Journal of Alloys and Compounds 622 (2015) 408–417

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Synthesis of air stable FeCo alloy nanocrystallite by proteic sol–gel method using a rotary oven

Tiago Pinheiro Braga [c,*], Diego Felix Dias [a], Matheus Falcão de Sousa [a], João Maria Soares [b], José Marcos Sasaki [a]

[a] Laboratório de Raios X, Departamento de Física, Universidade Federal do Ceará, Campus do Pici, CEP 60455-970, Fortaleza, CE, Brazil
[b] Departamento de Física, Universidade do Estado do Rio Grande do Norte, 59625-620 Mossoró, RN, Brazil
[c] LABPEMOL-Laboratório de Peneiras Moleculares, Instituto de Química, Universidade Federal do Rio Grande do Norte, Lagoa Nova, 59078-970 Nata, RN, Brazil

ARTICLE INFO

Article history:
Received 11 August 2014
Received in revised form 1 October 2014
Accepted 13 October 2014
Available online 22 October 2014

Keywords:
FeCo
Alloy
Nanoparticles
High stability

ABSTRACT

Highly air stable FeCo nanocrystals were synthesized by the proteic sol–gel method using a rotary oven. The synthesized materials were characterized by TG, DTA, XRD, TPR, VSM, Mössbauer spectroscopy and FEG-SEM. The results showed the effect of temperature and the influence of the hydrogen flow rate on the formation of pure FeCo alloy and on the average crystallite size. The use of a rotary oven is efficient, directly influencing the homogeneity and the purity of the FeCo alloy. The synthesized alloy has high values of saturation magnetization according to the VSM results. The performed characterizations confirmed that the synthetic route is interesting in the formation of FeCo alloy nanocrystallites with high chemical stability.

1. Introduction

It very is well known that the characteristics of nanomaterials differ strongly from those of bulk materials since the fraction of surface atoms is higher compared to the microparticles or bulk, presenting high surface energy [1]. The FeCo-based soft magnetic alloys belong to a class of nanomaterials which has some unique features, such as large permeability, high saturation magnetization, and high Curie temperature [2–4]. The FeCo alloys are being widely studied due to the great technological importance and their multiple applications, such as the medicine related to cancer treatments [5], the biomedicine to the controlled release of drugs in the body [6], in the catalytic process [7–9], in magnetic bearings [10], and thin films [11].

The properties of nanoparticles are extremely dependent on the particles size and synthesis methodology employed. The major synthetic routes reported in the literature for the synthesis of magnetic alloys are: conventional sol–gel [12], mechanical-ball milling process [13], polyol method [14], and co-precipitation route [15]. In spite of the several methods for the synthesis of nanoparticles, the development of a simple and inexpensive material with high chemical stability against oxidation remains a great challenge to be explored. Furthermore, there are few studies that use oxidation and reduction steps, respectively, during the preparation of magnetic alloys [16,17]. The proteic sol–gel method is quite interesting for the preparation of oxide materials containing nanoparticles, as described before [18–21], however, this method was not applied for the synthesis of magnetic alloys. The method designated proteic sol–gel method was recently developed, which uses the organic edible gelatin from marine fish or bovine species as organic template. It is important to highlight that this synthetic route presents smaller values of particle size compared to those listed above, including conventional sol–gel and uses organic precursors from a renewable source, providing an eco-friendly method [18–21]. With the aim of obtaining FeCo nanoparticles more stable against oxidation using a modified method, this work presents the first study for the preparation of FeCo magnetic alloys employing the proteic sol–gel route combined with the use of a rotary oven [22].

