# Influence of Synthesis Parameters of FeNi<sub>3</sub> Alloy Nanoparticles Obtained by Chemical Reduction Method in Aqueous Solution

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This paper reports the synthesis of FeNi<sub>a</sub> alloy nanoparticles by chemical reduction of the Fe<sup>2+</sup> and N<sup>2+</sup> ions, from the corresponding chlorides, with hydrazine ( $N_2H_4$ · $H_2O$ ) as a reducing agent in aqueous solution at room temperature by modifying the molar ratio of the fons Fe<sup>2+</sup>: N<sup>2+</sup>, reaction time, with and without amine-type growth promoter, and reducing both, with or without ultrasonic aid. The FeNi<sub>3</sub> alloy nanoparticles have been investigated by XRD, EDS spectrum analysis, SEM and VSM. When the molar ratio of Fe<sup>2+</sup> and N<sup>2+</sup> is equal to 1:3, reducing both, with or without ultrasonic aid, Fe<sup>2+</sup> and N<sup>2+</sup> were completely reduced into Fe and Ni, resulting FeNi<sub>3</sub> alloy with a face-centered cubic (fcc) crystal structure. EDS analysis supported the presence of metal ions in atomic weight corresponding to the stoichiometric ratio of initial reaction. SEM analysis showed that nanoparticles of FeNi<sub>3</sub> alloy nanoparticles at room temperature.

Keywords: FeNi, alloy, reduction method, magnetic properties, saturation magnetization

In the past decades, transition metal alloys, especially iron-nickel alloys, have been extensively studied due to their magnetic properties useful for applications in electrical and electronic devices such as antennas, transformers, recording heads and magnetic sensors, etc. [1, 2]. FeNi, alloy nanoparticles are part of the class of soft magnetic materials with high saturation magnetisation and low coercivity, which have been successfully applied in areas with high frequency and low losses applications, as materials for absorbing electromagnetic waves [3], energy storage [4] or hyperthermia [5]. The size and shape of magnetic nanoparticles are considered to be two of the most important features that affect the magnetic properties of nanoparticles. In the case of metal alloy nanoparticles, it is possible to fine-tune the interdependence between structure and properties through processing parameters. Chemical processing must control composition, phase purity, morphology, particle size, aggregation, and size distribution. Also for a safe reproducibility of the desired characteristics, it is necessary to establish optimal parameters for nanoparticles synthesis by the desired processing method. Thus, for the synthesis of magnetic metallic nanoparticles with controlled shape and size, additional efforts are needed to control experimental conditions. Therefore, additional efforts are needed to control experimental conditions for the synthesis of magnetic nanoparticles with controlled shape and size. FeNi, alloy nanoparticles were prepared by various methods such as: mechanical alloy [6, 7], chemical reduction in solution [8, 9], sol-gel combined with H, reduction [10], sol-gel autocombustion [11], sol-gel method [12], sol-gel route with benzyl alcohol [13], coprecipitation [14], chemical reduction based on the polyol process [15], reverse micelle technique [16], thermal decomposition of carbonyl compounds [17], hydrothermal reduction [18], to microwave assisted synthesis [19].

In this study, nanoparticles of FeNi<sub>3</sub> alloy were prepared by a chemical reduction process in aqueous solution using hydrazine as reducing agent. The influence of the different synthesis conditions on the structural, morphological and magnetic properties were also investigated in order to establish optimal parameters for the synthesis of FeNi, alloy nanoparticles powder with predefined properties in the mass conditions.

# **Experimental part**

#### Materials

Iron (II) Chloride Tetrahydrate FeCl<sub>2</sub>·4H<sub>2</sub>O ( $\geq$ 98 %) purchased from SIGMA-ALDRICH and Nichel Chloride Hexahydrate NiCl<sub>2</sub>·6H<sub>2</sub>O ( $\geq$ 98 %) from CHEMICAL COMPANY were used as reagents. Sodium Hydroxide NaOH (98 %), Hydrazine Hydrate NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O (65 %) and Hexadecylamine CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>NH<sub>2</sub> (98 %) from SIGMA-ALDRICH, Ethylic Alcohol Absolute C<sub>2</sub>H<sub>5</sub>OH (99.9 %) purchased from MERCK and Deionized Ultrapure Water, obtained from a Millipore Simplicity - UV equipment.

