

MAGNETIC AND TEXTURAL STUDIES OF XEROGEL AND AEROGEL NANOCOMPOSITES FORMED BY Ni FERRITES DISPERSED IN SILICA MATRIX

Nelcy D. S. Mohallem¹ and Juliana Batista da Silva^{1,2}

¹Laboratório de Materiais Nanoestruturados, DQ/ICEX – UFMG, 31270-450, Belo Horizonte, MG, Brazil

²CDTN/CNEN –30123-970, Belo Horizonte, MG, Brazil,

nelcy@ufmg.br

Introduction

Nickel ferrites have been extensively studied due to their numerous applications in electronic devices, microwave adsorbents, corrosion protectors, magnetic fluids and catalysts [1-5], among others. Nickel ferrite is a soft material with inverted spinel with the tetrahedral site (A) occupied by Fe³⁺ and the octahedral site occupied by Fe³⁺ and Ni²⁺. It is applied to devices that require easy magnetization and demagnetization to produce high magnetic flux and magnetic induction by an external field [3]. Usually, nickel ferrites is synthesized as dispersed particles or nanoparticles, but these kind of materials have a strong tendency to aggregate, mainly when these particles have nanometric dimension. The dispersion of ferrites in an inert matrix reduces particle agglomeration and controls the particle distribution. This procedure reduces energy loss of the material and provokes coupling effects, with resulting property enhancement. Important materials to be used as inert matrices are silica xerogels and aerogels obtained by sol-gel process.

Previous paper on nanocomposites prepared by the sol-gel process indicated that there is no direct interaction between the silica oxide and the ferrites [6], which could influence the properties of the nanocomposites. In the absence of such interactions, the distribution of the nanoparticles depends on the pore structure of the matrix network, which affects the maximum size of particles formed. The drying step also plays an important role in determining the final pore structure of the materials obtained by sol-gel. When the solvent is slowly removed from the wet gel at room pressure and temperature, the xerogel formed presents a large structure shrinking and pore size, but when the solvent is removed by supercritical drying, aerogels with higher pore volumes are obtained.

Some parameters are important in the control of magnetic properties of nanocomposites, such as crystallite size, concentration and distribution of the magnetic phase in the matrix. The crystallite size control is justified by existence of an average diameter range of single domain crystallites, between 10 nm < d < 70 nm, depending on the desired optimal magnetic properties. Crystallites with diameter smaller than 10 nm show superparamagnetic behavior, while with diameters larger than 70 nm (critical particle size/Dc) show multi-domain microstructure, with the consequent decrease in coercivity. When the ferrite concentration is low (< 10%), the crystallites are isolated, having single domains and showing superparamagnetism. Concentrations above 50% of ferrite provoke the agglomeration of the crystallites, which results in multi-domains. Other important

characteristic of magnetic nanocomposites is the texture of the matrix, which has important influence in their final applications such as magnetic devices and catalysts, due to the transport and interaction of fluids within their connected network formed by meso and macropores.

Experimental

NiFe₂O₄/SiO₂ wet gels were obtained from the mixture of tetraethylorthosilicate, ethyl alcohol, water (1/3/10), nitric acid, and nitrates, Ni(NO₃)₂·6H₂O and Fe(NO₃)₂·9H₂O. The precursor solutions were stirred for one hour for homogenization and left to rest for gelation, which happened due to the hydrolysis and polycondensation of the metallic alkoxide. The wet gels obtained were submitted to aging at 60 °C for 24 hours, dried at 110 °C for 12 hours, leading to the formation of xerogels. The aerogels were obtained by supercritical drying by raising the temperature up to 300 °C at 5 °C /min and 180 atm. The system was kept in this condition for 2 hours. The nanocomposites with 30%wt of ferrite were treated at 300, 500, 700, and 900 and 1100°C and the nanocomposites obtained with ferrite contents from 1 to 20% wt were treated at 700°C, both for 2 hours.

All samples were analyzed by X-ray diffractometry (Rigaku, Geigerflex 3034), and by infrared spectroscopy (ABB Bomem, model MB 102) to determination of the structures. Crystallite size was determined by Scherrer equation. The composition and morphology of the composites were evaluated by an electron microprobe (Jeol JXA, model 8900RL) with an energy dispersive spectrometer (EDS), and by scanning electron microscopy. Apparent and true density measurements were obtained by mercury and helium pycnometry (Quantachrome), respectively. Sample textural characteristics were determined through nitrogen gas adsorption (Autosorb - Quantachrome Nova 1200). Magnetization and coercivity were determined by vibrating sample magnetometry (VSM) at 300 K with a maximum applied magnetic field of 1 Tesla.