2. Methodology

This method is derived from the conventional sol–gel and use as organic precursor the edible bovine gelatin. The samples were prepared in order to obtain 5 g of FeCo alloy with molar ratio between Fe and Co of 1:1. The mass ratio between metal and gelatin was 1:0.5. Initially, they are prepared two different solutions, the first solution consists of 21.1 g of iron (III) nitrate nonahydrate $\{Fe(NO_3)_3{\cdot}9H_2O\}$ diluted in distilled water and then mixed with 10.6 g of gelatin (GELITA™) under constant thermal agitation to obtain a uniformly dispersed mixture. Concomitantly, the second solution containing 15.2 g of cobalt (II) nitrate hexahydrate $\{Co(NO_3)_2{\cdot}6H_2O\}$ diluted in distilled water and mixed with 7.6 g of gelatin also under continuous agitation. Subsequently, the solutions containing the gelatin and the nitrates

* Corresponding author. Tel./fax: +55 84 3342 2323.
E-mail address: tiagoquimicaufrn@gmail.com (T.P. Braga).

http://dx.doi.org/10.1016/j.jallcom.2014.10.074
0925-8388/

compounds were mixed in a single container and maintained under constant thermal agitation at 100 °C until the mixture acquire the consistency of a uniform gel. Afterward, this mixture was placed in a drying oven and remained for 48 h at 100 °C. The obtained xerogel was milled and calcined at different temperatures using a rotary oven according to the scheme illustrated in Fig. 1 [23]. The illustrative flow chart for the different steps of synthesis is present in Fig. 2.

For the preparation of the samples, it was carried out an oxidation process followed by a reduction step, whereas the oxidation was fixed at 700 °C under air flow (40 ml/min) for 2 h. However, two series of samples were prepared by reduction: (i) fixing the H_2 flow rate (30 mL/min) and varying the reduction temperature (500, 600, 700 and 800 °C) for 1 h; (ii) fixing the reduction temperature at 500 °C and varying the H_2 flow rate (20, 30, 40 and 50 mL/min) for 1 h, the different conditions employed are illustrated in Fig. 3.

The samples were named FeCo–*X*–*Y*–*Z* where *X* is the oxidation temperature, *Y* the reduction temperature and *Z* represents the hydrogen flow rate used (Fig. 3). In order to study the effect of the sample rotation during the oxidation/reduction process on the microstructure (crystallite size and microstrain), the oxidation and reduction steps of the sample FeCo-700-500-40 were performed without rotation. The solid without rotation was designated FeCo-700-500-40-WR.

To evaluate the chemical stability of the FeCo alloy against oxidation, a reoxidation was performed at temperatures of 250, 400 and 450 °C under air flow (40 ml/min) for the solid FeCo-700-700-30. The obtained samples were denominated FeCo-700-700-30-W, where W is the temperature of reoxidation.

The synthesized materials were analyzed by X-ray diffraction using a diffractometer for polycrystalline samples model X-Pert PRO MPD-Panalytical. The identification of the crystalline phases was performed using the software X-Pert HighScore (Panalytical) and the crystallography data for all phases were obtained using the Inorganic Crystal Structure Database (ICSD). The Rietveld refinement method [24] was employed using the code DBWS 9807 through the graphical interface DBWSTools [25]. The Pseudo-Voigt function was used to calculate the diffraction peaks profiles. The Full width at half maximum (FWHM) was used to calculate the crystallite size by the Scherrer equation [26]. The crystallite size, microstrain and homogeneity of the crystallites was evaluated through the value of correlation coefficient and were calculated using the Williamson–Hall equation (WH) [27].

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were also carried out using a Shimadzu DTA-60H. The measurements were made under air flow (40 ml/min) with a temperature range between 23 and 1000 °C, heating rate of 10 °C/min.

The effect of reduction temperature on the formation of FeCo alloy was observed by temperature programmed reduction (TPR-H_2) analysis from 25 to 930 °C in a quartz reactor using a 8% H_2/N_2 mixture (25 mL min^{-1}) at a heating rate of the 10 °C min^{-1} to reduce 20 mg of the solid. A thermal conductivity detector (TCD) was used to follow the H_2 consumption.