## Synthesis of FeNi<sub>3</sub> alloy nanoparticles

The FeNi, alloy nanoparticles were prepared by chemical reduction of the Fe<sup>2+</sup> and Ni<sup>2+</sup> ions chlorides, with hydrazine  $(N_2H_4\cdot H_2O)$  as a reducing agent in aqueous solution in the basic medium (in presence of NaOH) and at room temperature. Various synthesis parameters are presented in table 1.

FeCl<sub>2</sub>·4H<sub>2</sub>O (as Fe precursor) and NiCl<sub>2</sub>· 6H<sub>2</sub>O (as a Ni precursor) in the different molar ratio of the ions of Fe<sup>2+</sup> and Ni<sup>2+</sup> (table 1) were dissolved in deionized water to form solution of 0.5% concentration . The solution of the mixture of the two metals salts was moderately stirred until complete salts dissolution and then a volume of NaOH solution (50% concentration) was added until pH = 12 was reached. After this, at the solution mixture a volume of 6 mL of aqueous hydrazine (65% concentration) was rapidly added. The reaction mixture was magnetically stirred (at 600 rpm) at room temperature for 1h and then it was allowed to react without magnetic stirring at room temperature time for 20 h. The black precipitate formed was magnetically separated, washed three times with deionized water and with absolute ethylic alcohol at the end, then it was dried at temperature of 100°C in air.

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Sample	Molar ratio Fe <sup>2+</sup> : Ni <sup>2+</sup>	Reaction time (h)	Reduction reaction conditions	Growth agent
S1	1:3	22	hydrazine , pH =12, room temperature	-
\$2	1:1	22	hydrazine, pH =12, room temperature	-
S3	3:1	22	hydrazine, pH =12, room temperature	-
S4	1:3	22	hydrazine, pH =12, room temperature	hexadecylamine
<b>S</b> 5	1:3	2	hydrazine , pH =12, room temperature, ultrasonic	hexadecylamine

 Table 1

 SYNTHESIS PARAMETERS OF FeNi<sub>3</sub>

 ALLOY NANOPARTICLES SAMPLES.

For the synthesis of the FeNi<sub>3</sub> alloy nanoparticles with the 1:3 molar ratio of the Fe<sup>2+</sup>:  $Ni^{2+}$  ions in presence of hexadecylamine, first a 0.25M solution was prepared by dissolving hexadecylamine in absolute ethanol at room temperature. Then 10 mL of the hexadecylamine solution was added to the mixture of the two metal salts in the molar ratio of Fe: Ni of 1: 3.The reduction process was carried out respecting the above-described procedure.

Synthesis of the FeNi<sub>3</sub> alloy nanoparticles with the 1:3 molar ratio of the Fe<sup>2+</sup>: Ni<sup>2+</sup> ions in presence of hexadecylamine and the reducing process ultrasonic assisted (at 65 KHz) was performed similarly but in this case the reducing time of the reaction was reduced to only 2h.

## **Characterization**

The powder of FeNi, nanoparticles was characterized by X-ray diffraction (XRD) analysis for the determination of the crystallographic structure, estimation of crystallite size and lattice parameter. The X-ray diffraction pattern of the powder samples was recorded on a D8 Discover, Bruker-AXS (Germany) diffractometer with CuK $\alpha$  (1.5406Å) at room temperature in the range of 10 to 100° in the 20 scale, with a scanning speed of 0.04°/s and a time step of 10s. The morphology and particle size of samples as prepared were investigated by FESEM-FIB (Workstation Auriga) scanning electron microscope equipped with a dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments). Chemical compositions were estimated by an area analysis using energy dispersive X-ray spectroscopy (EDS) system. The magnetic properties of the FeNi, samples were measured with a vibrating - sample magnetometer (VSM) Lake Shore 7300 model at room temperature.

