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Synthesis and characterization of Co and Ni magnetic nanoparticles

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This paper reports some results on the synthesis and magnetic properties of cobalt and nickel nanoparticles. Cobalt and nickel nanoparticles have been synthesised by polyol method and the obtained magnetic nanoparticles have a superparamagnetic behaviour. The morphology and size of the nanoparticles were studied by scanning electron microscopy (SEM) and dynamic light scattering (DLS). The micrographs reveal that the nanoparticles are mostly spherical. The size of Co nanoparticles ranges between 30 – 340 nm and size of Ni nanoparticles ranges between 90 – 400 nm. Magnetic characteristics of the obtained nanoparticles were determined at room temperature by using a vibrating sample magnetometer (VSM), in an external magnetic field of 600 kA/m.

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Keywords: Cobalt nanoparticles, Nickel nanoparticles, Polyol process, Superparamagnetic behaviour

1. Introduction

The synthesis and investigation of magnetic properties of nanostructured magnetic materials present interest from both fundamental and technological point of view. Magnetic nanoparticles are used and are explored for use in fields as diverse as biology and data storage. In these applications, the ability to control particle size, shape, composition, and surface chemistry is critical in obtaining the desired magnetic properties. For biomedical applications the use of particles that present superparamagnetic behaviour at room temperature (no remanence along with a rapidly changing magnetic state) is preferred. In biomedicine, superparamagnetic particles are used for cell sorting and are explored for radiation treatment. Such particles are also being explored for use in drug delivery and gene therapy [1]. In magnetic data storage, the self-assembly of ferromagnetic particles is being explored for high-density magnetic media. The diverse range of applications has resulted in interest for nanoparticles with a wide range of magnetic properties. For example, the magnetic beads used in cell sorting are superparamagnetic in order to avoid aggregation; however, it is desirable that they have a relatively high magnetic moment so that they can be separated from the suspension at relatively low fields. In contrast, magnetic particles for magnetic recording should be ferromagnetic, with high saturation magnetization and high coercivity [2].

In this paper we reports some experimental results concerning the synthesis and magnetic properties of cobalt and nickel nanoparticles obtained by a chemical method called the polyol process [3]. In the polyol process, the liquid polyol acts as the solvent of the metallic precursor, the reducing agent and in some cases as a complexing agent for metallic cations. The solution is heated to a given temperature reaching the boiling point of the polyol for less reducible metals.

2. Experimental

Magnetic nanoparticles of Co and Ni were prepared by refluxing an ethylene glycol solution containing their suspended sulphates. To obtain cobalt and nickel nanoparticles we used cobalt sulphate hexahydrate and nickel sulphate hexahydrate solutions having molar concentrations of 0.035 M in ethylene glycol. The accurate and reproductible control of the mean diameter of the particles was achieved in the nanometer size by heterogeneous nucleation for both Co and Ni nanoparticles. The seeding of the reaction medium was achieved by adding silver nitrate (0.1 g/l) or platinum (II) acetylacetonate (0.05 g/l**)** as nucleating agents. The precious metal cations are easily reduced and generate in situ numerous tiny metal particles, which then act as suitable sites or the further growth of the ferromagnetic metals.

For the preparation of Co and Ni nanoparticles, the pH of solutions was adjusted to 11 – 12 by addition of NaOH prior to reduction process. The sodium hydroxide was used to promote the reduction and to help control the particle size.

The refluxing temperature and the reaction time are specific for obtaining either nanoparticles type: 185 ˚C – 190 ˚C and 4 hours for Co nanoparticles and 190˚C – 195˚C and 6 hours for Ni nanoparticles, respectively. In all cases, the solutions turned black within a few minutes of reaching refluxing temperature.

The metal-ethylene glycol mixtures were cooled to room temperature, filtered, and then the collected precipitates were dried in vacuum.

The morphology and size distribution of the magnetic nanoparticles were determined by scanning electron microscopy (SEM) and by dynamic light scattering (DLS) with a Microtrac Nanotrac 250 Particle Size Analyser. The structure of the nanoparticles was examined by X-ray diffraction (XRD) using Co Kα radiation (λ=0.7189 nm) or Cu Kα (λ = 1, 54056 Å). Room temperature magnetic

characteristics of the nanoparticles were determined by using a vibrating sample magnetometer (VSM) in an external field of 600 kA/m.

3. Results and discussion

3.1. Morphology and size of prepared magnetic nanoparticles

In Fig. 1 is shown a SEM micrograph of Co magnetic nanoparticles obtained by homogenous nucleation (without nucleating agent) and in Fig. 2 is presented a SEM micrograph of Co nanoparticles obtained by heterogeneous nucleating (using Ag as nucleating agent).