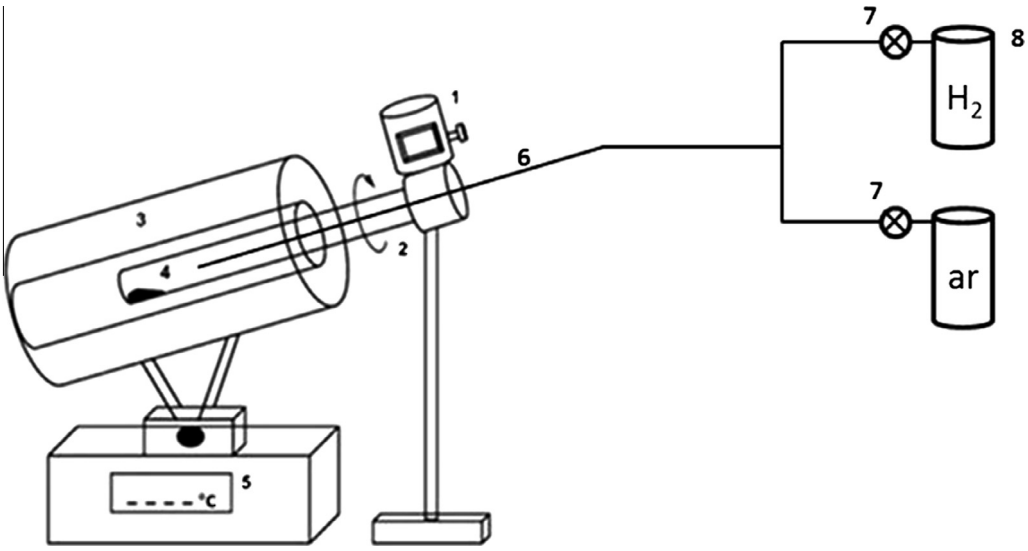

Fig. 1. Scheme for the rotary oven; 1 – rotational speed controller, 2 – alumina rotary tube (sample holder), 3 – oven, 4 – sample, 5 – temperature controller, 6 – alumina thin tube (gas inlet), 7 – flow rate control valve, 8 – gas cylinders.

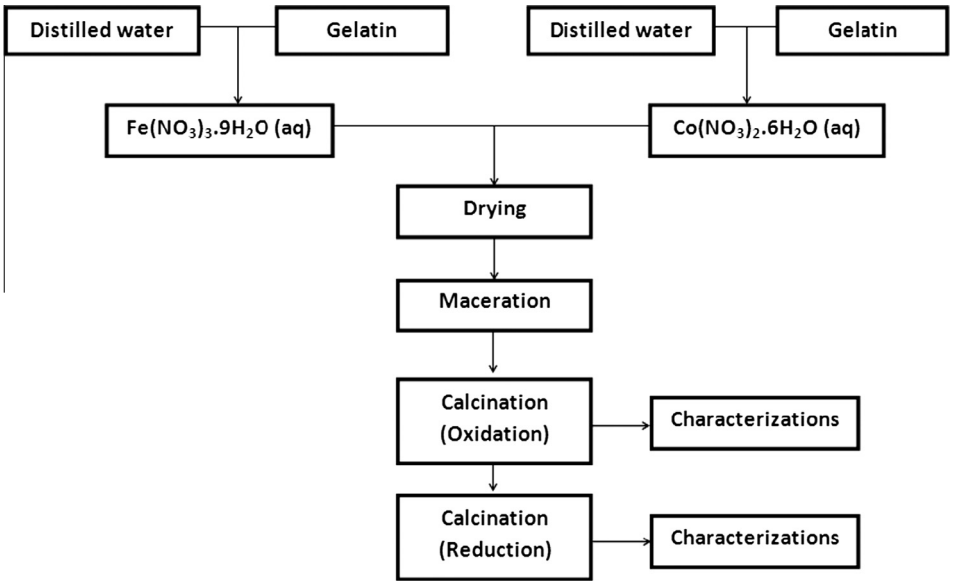

Fig. 2. Flow chart for the different steps of synthesis using the proteic sol–gel route.