# **Results and discussions**

## X-ray analysis

The XRD patterns of the samples of FeNi<sub>3</sub> alloy nanoparticles powder as obtained with different molar ratio of Fe<sup>2+</sup>: Ni<sup>2+</sup> was showed in figure 1 (a) - (c). When the molar ratio of Fe<sup>2+</sup>: Ni<sup>2+</sup> is 1:3 (sample S1),

When the molar ratio of  $Fe^{2+}$ : Ni<sup>2+</sup> is 1:3 (sample S1), from the X-ray diffraction pattern, figur e 1 (a) reveals five peaks at 2 $\theta$  of 44.038°, 51.307°, 75.674°, 92.080° and 97.488°, corresponding of the crystalline planes (111), (200), (220), (311) and (222) characteristics of fcc structure - FeNi<sub>3</sub>, F<sub>m</sub>-3<sub>m</sub> (225) space group in according with ICDD PDF 2 database file number PDF 01-071-8324. It was not noticed other specific peaks for nickel oxides, (FCC)-Ni, Fe<sub>2</sub>O<sub>3</sub>, alfa-Fe or other impurity in the XRD pattern, concluding that at this molar ratio the obtained nanoparticles contains pure FeNi<sub>3</sub> phase with cubic structure. The reduction reaction proceeds according to the following equation:

$$3Ni^{2+} + Fe^{2+} + 2N_2H_4 + 8OH \rightarrow FeNi_3 + 2N_2 + 8H_2O$$

$$(pH = 12)$$
(1)





The crystallite size was obtained using Debye-Scherer equation (2) taking into account the main peak (111):

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{2}$$

where: D is the crystallite mean size,  $\lambda = 1.5406$  Å is the wavelength of the X-rays, B is the full width at half maximum (FWHM) of the peak and  $\theta$  is the Bragg angle. The calculated crystal size was of 12 nm.

Increasing Fe<sup>2+</sup> content to the molar ratio Fe<sup>2+</sup> : Ni<sup>2+</sup> of 1 : 1 (sample S2) (fig.1b) it was noticed the presence of six additional peaks at 20 of 30.086°, 35.447°, 53.545°, 57.094°, 62.639° and 90.071°, which correspond to the crystalline planes (220), (311), (422), (511), (400), (731) of the fcc Fe<sub>3</sub>O<sub>4</sub> structure, F<sub>4</sub>-3m(227) space group according to ICDD PDF 01-071-6336, along with those four characteristic peaks at 20 of 43.950°, 51.185°, 75.450° and 91.685° associated with the crystalline planes (111), (200) (220) and (311) of the fcc FeNi<sub>3</sub> structure, F<sub>m</sub>3<sub>m</sub>(225) space group (according to ICDD PDF 01-071-8324).

Reducing the Ni<sup>2+</sup> content to a Fe<sup>2+</sup>: Ni<sup>2+</sup> molar ratio of 3:1 (sample S3) figure 1 (c) results in the main formation of the Fe<sub>3</sub>O<sub>4</sub> phase with fcc structure and only two weak peaks of fcc FeNi<sub>3</sub> of the (111) and (200) crystallographic

planes are present in the X-ray pattern. This result reveals that  $Fe^{2+}$  is more likely to be oxidized to  $Fe^{3+}$  resulting in  $Fe_3O_4$  and a very small fraction is reduced to Fe and a small trace of  $FeNi_3$  was detected. Similar results have been reported also in other papers [1, 20].

Figure 2 (a) shows the X-ray diffractogram for the sample S4 prepared keeping the same synthesis parameters as for sample S1, but reduction process with hydrazine was performed in the presence of hexadecylamine. It is noticed the presence of five peaks at the 20 of 44.138°, 51.423°, 75.702°, 92.201° and 97.469° which are associated with the crystalline planes of the fcc FeNi<sub>3</sub> structure (PDF 01-071-8324). Other four peaks are present here at 20 of 30.069°, 35.414°, 56.951° and 62.606° assigned to Fe<sub>3</sub>O<sub>4</sub> phase indexed according to the PDF 01-071-6336, which leads to the conclusion that in presence of hexadecylamine the Fe<sup>2+</sup> reduction is not totally achieved, a small amount is oxidized, Fe<sub>3</sub>O<sub>4</sub> phase being present along with the FeNi<sub>3</sub> one.

