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Dedicated to Professor Dr. Cozar Onuc on His 70th Anniversary

Fe_2O_3 PARTICLES AS PRECURSORS FOR α''-$Fe_{16}N_2$ PHASE SYNTHESIS

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ABSTRACT. In this work we investigate the structural properties and microstructure of Fe_2O_3 particles synthesized using the sol-gel method. Differential thermal and thermogravimetric analysis showed that the organic matrix is completely burned off at temperatures higher than 520 °C. The sample annealed at 550 °C for 12 h contained only the Fe_2O_3 phase. The obtained hematite particles are micrometer sized and have an elongated shape. Taking into account the cheap and available sol-gel precursors, the possibility of using these particles in α''-$Fe_{16}N_2$ synthesis is discussed.

Keywords: *Hematite, Sol-gel synthesis, Shape anisotropy, X-ray Diffraction, Calorimetry, Annealing.*

INTRODUCTION

In the last 20 years an increased interest for rare earth free magnetic materials has been observed [1]. The recent rare earth crisis has led to the opening of various research directions for studying rare earth free magnetic materials and since then many alloys, compounds and synthesis pathways have been investigated [2-4]. A promising alternative to rare earth-based magnets is the α''-$Fe_{16}N_2$ phase which presents enhanced magnetic properties compared to those of α-Fe [5]. Different synthesis techniques for obtaining the α''-$Fe_{16}N_2$ phase have been reported, however, they faced difficulties regarding phase purity and expected properties [5-9]. One of the main difficulties in obtaining the α''-$Fe_{16}N_2$ phase is its low decomposition temperature, around 200 °C [10].

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The α”-$Fe_{16}N_2$ phase synthesis method with the highest yield proposes the nitridation of metallic iron under anhydrous ammonia at low temperatures [11, 12]. The metallic iron is usually obtained from iron oxides by reduction under hydrogen at temperatures around 400-500 °C [11]. It was reported that the Fe particle size strongly affects the yield of α”-$Fe_{16}N_2$ phase formation during the nitridation reaction, smaller particles leading to higher α”-$Fe_{16}N_2$ phase concentrations [11]. In this work we investigate the crystal structure and microstructure of Fe_2O_3 powders synthesized using the sol-gel method. Fine Fe_2O_3 powders with nanometer-size particles and various microstructures can be obtained using the sol-gel process [13], which could then be used as starting materials for preparing $Fe_{16}N_2$. The possibility of using these particles as precursors for synthesizing α”-$Fe_{16}N_2$ magnetic materials is discussed.

EXPERIMENTAL DETAILS

The hematite particles were obtained via the sol-gel combustion method. Iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) was used as an iron source. Pectin and sucrose were added as polycondensation, respectively gelation agents, in order to prevent Fe_2O_3 particle growth during the gel combustion. The mixture was stirred vigorously for 25 minutes. The sol was dried for 48 h at 90 °C in a sand bath in open air. The dried gel was annealed at 550 °C for 12 h in air. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) measurements were performed in air using a Q600 SDT thermal analyzer made by TA instruments. The heating rate during the DSC/TGA measurements was 20 °C/min. SEM images were collected using a Hitachi SU8230 scanning electron microscope. X-ray diffraction (XRD) measurements were performed at room temperature using a Bruker D8 Advance diffractometer using Bragg-Brentano focusing geometry and Cu Kα radiation. The lattice parameters were determined using the Powdercell software.

RESULTS AND DISCUSSIONS

The X-ray diffraction patterns of the dried gel and the sample annealed at 550 °C for 12 h in air are shown in Figure 1. The as-obtained dried gel shows a diffraction pattern which is characteristic for amorphous materials, consisting of a background signal of decreasing intensity with increasing 2θ angle. This behaviour could be attributed to the organic part bonded with the iron oxide in the gel which prevents the crystalline ordering of the iron oxide.

