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Letter

Nd-enriched particles prepared from NdFeB magnets: A potential separation route

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ABSTRACT

The preparation of Nd-enriched particles from NdFeB sintered magnets using no acid or basic solution is reported. The combination of a hydrogenated–disproportionated alloy with a H_2O_2 solution at room temperature allows that $Nd(OH)_3$ be obtained as major phase whilst Fe concentration is reduced 27 times compared to the starting material. The chemical reactions which take place in the system during the reaction are proposed based on X-ray diffraction results. After an oxidizing heat treatment a mixture of neodymium oxides is achieved.

1. Introduction

Throughout the last three decades the NdFeB-based magnetic compound became indispensable in several strategic areas for human society such as power generation and communications. Magnets production has increased continuously, achieving 80,000 tons in 2010 [1]. As a result, a growing concern about its recycling has been observed due to the increase of both supply risk and price of the rare earth elements [2,3].

The NdFeB-based compound reprocessing might have, in principle, two distinct aims: (i) the preparation of new engineering products and (ii) the elements' recovery. Regarding the former, the possibility in obtaining electromagnetic radiation absorbers, magnets or nanoparticles to be used for magnetic hyperthermia has been shown [4–8]. Concerning the elements' recovery, the extraction of Nd from NdFeB magnets can be performed mainly based on acid or basic solutions (consuming large quantities of no environmentally friendly materials), or molten elements, as detailed elsewhere [9,10].

NdFeB alloys possess high chemical affinity with H_2. Under such atmosphere and for temperatures below 500 K the hydride $Nd_2Fe_{14}BH_x$, where x is a function of the H_2 pressure, is obtained. For temperatures above 800 K a mixture of NdH_y (y is also a function of H_2 pressure) and a soft magnetic phase is achieved by means of the disproportionation reaction. In this work, a new alternative procedure able to prepare a Nd-enriched material from hydrogen treated powders without any acid or basic solution is presented.

2. Experimental

Commercially available NdFeB-based sintered magnets (grade N42) were used as starting material. The parts were demagnetized in air at 723 K and crushed into pieces smaller than 10 mm. Next, the resultant material was inserted into a vessel which was cleaned (mechanical pump pressure) and subsequently filled with H_2 (analytical grade) up to a pressure of 0.2 MPa. The system temperature was increased up to distinct values to prepare two types of samples: (i) to 523 K to obtain the hydrogen decrepitated (HD) powder or (ii) to 853 K $\leqslant T \leqslant$ 903 K in order to allow that the disproportionation reaction took place. In both cases, once the hydrogen absorption was completed, the material was removed from the vessel, comminuted and sieved to particles <53 μm.

Next, twenty grams of each powder were separately immersed in 200 g of a solution of purified water and H_2O_2 (3% H_2O_2 vol. concentration). Such mixture was stirred at 600 rpm during 180 min at room temperature, being interrupted each 60 min for liquid change. This procedure was repeated twice for every sample type. The reaction behavior of the hydrogenated and disproportionated materials with the (H_2O_2 + H_2O) solution occurred as follows. Regarding the former, the liquid became dark-red along the time and a gas release, together with the formation of bubbles in the solution, were observed. Its temperature achieved 313 K during

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the experiment and the reaction stopped completely about 30 min after the liquid was added to the powder for every solution change. For the latter (disproportionated material + solution), the liquid color became grey along the reaction time. Gas release was also noticed, but in lower amount compared to the previous case. No temperature increase has been verified.

The solid–liquid phase separation was carried out magnetically and the liquid was evaporated in air at 383 K until the resultant powder previously dissolved/precipitated in the liquid was collectable. In order to evaluate the possibility to prepare an oxide, the obtained powders after the mentioned procedure were heat treated at several temperatures ($823\ K \leqslant T \leqslant 1223\ K$) at a heating rate of $5\ K\ min^{-1}$ during 120 min.

Structural characterization of the starting material and obtained powders were carried out by X-ray diffraction (Co Kα radiation, scanning rate $0.005^\circ\ s^{-1}$) together with Rietveld analyses (TOPAS – academic software, v. 4.1), where the later is detailed in [11,12]. The powders' microstructure was analyzed by high-resolution scanning electron microscopy (HRSEM) and its chemical composition was semi-quantitatively evaluated by energy dispersive spectroscopy (EDS).

3. Results and discussion

The starting HD and disproportionated materials are visually similar to each other from HRSEM images with low magnification (irregular particles with flat surfaces due mainly to cleavage) as shown in Fig. 1(a) and (b), but structurally distinct analyzing their respective XRD patterns, as depicted in Fig. 2(a). The former presented all diffraction peaks of the 2:14:1 original tetragonal phase with a shift to lower angles, indicating the expansion of the unit cell parameters. Our result is in quite well agreement with the compound $Nd_2Fe_{14}BH_{4.73}$ ($a = 0.8917$ nm and $c = 1.2344$ nm) although a peak at 35° refers to the presence of Nd_2O_3 in a quantity not larger than 3%. The disproportionated material presented six peaks in the 2θ range evaluated, ascribed to a mixture of FCC NdH_2, BCC α-Fe and tetragonal Fe_2B phases (the last two present a superposition in their highest intensity peaks). This result is in agreement with that reported in [13]. From Rietveld analyzes (refinements not shown), NdH_2 presents a lattice parameter $a = 0.547$ nm and constitutes about 30% of the disproportionated material; concerning the latter (α-Fe + Fe_2B), it represents about 70% of the sample. The estimated mean crystallite sizes of NdH_2 and α-Fe are 25 nm and 45 nm, respectively.