The X-ray diffraction pattern of the S5 sample is shown in figure 2 (b). In this experiment reduction of Fe<sup>2+</sup> and Ni<sup>2+</sup> to Fe and Ni in solution, with hydrazine and hexadecylamine, ultrasound assisted leads to the formation of a pure FeNi<sub>3</sub> phase. The characteristic peaks at 2 $\theta$  of 44.182°, 51.462°, 75.855°, 92.225° and 97.569° are sharp,



Fig. 2 X-ray powder diffraction patterns for FeNi<sub>3</sub> alloy nanoparticles samples prepared in the molar ratio of Fe<sup>2+</sup>:Ni<sup>2+</sup> = 1:3, in the presence of hexadecylamine and reduction: (a) without ultrasound assistance and (b) ultrasonic assisted reduction

Table 2										
THE RESULTS OF XRD	ANALYSIS FOR PREPAREI	) FeNi	, ALLOY NAM	VOPARTICLES						

Sample	Curretelline phase	Lattice parameter		Crystallite size
Sample	Crystanne phase	ateor (A)	aexp (A)	(nm)
S1	FeNi <sub>3</sub> - face centered cubic structure, space group Fm-3m(225)	3.555	3.559	12
S2	FeNi <sub>3</sub> - face centered cubic structure, space group Fm-3m(225)	3.555	3.565	26
	Fe <sub>3</sub> O <sub>4</sub> - centered cubic structure, space group F <sub>d</sub> - 3 <sub>m</sub> (227)	8.378	8.378	25
S3	FeNi <sub>3</sub> - face centered cubic structure, space group Fm-3m(225)	3.555	3.572	18
	Fe <sub>3</sub> O <sub>4</sub> - centered cubic structure, space group F <sub>d</sub> - 3 <sub>m</sub> (227)	8.378	8.064	33
S4	FeNi <sub>3</sub> - face centered cubic structure, space group Fm-3m(225)	3.555	3.551	13
	Fe <sub>3</sub> O <sub>4</sub> - face centered cubic structure, space group F <sub>d</sub> -3 <sub>m</sub> (227)	8.378	8.399	13
<b>S</b> 5	FeNi <sub>3</sub> - face centered cubic structure, space group Fm-3m(225)	3.555	3.547	16

which means that the  $\text{FeNi}_3$  nanoparticles are better crystallized and a larger crystalline size is achieved (16 nm).

The results of XRD analysis for the prepared samples are summarized in table 2. *EDS-analysis* 

The results of the EDS analysis performed on FeNi<sub>3</sub> nanoparticles obtained by chemical reduction of the two metals chlorides in the aqueous solution at room temperature, ranging the experimental parameters and the synthesis conditions are presented in figure 3 (a) - (e).

All five EDS spectra, reveals the presence of the Fe and <u>Ni, corresponding to the a</u>tomic weight of the elements in



Fig. 3 Results of EDS analysis for the prepared FeNi<sub>3</sub> alloy nanoparticles samples

the initial synthesis. Together with Fe and Ni peaks it is also noticed the presence of the Oxygen, as presented in figure 3 (a), (d) and (e) and its low weight ratio may be due to the formation of a weak oxidation layer on the surface of the FeNi<sub>3</sub> alloy nanoparticles [21]. The presence of a small amount of C detected in the spectra in figure 3 (d) may be due to the impurities due to the presence of the trace of the amine remaining after washing.

the amine remaining after washing. The highest amount of Oxygen in the reported spectra in figure 3 (b) and (c) can be explained by the presence of the  $Fe_3O_4$  phase together with  $FeNi_3$  one. The result is consistent with the XRD analysis.