Results and discussion

The NiFe₂O₄/SiO₂ xerogel and aerogel exhibited amorphous behaviour up to 300°C. XRD analyses showed the formation of a single phase of Ni ferrite with spinel structure inside the silica matrix in all calcined materials above 300°C. The characteristic peaks of NiFe₂O₄ phase increased in intensity above this temperature and by the increasing in ferrite amount. No diffraction lines of other phases were observed.

Xerogel and aerogel composites are porous materials, with total porosity between 60 and 47% and between 91

and 93%, respectively, for samples treated in the range of 300 to 900°C. The xerogel porosity decreased sharply between 900 and 1100°C due to pore collapse with consequent encapsulation of nickel ferrite particles. Aerogels treated at 1100°C kept their porous characteristics ($\sim 16 \pm 1\%$).

The specific surface area of the composites and crystallite size of the dispersed phase are shown in Tables 1, 2 and 3.

Table 1 – Textural and magnetic characteristics of NiFe₂O₄/SiO₂ xerogels heating at various temperatures.

Heating (°C)	Crystallite size* (nm)	SSA (m ² .g ⁻¹)	Spontaneous Magnetization (emu.g ⁻¹)	Coercivity (Oe)
500	19	349	2.7	-
700	25	347	5.9	66
900	34	285	7.5	88
1100	66	2	13.0	166

*by XRD

Table 2 – Textural and magnetic characteristics of NiFe₂O₄/SiO₂ xerogels heating at various temperatures.

Ni ferrite %	Crystallite size* (nm)	SSA (m ² .g ⁻¹)	Spontaneous Magnetization (emu.g ⁻¹)	Coercivity (Oe)
1	-	427	0.13	120
5	24	544	0.48	122
10	28	515	2.4	182
20	21	411	4.5	107
30	25	347	5.9	160

*by XRD

Table 3 – Textural and magnetic characteristics of NiFe₂O₄/SiO₂ aerogels heating at various temperatures.

Heating (°C)	Crystallite size* (nm)	SSA (m ² .g ⁻¹)	Spontaneous Magnetization (emu.g ⁻¹)	Coercivity (Oe)
900	14	263	1.8	106
1100	31	43	8.0	120

*by XRD

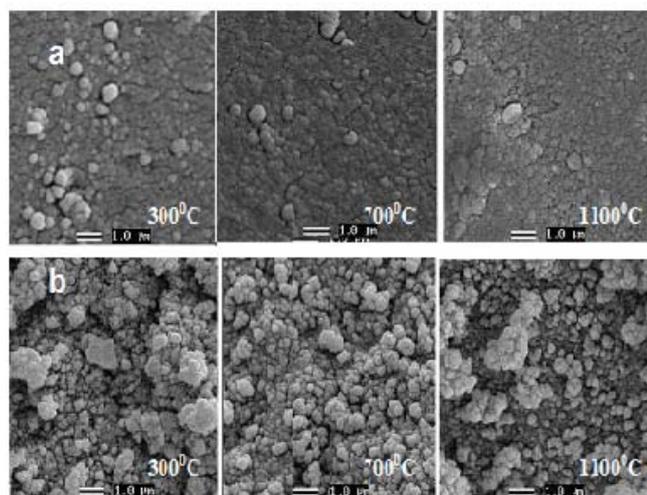


Fig. 1 - MEV image of NiFe₂O₄/SiO₂ composites, treated at different temperatures, (a) xerogel and (b) aerogel .

Figure 1 shows the morphologies of xerogel and aerogel samples treated between 300 and 1100°C. It is evident the formation of spherical grains with no porosity in the xerogel. In turn, the structure of the aerogel is similar to a “cauliflower”, which is characteristic of porous materials with meso and macropores. Between 300 and 1100°C the aerogels presented no significant morphological differences

The magnetic characteristic of the xerogels at room temperature changed from superparamagnetic to ferrimagnetic with increasing in the thermal treatment temperature. The aerogel samples calcined between 300 and 900°C presented paramagnetic behavior and the sample calcined at 1100°C had significant superparamagnetic fraction. Saturation magnetization and coercivity of the nanocomposites under 1T varied from 0.1 to 13.0 emu/g and 66 to 182 Oe, respectively, for the different morphologies and textures of the analyzed material (Tables 1, 2 and 3). The results showed that thermal treatment temperature, ferrite content and matrix porosity influence the magnetic behavior of the nanocomposites.

Conclusion

Nanocomposites formed by nickel ferrite crystallites with average diameters ranging from ~ 14 to 66 nm dispersed in silica matrix were obtained by sol-gel process. The xerogels as prepared were superparamagnetic and changed to ferromagnetic with increasing thermal treatment temperature, while the aerogels showed significant superparamagnetic fractions for all the samples, even when prepared at 1100°C.

The results show that heating temperature, crystallite size, ferrite content, synthesis conditions, and mainly the porosity and specific surface area influence the nanocomposite magnetic behavior.

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Acknowledgments

CNPq, and FAPEMIG