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Synthesis and magnetic properties of nickel micro urchins

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ABSTRACT

Urchin-like nickel micro particles were produced in aqueous solution through a simple auto-catalytic chemical reduction method without any complexant or surfactant by slowly increasing the temperature of the bath from 25 °C to an aging plateau at 85 °C. The overall time of synthesis is around 40 min. The micro urchins are nanostructured, formed by only one fcc-Ni phase with mean crystallite size of 27.6 nm; they have mean diameter of 1.36 μm with spherical core and blade shaped spikes rising from its surface. In order to study the nucleation and growth process, we also repeated the synthesis changing its plateau temperature and aging time. Based on the reaction temperature and time investigations, a scheme for the micro urchins formation was proposed and discussed. Vibrating sample magnetometry measurements of the particles present coercivity (Hc = 107.12 Oe) and relative remanence (Mr/Ms = 0.15) much higher than the nickel bulk and lower saturation magnetization (Ms = 50.8 emu/g) due to their shape and nanosized structure.

1. Introduction

The production of magnetic materials within the micro and sub-micro scale, with controllable size distribution and shape, has great interest in technological applications like chemical catalysis [1], magnetic recording [2], and medical diagnosis [3], since it is widely accepted that the intrinsic properties of these materials are very dependent on its morphology, size, size-distribution, and crystallinity.

As one of the transition metals that exhibits magnetism as bulk material, nickel structures have attracted high interest in electronic devices, besides its good catalytic properties. Nickel micro and sub-micro particles of various different morphologies, such as spheres [4], hollow spheres [5], flowers [6], chains of spherical particles, and hexagonal flakes [7] have been successfully synthesized *via* various methods, including sonochemistry, thermal decomposition, chemical or electrochemical reduction, and solvothermal method. Nickel micro crystals with flower-like and urchin-like morphologies exhibit excellent microwave absorption performance due to the relatively low eddy current from its particle shape [8]. Therefore, it is of interest to study their formation process to find better routes of synthesis with low size dispersion and good morphology control.

The electroless method is an auto-catalytic chemical reduction wherein a metallic salt is reduced by a chemical reducing agent such as hydrazine, sodium hypophosphite, or sodium borohydride. Depending on the reducing agent, the resulting material can be made of pure metal (*e.g.*, with hydrazine) or have some grade of impurity (*e.g.*, phosphorous with phosphorous hypophosphite or boron with sodium borohydride). This method is well known for its high yield, efficiency, and scalability, though the strong dependence on the temperature, concentrations, and pH may present some challenge of control [9].

This work shows a simple and fast synthesis route of urchin-like nickel micro particles in aqueous solution by electroless at fairly low temperature (85 °C) without the use of any complexant or surfactant. The overall reaction time is about 40 min and the particles have 1.36 μm of mean diameter. Nickel sulfate hexahydrate was used as nickel source, sodium hydroxide for pH adjustment and hydrazine monochlorohydrate acted as reducing agent. The formation process for the micro urchins and an investigation of its reaction temperature dependence is discussed.

Urchin-like self-assembled chains of Ni were obtained by Zhu et al. [10] by a solvothermal method in autoclave with an ethylenediamine(EDA)-assisted self-assembly process at 115 °C, but they realized that, there was no formation of urchin-like particles without the presence of EDA. Therefore, in the present paper we show an economic, faster, and simpler process of obtaining urchin-like loose particles.

XRD, SEM, and FESEM were used to characterize the phase composition, size, and morphology of the particles. VSM was used

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to measure magnetic properties of the samples. Due to the low flowability of fine powders, depending on how the powder accommodate on the sample holder, the field variation during the magnetic measurements may move and re-accommodate the particles interfering on the hysteresis curve. A powder preparation method using coffee ring effect [11] was used to better accommodate the samples before the measurements, obtaining more accurate and reproducible values.

2. Experimental

2.1. Reagents

The reagents used for the synthesis were $NiSO_4 \cdot 6H_2O$ (MERCK), NaOH (VETEC – Brazil), $N_2H_4 \cdot HCl$ (VETEC – Brazil), ethanol 99% (LAFAN – Brazil). All reagents present analytical grade and were used as received.

2.2. Synthesis of Ni micro urchins (sample S1)

3.000 g of $NiSO_4 \cdot 6H_2O$ and 920 mg of NaOH were dissolved in 30 ml of distilled water and magnetic stirred for 10 min at room temperature. Then, 20 ml of an aqueous solution containing 2.843 g of $N_2H_4 \cdot HCl$ and 1.660 g of NaOH was added to the main solution. At this stage, the pH was 13. After addition of the reducing mixture, the solution was heated at a rate of 5 °C/min from 25 °C to a final plateau temperature at 85 °C. As soon as the temperature reached 80 °C, the solution started to darken, indicating the beginning of the growing process. Once its temperature reached 85 °C, the solution started to strongly release gas, indicating an accentuated increase in the reduction of the nickel cations. To avoid the particles smashing, the magnetic stirring was decreased. The gas evolution stopped 25 min after its start at 85 °C, leaving a magnetic dark gray powder precipitated over the magnetic bar and a transparent liquid solution with pH 10. The precipitate was washed with water and ethanol, respectively, with assistance of a magnet and dried under vacuum at 60 °C for 12 h. The final product typically has around 610 mg, representing a yield of 91% in relation to the Ni involved in the reaction.