## SEM analysis

The SEM images of the synthesized FeNi<sub>3</sub> alloy nanoparticles powder are presented in figure 4 (a) - (e). From the analysis of SEM images it results that the synthesis parameters clearly influence the morphology and particle size distribution of the synthesized FeNi<sub>3</sub> alloy nanoparticles. The SEM image of figure 4 (a) shows a spherical structural morphology with a wide range of size distribution from 60 to about 180 nm. Due to the magnetic interaction of crystallites of approximately 10-15 nm leads to nanospheres occurrence, which is in agreement with the XRD results. The SEM image of figure 4 (b) and (c) also show the formation of spherical form resulting from the aggregation of spherical crystallites representing the structural phase of FeNi<sub>3</sub> alloy and polyedric sheets representing the phase of Fe<sub>3</sub>O<sub>4</sub> as shown by XRD analysis.

In figure 4 (d) and figure 4 (e) is presented the influence of hexadecylamine on the dimensions and the morphological aspect of the FeNi<sub>3</sub> alloy nanoparticles. Therefore, the hexadecylamine in the process of reducing of the two metals chlorides, with hydrazine, at room temperature for 20 h reaction time, leads to the formation of spherical structures with a mace look and dimensions in the range of 370 - 470 nm (fig.4 (d)). The nanospheres are formed by the aggregation of the pyramidal crystals with the sizes of 20 - 53 nm.

Through the assisted ultrasonic reduction process with reduced reaction time (fig. 4(e)) similar morphology of the nanospheres is obtained, but smaller size, in range of 200 nm to at 400 nm. In this case ultrasounds help the crystallization process, the nanospheres being formed by the aggregation of the pyramidal sharp crystals with dimensions up to 75 nm. *VSM analysis* 





Figure 5 (a)-(b) shows the magnetization vs. magnetic field loops measured at room temperature for all the five samples of the FeNi<sub>3</sub> alloy nanoparticles as prepared. Hysteresis loops show that the nanoparticles have ferromagnetic behaviour at room temperature.

Table 3 shows the magnetic parameters of the FeNi<sub>3</sub> alloy nanoparticles sample. The saturation magnetization values are less than the FeNi<sub>3</sub> bulk value (125 emu/g). This reduction of the saturation magnetization (Ms) is explained by the particle size reduction or surface disorder [21]. The Ms value increases with increasing of Fe content, the highest Ms value of 82.05 emu/g was obtained for sample S2 in which the Fe: Ni atomic ratio is 1: 1. The lower Ms for sample S3 in comparison with sample S2 may be due to the presence in their composition of the majority phase Fe<sub>3</sub>O<sub>4</sub>. The reduction of Ms for sample S4 compared to S1 and S2 can be explained by the additional contribution of the C impurities presence. The Ms value of 70.4 emu/g of sample

S1 can be explained by the increase of the specific area due to the ultrasound-induced increase of crystals.

The large coercivity of FeNi<sub>3</sub> alloy nanoparticles samples compared to that of the FeNi<sub>3</sub> bulk (0.5 Oe) is due to large intrinsic magnetocrystalline anisotropy of intermetalic compound [22]. Also high coercivity can be explained by the presence of a magnetic inert layer on their surface with an oxide layer in accordance with the EDS analysis [23].

The  $M_r/M_s$  ratio of synthesized FeNi<sub>3</sub> alloy is less than 0.5, indicating a relatively low inter-particle distance between FeNi<sub>3</sub> alloy nanoparticles [24].

## Conclusions

The synthesis conditions by chemical reduction in aqueous solution are important on the structural, morphology, size and magnetic behaviour of FeNi<sub>3</sub> alloy nanoparticles processing. Only for the 1:3 molar ratio of Fe<sup>2+</sup>: Ni<sup>2+</sup> it was obtained a pure FeNi<sub>3</sub> fcc crystalline phase. In the reducing process the total reaction time is reduced from 20h to only 2h when ultrasound assisted. The

hexadecylamine growth agent contributes to the morphological development of mace like spherical structures and the decrease of their size when ultrasound assisted reducing process is used. The magnetic properties of the FeNi<sub>3</sub> showed a soft ferromagnetic behaviour at room temperature. The highest value of M<sub>s</sub> it is reported for sample S2, of 82.05 emu/g. It can be concluded that by controlling the synthesis conditions it is possible to obtain FeNi<sub>3</sub> nanoparticles with predefined properties at low costs.

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