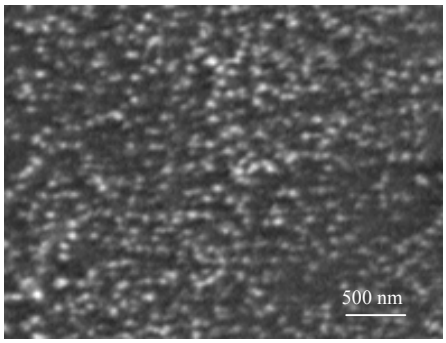

Fig. 1. SEM micrograph of Co nanoparticles prepared by homogeneous nucleation.

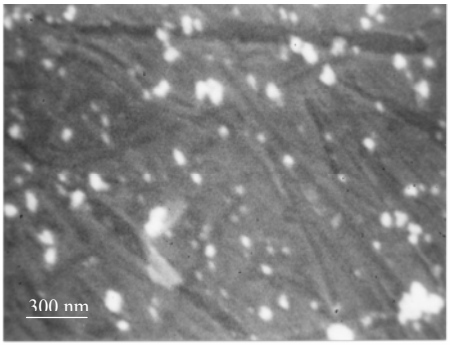

Fig. 2. SEM micrograph of Co nanoparticles prepared by heterogeneous nucleating (Ag as nucleating agent).

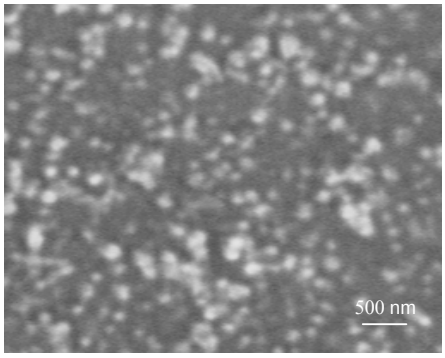

Fig. 3. SEM micrograph of Ni nanoparticles prepared by homogeneous nucleation.

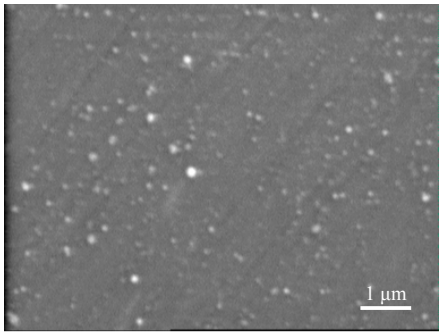

Fig. 4. SEM micrograph of Ni nanoparticles prepared by heterogeneous nucleating (Pt as nucleating agent).

The SEM micrographs presented in Fig. 1 and Fig. 2, respectively, reveal that the shape of Co nanoparticles is mostly spherical. Due to the large surface to volume ratio and strong magnetic attraction forces, the nanoparticles tend to agglomerate in order to minimize the total surface energy of the system. In Fig. 3 is shown a SEM micrograph of Ni magnetic nanoparticles obtained by homogeneous nucleation and in Fig. 4 is presented a SEM micrograph of Ni nanoparticles obtained by heterogeneous nucleating (using Pt as nucleating agent). From the SEM micrographs of Ni nanoparticles it can be observed that their shape is spherical.

In Fig. 5 is presented the comparison plot of size distribution of Co nanoparticles obtained by homogeneous nucleating and by heterogeneous nucleating and in Fig. 6 is presented the comparison plot the size distribution of Ni nanoparticles, respectively.

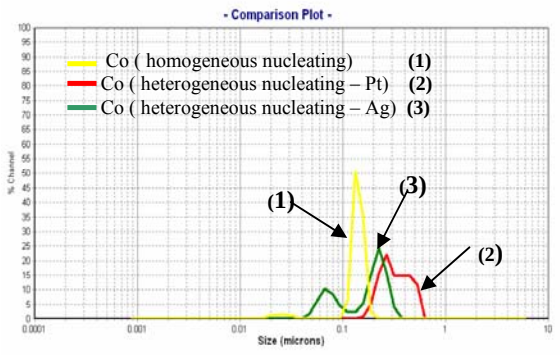

Fig. 5. Size distribution of Co nanoparticles.

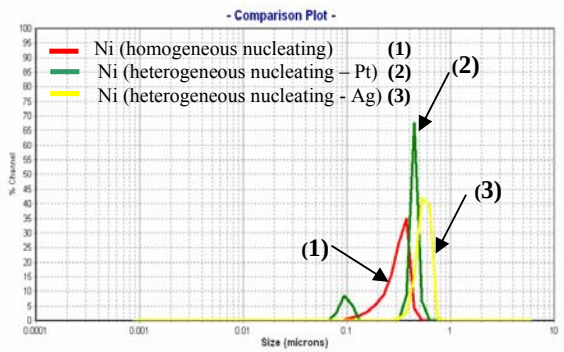

Fig. 6. Size distribution of Ni nanoparticles.

