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 H2O2 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 non-environmentally friendly materials), or molten elements, as detailed elsewhere [9,10].

NdFeB alloys possess high chemical affinity with H2. Under such atmosphere and for temperatures below 500 K the hydride Nd2Fe14BHx, where x is a function of the H2 pressure, is obtained. For temperatures above 800 K a mixture of NdH3 (y is also a function of H2 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 H2 (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 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 l m.

Nd2Fe14BHx, where x is a function of the H2 pressure, is obtained. For temperatures above 800 K a mixture of NdH3 (y is also a function of H2 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.
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 ≤ T ≤ 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’’ 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 Nd₂Fe₁₄BH₄.₇₃ (a = 0.8917 nm and c = 1.2344 nm) although a peak at 35° refers to the presence of Nd₂O₅ in a quantity not larger than 3%. The disproportionated material presented six peaks in the 2θ range evaluated, ascribed to a mixture of FCC NdH₂, BCC α-Fe and tetragonal Fe₂B 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), NdH₂ presents a lattice parameter a = 0.547 nm and constitutes about 30% of the disproportionated material; concerning the latter (α-Fe + Fe₂B), it represents about 70% of the sample. The estimated mean crystallite sizes of NdH₂ 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 Nd₄Fe₁₄BH₄.₇₃ 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 Nd₄Fe₁₄B grains in sintered magnets (grain size – 5–10 μm), it will not be considered. When the Nd₄Fe₁₄BH₄.₇₃ 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 drying the resultant material is not a powder, but friable “chips”). The XRD pattern of such material (in powder form after manual drying the resultant material is not a powder, but friable “chips”).

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

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 (Nd₄Fe₁₄BH₄.₇₃ + H₂O₂). 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**

\[
\text{Nd}_4\text{Fe}_{14}\text{BH}_4(s) + 35\text{H}_2\text{O}_2(l) \rightarrow 2\text{Nd(OH)}_2(s) + 14\text{Fe(OH)}_2(s) + 20\text{H}_2\text{O}(l)
\]

(1)

**Subproducts reactions:**

\[
2\text{Fe(OH)}_2(s) + \text{H}_2\text{O}_2(l) \rightarrow 2\text{Fe(OH)}_3(s)
\]

(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

\[
\text{Fe(OH)}_3(s) \leftrightarrow \text{Fe}^{3+} + 3\text{(OH)}^-. 
\]

(2b)

It is known from the literature that Fe³⁺ is a catalyst for H₂O₂ decomposition [15,16]. Thus, it is possible that will exist a competition between reactions (2a) and (2c):
Fe$_{3}^{3+}$ + H$_{2}$O$_{2}$(l) $\rightarrow$ [Fe$^{III}$O(OH)]$_{2}^{2+}$ + H$^{+}$
\[ \rightarrow$ [Fe$^{II}$]$^{3+}$ + H$_{2}$O$\xrightarrow{H_{2}O_{2}}$Fe$^{3+}$
\[ = 2H_{2}O_{(g)} + O_{2(g)} \] (2c)

For this reason, the mixture of powder and H$_{2}$O$_{2}$ was interrupted at each 60 min to replace H$_{2}$O$_{2}$ (as described in the previous section), since it was consumed as described in the reactions (2a) and (2c). Finally after heat treatment Fe$_{2}$O$_{3}$ is formed, according to

\[ 2$Fe(OH)$_{3(s)} \xrightarrow{\Delta Fe_{2}O_{3(s)} + 3H_{2}O_{(g)}} \] (2d)

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

\[ 2$Nd(OH)$_{2(s)} + H_{2}$O$_{2(s)}$ $\rightarrow$ 2$Nd$O$_{3(s)} \] (3a)

\[ 2$Nd(OH)$_{2(s)}$\xrightarrow{\Delta Nd_{2}O_{3(s)} + 3H_{2}O_{(g)}} \] (3b)

**Subproducts reactions:** B(OH)$_{3}$

\[ 2$B(OH)$_{3(s)}$\xrightarrow{\Delta B_{2}O_{3(s)} + 3H_{2}O_{(g)}} \] (4a)

\[ Nd_{2}O_{3(s)} + B_{2}O_{3(s)} \xrightarrow{\Delta 2NdBO_{3(s)}} \] (4b)

\[ Nd_{2}O_{3(s)} + Fe_{2}O_{3(s)} \xrightarrow{\Delta 2NdFeO_{3(s)}} \] (4c)