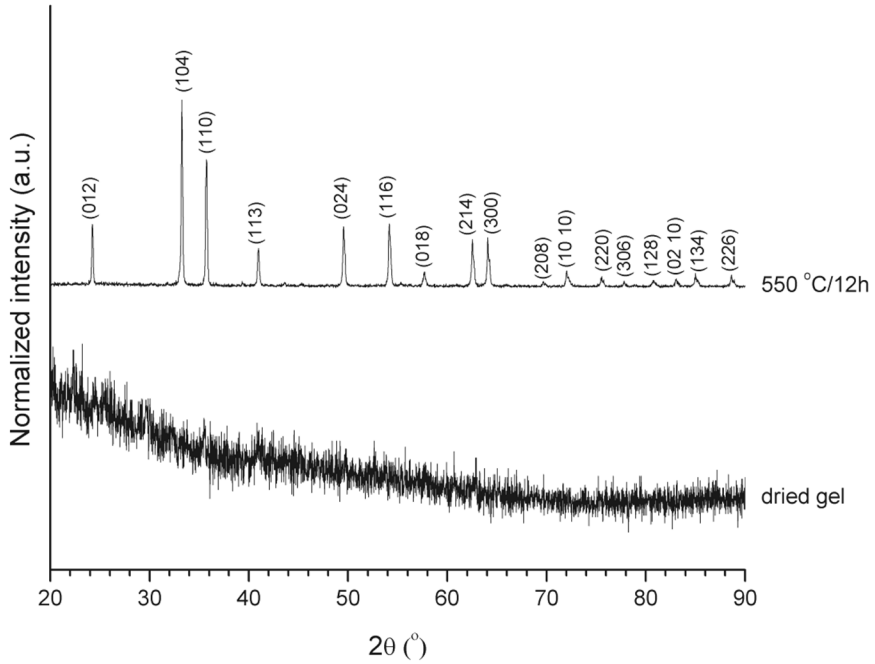

Fig. 1. X-ray diffraction patterns of the as-obtained dried gel and the sample annealed at 550 °C for 12 hours in air. The miller indices of the Fe_2O_3 phase are indicated on top of their respective peaks.

To find out about the optimum annealing temperature, in order to burn the organic part of the dried gel, we performed a simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) measurement from room temperature up to 1000 °C. The DSC/TGA curves are shown in Figure 2. The DTA curve shows one broad peak centered on 250 °C, an intense peak at 460 °C and a small shoulder around 520 °C. The TGA derivative versus temperature curve showed one narrow peak at 200 °C with a shoulder around 250 °C and an intense peak at 460 °C with a small shoulder at 520 °C. The peaks at 200 and 250 °C correspond to the elimination of water from the gel structure, accounting for a weight loss of around 40% - Figure 2 inset. The peaks at 460 and 520 °C were attributed to the burning of the organic part of the gel, the sample mass decreasing from 60% to around 10% of the initial mass. The TGA signal remains constant from 550 °C to 1000 °C, meaning that the burning of the organic part was complete after 520 °C.

To ensure the complete elimination of the organic part we chose to anneal the gel at 550 °C for 12 h in air. The X-ray diffraction pattern of the annealed gel - Figure 1 - shows that the sample is single phase, consisting of hematite (Fe_2O_3).

The lattice parameters of the obtained Fe_2O_3 phase are a = 5.03 Å and c = 13.77 Å, in good agreement with previously reported data [14]. The XRD peaks of the annealed sample are intense and narrow, indicating micrometer size crystallites.

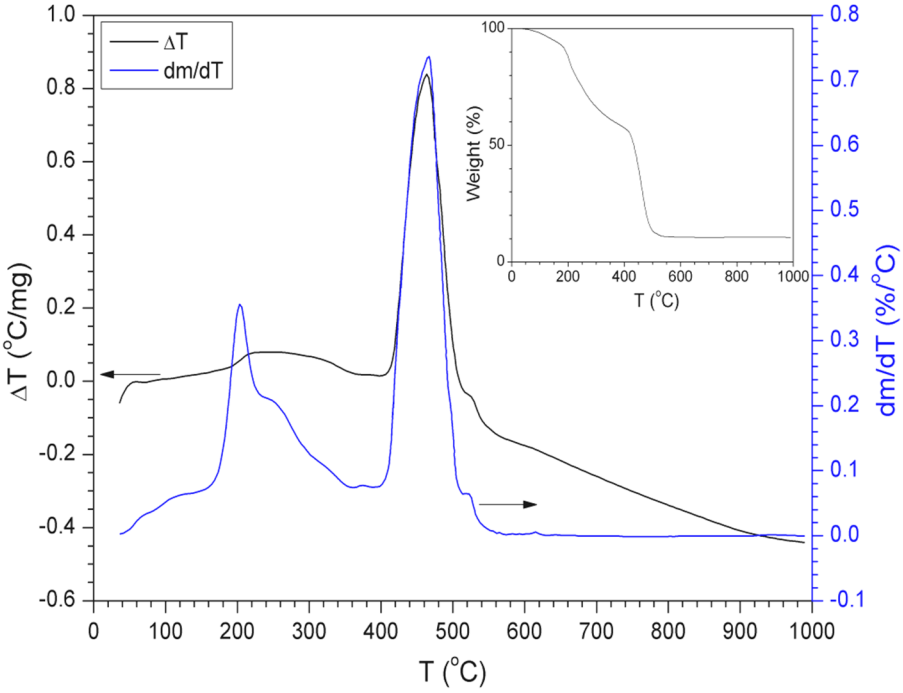

Fig. 2. DTA/TGA curves of the dried gel sample. The main figure shows the DTA signal and the derivative of the TGA signal as a function of temperature. The TGA signal is shown in the inset.