In Fig. 5 and in Fig. 6 are presented the comparison plots of the size distribution of Co and Ni nanoparticles obtained by homogenous and by heterogeneous nucleating. The size distribution presented in Fig. 5 reveals that the Co nanoparticles diameter ranges between 30 – 340 nm. Spherical particles of Co with mean diameter between 60 and 200 nm were obtained by using Ag as nucleating agent, whereas when Pt was employed larger particles, with mean diameters between 200 and 600 nm, were obtained.

It can be observed that the Ni nanoparticles (Fig. 6) diameter varies between 90 and 400 nm. For Ni were obtained spherical particles with mean diameter between 400 and 540 nm by using Ag as nucleating agent, whereas when Pt was employed smaller particles, with mean diameters between 90 and 400 nm, were obtained. The material appears as individual nanoparticles, rather in spherical shape, and presents a very narrow size distribution as expected for a material synthesized by the polyol process.

3.2. Structural features of Co and Ni nanoparticles

The X-ray diffraction pattern of Co nanoparticles prepared by homogeneous nucleation (Fig. 7) shows the presence of sharp reflexes, corresponding to crystalline phases of Co (111), (200) and (220). In Fig. 8 is presented the X-ray diffraction pattern of Co nanoparticles prepared by heterogeneous nucleation (Ag as nucleating agent). The diffraction peaks of the XRD pattern correspond to the Co reflections and (111) fcc Ag reflections, respectively.

The X-ray diffraction patterns of Ni nanoparticles prepared by heterogeneous nucleation with Pt as nucleating agent (Fig. 9) and with Ag as nucleating agent (Fig. 10) are presented. It can be observed the presence of (111) and (200) fcc Ni reflections in Fig. 9 and for the obtained Ni nanoparticles with Ag as nucleating agent are present for Ni the specific reflections and (111), (200) and (220) fcc Ag reflections in Fig. 10, respectively.

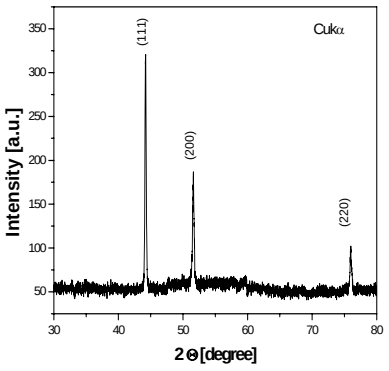

Fig. 7. X-ray diffraction patterns of Co nanoparticles

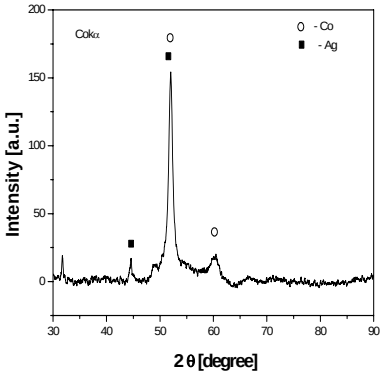

Fig. 8. X-ray diffraction patterns of Co (Ag as nucleating agent)

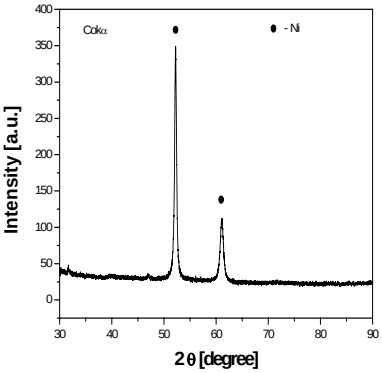

Fig. 9. X-ray diffraction patterns of Ni (Pt as nucleating agent).

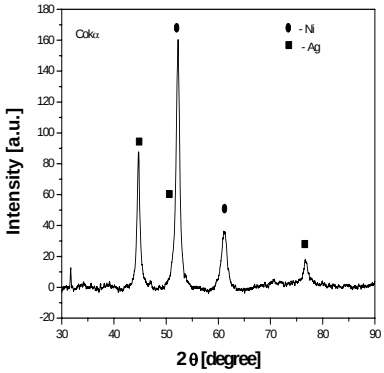

Fig. 10. X-ray diffraction patterns of Ni (Ag as nucleating agent).