The HD powder can be considered as a set of particles almost fully constituted by $Nd_2Fe_{14}BH_{4.73}$ since secondary phases such as neodymium hydride, formed from the grain boundaries of the original material, might also be encountered. However, the quantity of these secondary phases is proportional to the grain boundary volume and, as this last quantity is much smaller than the volume of $Nd_2Fe_{14}B$ grains in sintered magnets (grain size – 5–10 μm), it will not be considered. When the $Nd_2Fe_{14}BH_{4.73}$ particles are in contact with the liquid solution, a chemical reaction might occur until a complete dissolution of the solid compound is achieved or some element which constitutes the solution is completely consumed. In fact, the second proposition is apparently valid in our case because, in all experiments performed, the starting powder has still been found after the reaction has stopped. The resultant material dispersed in the liquid, depicted in Fig. 3(a), presents agglomerated particles with distinct sizes. The particle size distribution characterization was not performed because after drying the resultant material is not a powder, but friable "chips". The XRD pattern of such material (in powder form after manual comminution) is depicted in Fig. 2(b) and presented a halo, typical feature of amorphous materials. In order to evaluate the phases formed after a heat treatment, Fig. 2(c) shows the XRD pattern of the treated sample (1223 K – 120 min in air). It indicates a crystalline Fe-rich compound constituted by a mixture of $NdBO_3$, $NdFeO_3$ and Fe_2O_3. Table 1 lists its chemical composition obtained by EDS (comparisons can be performed with the spectra shown in Fig. 4(a) for the starting magnet and Fig. 4(b) for the product material). The amount of Fe in this material is about 79% of that existent in a

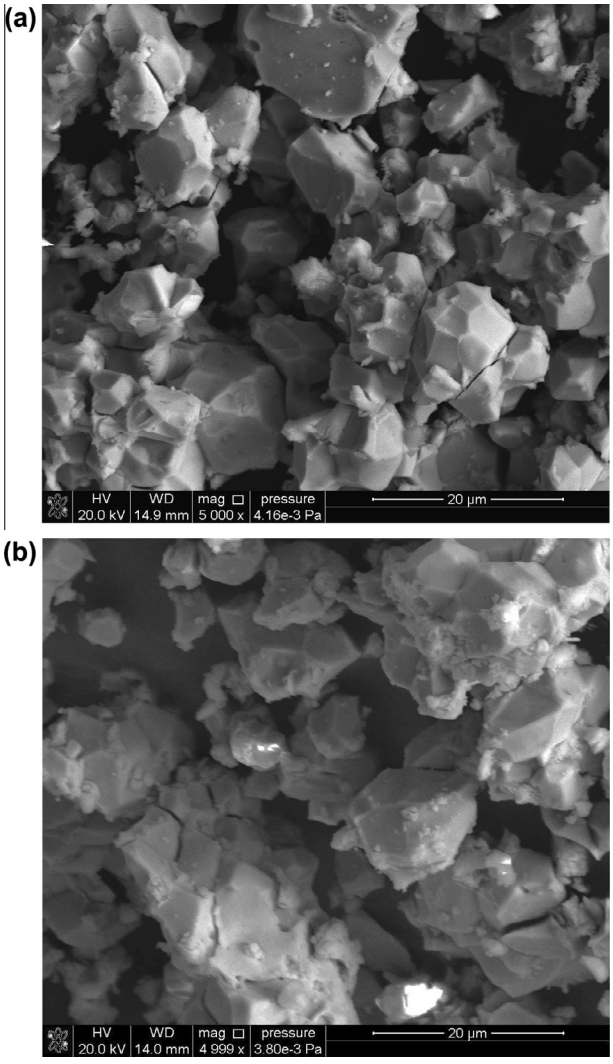

Fig. 1. HRSEM micrographs of the starting material: (a) hydrogenated material and (b) disproportionated material.

NdFeB-based starting magnet. Concerning its microstructure (shown in Fig. 3(b)), larger particle sizes (~1 μm) have been obtained from its amorphous precursor. At this point it is worth addressing the chemical behavior of the product from the reaction ($Nd_2Fe_{14}BH_{4.73} + H_2O_2$). In order to make easier its explanation, the H amount in the hydride will be assumed as five so that a possible sequence of reactions is:

Initial reaction

$$Nd_2Fe_{14}BH_{5(s)} + 35H_2O_{(l)} \rightarrow 2Nd(OH)_{2(s)} + 14Fe(OH)_{2(s)} + B(OH)_{3(aq)} + 20H_{2(g)} \quad (1)$$

Subproducts reactions: $Fe(OH)_{2(s)}$

$$2Fe(OH)_{2(s)} + H_2O_{2(l)} \rightarrow 2Fe(OH)_{3(s)} \quad (2a)$$

At this point it is worth mentioning that although $Fe(OH)_3$ presents a Kps of about 1.5×10^{-39} (at 298 K) [14], there is the equilibrium

$$Fe(OH)_{3(s)} \leftrightarrow Fe^{3+} + 3(OH)^-. \quad (2b)$$

It is known from the literature that Fe^{3+} is a catalyst for H_2O_2 decomposition [15,16]. Thus, it is possible that will exist a competition between reactions (2a) and (2c):