODUCTION

Today 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 process of nanomaterial synthesis have been investigated aiming to control their size, morphology, structure and chemical composition.
In this context, supercritical processes are an interesting alternative to synthesize nanomaterials. There are two main routes of material synthesis in supercritical media: processes using a physical transformation (RESS, GAS, ...) and less commonly processes using a chemical transformation of metal precursors in a supercritical fluid.

ICMCB process 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, precursor concentration [1, 2].
This study refers to the chemical transformation of nickel hexafluoroacetylacetonate in supercritical ammonia.

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

I- DECOMPOSITION OF A NICKEL PRECURSOR IN SUPERCRITICAL AMMONIA

I.1 Operating conditions

Solvent used for the 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 4.31 m) with a flow rate of 1 l/h [3]. Pressure was about 18 MPa and temperature was of 280 °C in order to perform thermal decomposition of nickel precursor (nickel(II) hexafluoroacetylacetonate, $Ni(hfac)_2$). Optimal decomposition temperature was determined by in situ UV-visible spectroscopy. Experimental conditions are reported in Table 1.

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

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

I.2 Characterization

Physico-chemical characterisation of materials was carried out by: i) chemical analysis, thermogravimetric analyses (TGA) coupled with mass spectroscopy; ii) conventional X-Ray powder diffraction (XRD: CuK_α radiation) and structural refinment [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.

I.2.1 Chemical composition and structure

Chemical analysis and structural refinment permit us 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 Å and c = 4.3084 Å).
Experimental and theoretical XRD patterns of $Ni_3NO_{0.18}$ are presented in Figure 1.

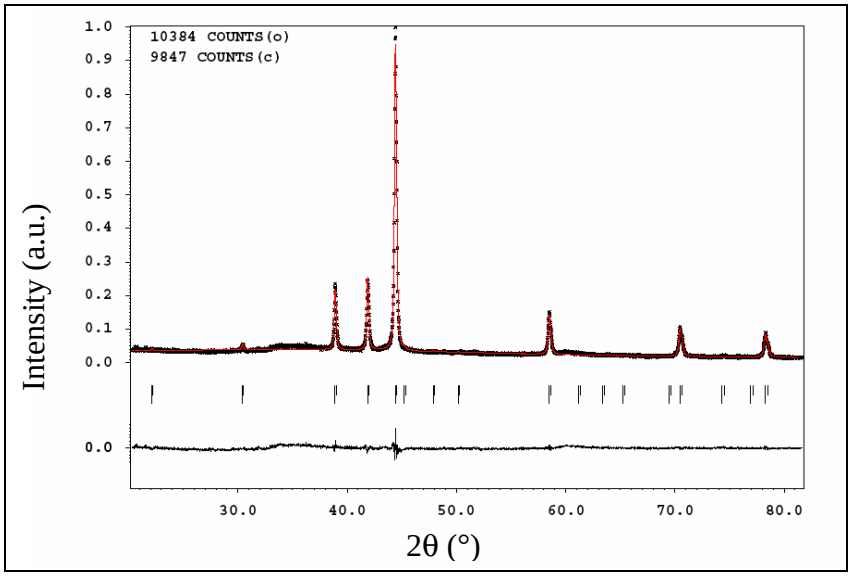


***Figure 1**: Experimental (in black) and theoretical (in red) XRD patterns of $Ni_3NO_{0.18}$.*

The structure refinment shows that oxygen atoms are insert 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.

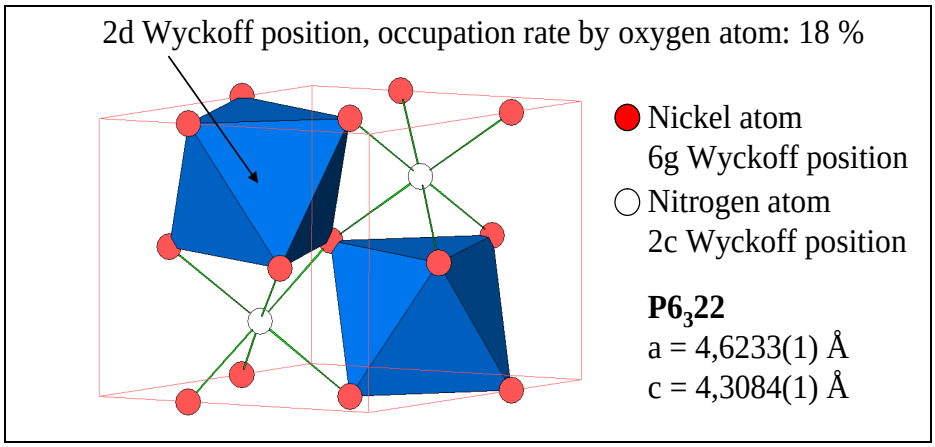
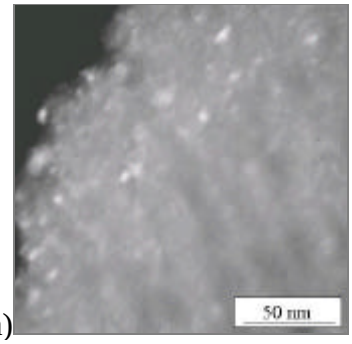


***Figure 2**: Unit cell of nickel oxinitride, $Ni_3NO_{0.18}$ determined with structural refinement.*

I.2.2 Powder morphology and particle size

Powders are composed of shapeless aggregates, constituted by crystallized nanoparticles. Aggregates were observed by SEM and nanoparticles by TEM in dark field. An example is presented in Figure 3.

a) 

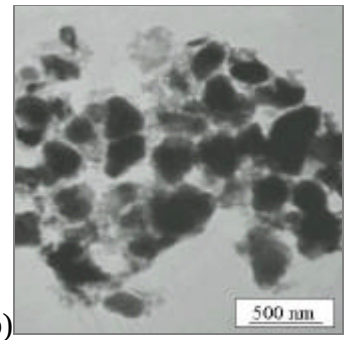
b) 

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

The particle size distribution of initial sample is presented in the following histogram (Figure 4). The mean particle size is of 4.4±2.5 nm (Table 1).