3.3. Magnetic properties of Co and Ni nanoparticles

The magnetic properties of nanosized particles arise from the competition between strong, short-range exchange interactions and long-range, dipolar couplings of electron spins- atoms that make up magnetic solids. These competing interactions favour parallel alignment of nearby spins and anti parallel alignment of distant spins forming magnetic domains in bulk magnetic materials.

The hysterezis curves of Co nanoparticles prepared by homogeneous and heterogeneous nucleating are presented in Fig. 11. From the hysterezis curve presented in Fig. 11 it can be observed that the Co nanoparticles have a superparamagnetic behaviour. The value of magnetization of Co nanoparticles prepared by homogeneous nucleating was 135 emu/g. The values of magnetization of Co nanoparticles prepared by heterogeneous nucleating with Ag was 110 emu/g and for the Co nanoparticles prepared by heterogeneous nucleating with Pt was 78 emu/g.

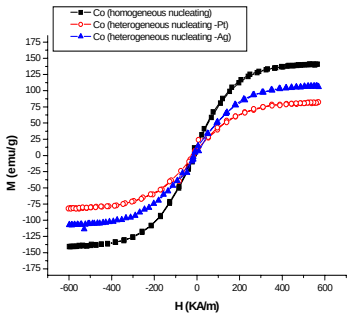

Fig. 11. Hysterezis curves of Co nanoparticles.

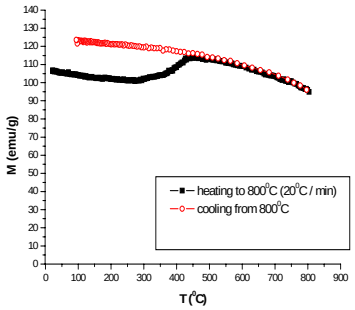

Fig. 12. Temperature dependence of the magnetization of Co nanoparticles (Ag as nucleating agent).

In Fig. 12 is presented the temperature dependence of the magnetization of Co nanoparticles prepared by heterogeneous nucleating (Ag as a nucleating agent). From the temperature dependence of the magnetization it can be observed that the value of magnetization is decreasing with the increasing of temperature. The hysterezis curves of Ni nanoparticles prepared by homogeneous and heterogeneous nucleating are presented in Fig. 13. It can be observed from Fig. 13 that the as-prepared Ni nanoparticles have a superparamagnetic behaviour. The value of magnetization of Ni nanoparticles prepared by homogeneous nucleating was 33 emu/g. The value of magnetization of Ni nanoparticles prepared by heterogeneous nucleating with Ag was 24 emu/g and for the Ni nanoparticles prepared by heterogeneous nucleating with Pt the value of magnetization was 40 emu/g. In Fig. 14 is presented the temperature dependence of the magnetization of Ni nanoparticles obtained by heterogeneous nucleation with Pt as nucleating agent. From this figure it can be observed that the Curie temperature of Ni nanoparticles is 390˚C.

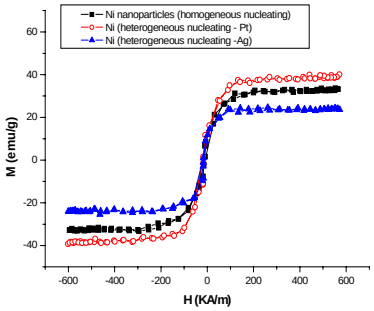

Fig. 13. Hysterezis curve of Ni nanoparticles.

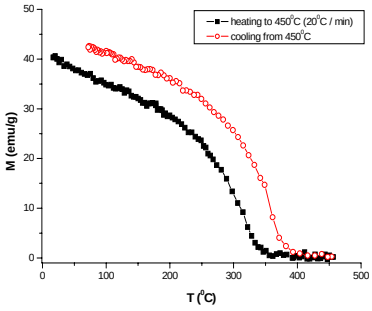

Fig. 14. Temperature dependence of the magnetization of Ni nanoparticles (Pt as nucleating agent).

4. Conclusions

The polyol process, which is known for providing monodisperse fine metal nanoparticles, afforded us the opportunity to synthesize ferromagnetic metal particles. The final particles have interesting morphological characteristics: an almost spherical shape, a narrow size distribution.

By control of the parameters of polyol process (molarity, pH, time and refluxing temperature of solutions), Co and Ni nanoparticles with good magnetic properties and a superparamagnetic behaviour were obtained. Control of particle size and size dispersion requires careful control of the nucleation and growth steps in the process and elimination of aggregation during growth.

The resulting magnetic behaviour of the obtained Co and Ni nanoparticles is rather complex, as it is strongly affected by the temperature - dependent interplay between finite size core effects, surface effects, and interface effects interactions. Such effects can complete, and the result of such competition is difficult to predict.

Acknowledgements

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