In order to study the morphology and microstructure of the as-obtained dried gel and annealed samples, we performed scanning electron microscopy (SEM) measurements on the two samples. The collected SEM images are shown in Figure 3. The as-obtained dry gel consists of elongated particles with sizes of the order of 10-100 nm - Figure 3 (a, b) - a characteristic of materials synthesized through the sol-gel method. However, after annealing the dry gel at 550 °C for 12 h in air, the SEM images show that the sample is comprised of micrometer size particles with elongated shapes and a rather narrow size distribution - Figure 3 (c, d). This behaviour could be explained by the fact that as the organic part is burned off, iron oxide particles start to crystallize. The fact that the particles are micrometer size could mean that the annealing time was too long. Shorter annealing times could lead to smaller particle

sizes within the 50-100 nanometer range, which are optimum for α"-$Fe_{16}N_2$ synthesis [11]. The elongated shape of the hematite particles makes them promising precursors for synthesizing α"-$Fe_{16}N_2$ magnetic materials with shape anisotropy.

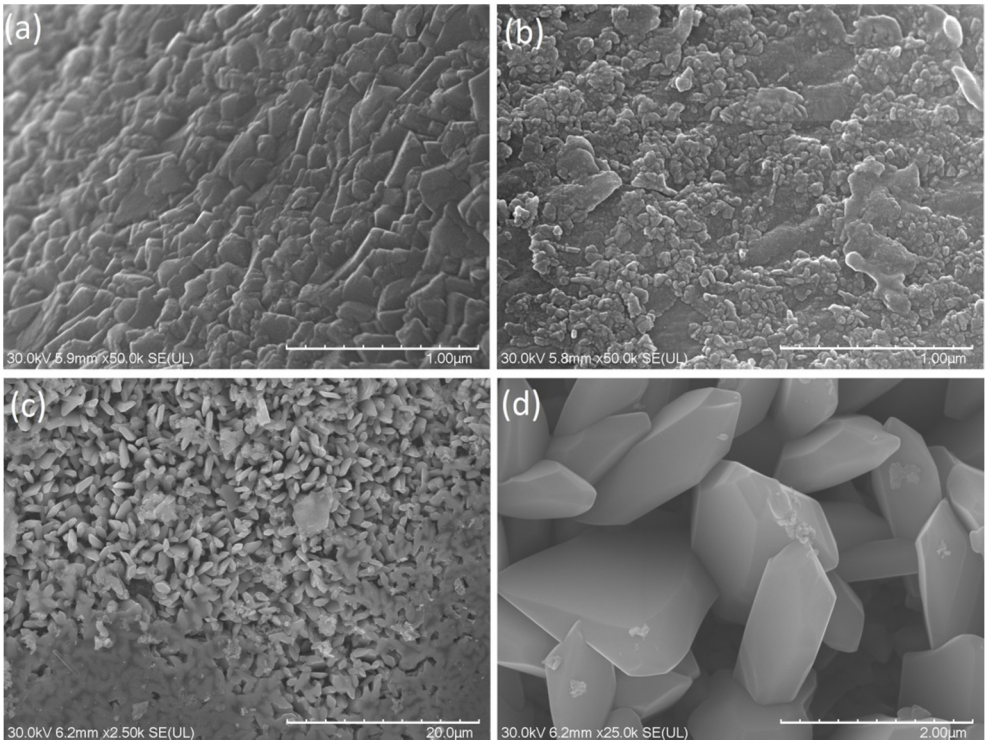

Fig. 3. SEM images of the as-obtained dry gel (a, b) and the sample annealed at 550 °C for 12 h in air (c, d).

CONCLUSIONS

The structure and microstructure of Fe_2O_3 particles synthesized by the sol-gel method were investigated. The X-ray diffraction pattern of the as-obtained dried gel showed that the sample was amorphous, characteristic for materials obtained using the sol-gel method. DTA/TGA measurements showed that the organic matrix of the gel is completely burned off at temperatures above 520 °C. The sample annealed at 550 °C for 12 h in air was found to be single phase, consisting of micrometer size Fe_2O_3 particles with an elongated shape and a rather

narrow size distribution. These results showed that the sol-gel technique can be used to synthesize particles with different geometries, making them suitable for magnetic materials preparation with induced shape anisotropy. The cheap and available precursors also make this method promising for large-scale synthesis of acicular Fe_2O_3 particles and consequently α"-$Fe_{16}N_2$ magnetic materials with enhanced shape anisotropy.

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