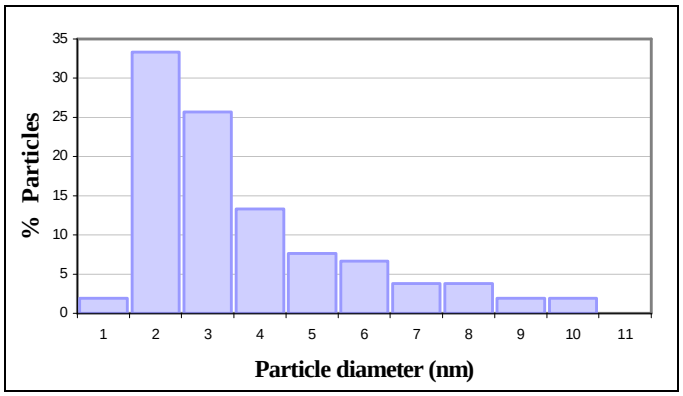


***Figure 4**: Histogram of studied sample*

To summarize this part, homogeneous powders constituted of aggregated nanoparticles were obtained.

II- PRELIMINARY STUDY OF NICKEL OXINITRIDE $Ni_3NO_{0.18}$ MAGNETIC PROPERTIES

Magnetic measurements were performed with a SQUID at 0°C. Two samples were studied: i) initial sample (4.4 nm), ii) annealing sample (250 nm). Annealing 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 nanoparticles aggregated with an elementary size of 4.4 nm in average, isolated monodispersed crystals with a size distribution of 250 nm were obtained. TEM pictures of these samples are presented in Figure 3. We can notify that material structure did not changed during the thermal treatment (same unit cell parameters).

The main characteristics of these samples and their magnetic properties are reported in Table 2 and Figure 5.

***Table 2**: Morphological, structural and magnetic properties. (s_s, saturation magnetization, R, remanence ratio (ratio=magnetization at 0 Oe/ magnetization at 20000 Oe) and H_c, coercivity)*

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

Nickel oxinitride shows a ferromagnetic behaviour [5]. This ferromagnetic behaviour is observed with the particles of 250 nm. The difference of the magnetic properties between our sample and the referenced one ([5]) can be explained by the insertion of oxygen in the Ni_3N cell. For the smallest particles (4.4 nm), the coercitivity and the remanence ratio decrease and tend toward the superparamagnetic behaviour. This phenomenon was already put in evidence [6].

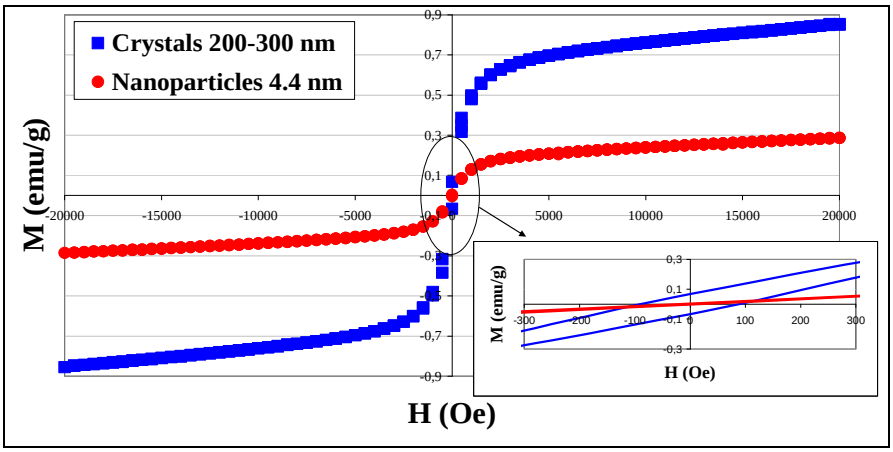


***Figure 5**: Magnetization evolution versus imposed magnetic field at 0°C. Particle size influence on magnetic properties.*

CONCLUSION

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

This preliminary study of magnetic properties of $Ni_3NO_{0,18}$ has shown that this material presents a ferromagnetic behaviour. 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] PESSEY, V., GARRIGA, R., WEILL, F., CHEVALIER, B., ETOURNEAU, J., CANSELL, F., Control of particle growth by chemical transformation in supercritical CO2/ethanol mixture,. J. Mater. Chem., Vol. 12(4), **2002**, p. 958-965.

[2] PESSEY, V., Elaboration de poudres inorganiques nanostructurées en milieux fluides supercritiques, Physico-chemistry. **2000**, Bordeaux 1.

[3] CANSELL, F., AYMONIER, C., SERANI, A., Review an materials science and supercritical fluids, Current Opinion in Solid State & Materials Science, in press.

[4] PETRICEK, V., DUSEK, M., *JANA2000* , Physical Institut, Prague, Czech Republic.

[5] GAJBHIYE, N.S., NINGTHOUJAM, R.S., WEISSMÜLLER, J., Phys. Stat. Sol. A, Vol 189, **2002**, p.691-695.

[6] NEEL, L., Théorie du traînage magnétique des ferromagnétiques en grains fins avec applications aux terres cuites. Ann. Géophys.,5, **1949**, p. 99-136.