2.3. Structure and morphology characterization

X-ray diffraction (XRD) was conducted on a X'PERT MPD–PRO (PANalytical) using Cu Kα radiation and the peaks were characterized using X'PERT HIGHSCORE PLUS software. Scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM) images were obtained on a JSM-6390L and a JSM-6701F Scanning Electron Microscope (JEOL), respectively, and analyzed with Image tool for windows 3.0 software.

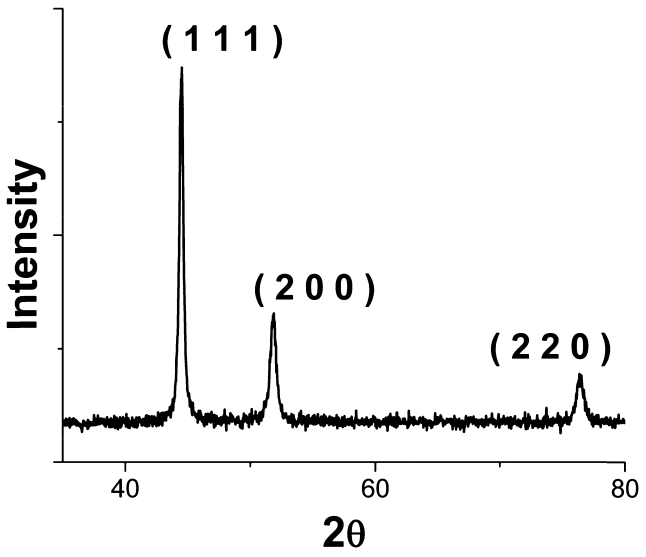

Fig. 1. XRD pattern of the sample S1 identifying a phase of fcc-Ni (JCPDS 01-087-0712) and crystallite size of 27.6 nm.

2.4. Magnetic characterization

Magnetic measurements were obtained with a Microsense EV9 Vibrating Sample Magnetometer (VSM). The magnetic properties of powders are dependent on the samples packing density [12]. Due to the low flowability of fine powders, depending on how the powder accommodate on the sample holder, the vibration and field variation during the measurements may dislocate the particles interfering on the hysteresis curve.

A powder preparation method using the coffee ring effect [11] with ethanol was used to better accommodate the samples before the measurements. The less powder in the flask, the better to prevent anisotropy of conformation. Therefore, about 4 mg of material was used for each measurement. After each sample was weighted, a drop of ethanol at 40 °C was released over it, making the powder retract and conform on the bottom of the sample holder as the ethanol evaporate.

3. Results and discussion

3.1. Structure and morphology characterization

A XRD pattern of the sample S1 is shown in Fig. 1. Diffraction peaks in $2\theta = 44.44°$, 51.78°, and 76.34° are observed, representing planes (1 1 1), (2 0 0) and (2 2 0) in accordance with the JCPDS card 01-087-0712 for face-centered cubic (fcc) nickel. Application of Scherrer formula on the (1 1 1) peak shows a mean crystallite size of 27.6 nm.

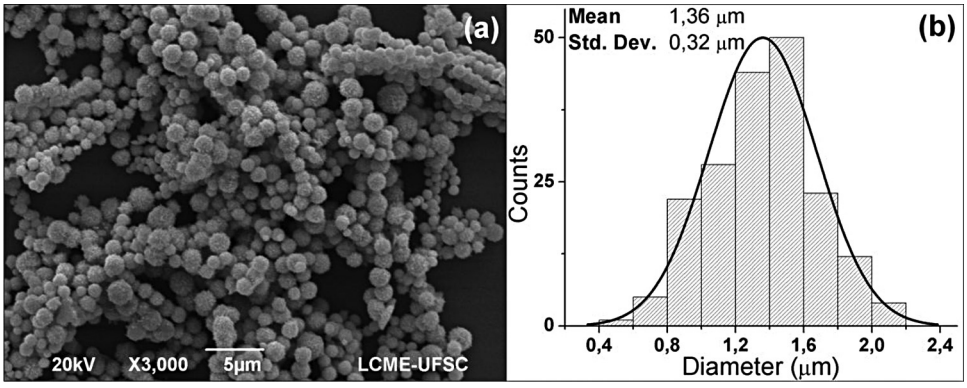

Fig. 2. SEM image of the sample S1 with magnification of 3000× (a) and histogram with the particles dispersion of diameters (b).