On the other hand, the starting disproportionated powder is constituted by three phases mixed at nanometric scale, possessing their respective contact area with the liquid and reacting chemically with the solution in a different way. The XRD pattern of the reaction product is presented in Fig. 2(b). At least three phases could be identified: Nd(OH)$_{3}$ (majority), Fe$_{2}$O$_{3}$ and Fe$_{2}$B. Several peaks have still not been identified due to the possibility of diffraction of several possible phases, including three allotropic forms of Nd$_{2}$O$_{3}$ (no other oxides have been considered, such as Dy and/or Pr oxides, because these elements have not been found). By analyzing its microstructure depicted in Fig. 3, agglomerates of about 5 μm, as well as smaller ones, are observed. With a more detailed verification in its characteristics, as depicted in Fig. 3, it is also possible to visualize particles ranging from 300 to 600 nm, which is one order of magnitude larger than that of the crystallite size of the disproportionated material. Based on EDS results also listed in Table 1 and whose spectrum is depicted in Fig. 4(c), the compound is about 21 times poorer in Fe compared to the that obtained by using the hydrogenated powder as starting material and 27 times compared to the original magnet. Therefore, quite reasonable to consider that a selective reaction occurs, although the mechanism still needs further studies to be completely clarified. In other words, NdH$_{2}$ is preferably “removed” from the disproportionated alloy forming a hydroxide, although some Fe also migrates in this process according to EDS results. One may also consider, in a different way that the reaction of either Fe or Fe$_{2}$B present a slower kinetics than that of the NdH$_{2}$. Therefore, the enrichment of Nd in this new formed phase means an enrichment of the Fe/Nd ratio in the remaining disproportionated alloy. Considering all phases of system (remaining initial material + new formed phase(s)), the Fe/Nd ratio is constant.

In order to check the influence of a heat treatment in the structure of the Nd-rich material, Fig. 2(d) shows the XRD patterns of...
the hydroxide powder exposed to distinct temperatures (883 K to 1223 K). It is observed a continuous transition which can be summarized as follows: after the treatment at 823 K, the phase with the largest amount is the hexagonal Nd$_2$O$_3$ (space group 164) and secondary phases are also identified (Fe$_2$O(BO)$_3$, NdFeO$_3$ and remaining Nd(OH)$_3$); after the treatment at 1223 K, the main phase is the cubic Nd$_2$O$_3$ (space group 206). Furthermore, both hexagonal and monoclinic Nd$_2$O$_3$ were also identified. The microstructure of the latter (material treated at 1223 K) is depicted in Fig. 3(e) where particles below 1 µm are present, although agglomerates with dimensions around 5 µm are also found.

As a first approach to explain the products obtained from the disproportionated material, a possible sequence of reactions is:

**Partial reaction:** NdH$_2(s)$

$$\text{NdH}_2(s) + 2\text{H}_2\text{O}_2(l) \rightarrow \text{Nd(OH)}_3(s) + 2\text{H}_2(g)$$

(5a)

$$2\text{Nd(OH)}_3(s) + \text{H}_2\text{O}_2(l) \rightarrow 2\text{Nd(OH)}_3(s) + 4\text{H}_2\text{O}_2(l)$$

(5b)

or

$$\text{NdH}_2(s) + 5\text{H}_2\text{O}_2(l) \rightarrow 2\text{Nd(OH)}_3(s) + 4\text{H}_2\text{O}_2(l)$$

(5c)

**Partial reaction:** Fe$_2$B$_2(s)$

$$\text{Fe}_2\text{B}_2(s) + 2\text{H}_2\text{O}_2(l) \rightarrow \text{Fe}_2\text{O}(\text{BO})_3(s) + 2\text{H}_2(g)$$

(6a)

**Table 1**

<table>
<thead>
<tr>
<th>Material</th>
<th>Element</th>
<th>O</th>
<th>Fe</th>
<th>Cu</th>
<th>Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting magnet</td>
<td>Not quantified</td>
<td>77.8 ± 0.4</td>
<td>&lt;1</td>
<td>22.2 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>Nd$_2$Fe$<em>4$B$</em>{14}$ + H$_2$O$_2$</td>
<td>18.0 ± 0.5</td>
<td>61.2 ± 0.4</td>
<td>2.7 ± 0.3</td>
<td>18.1 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>(NdH$_2$ + Fe + Fe$_2$B) + H$_2$O$_2$</td>
<td>37.0 ± 0.9</td>
<td>2.9 ± 0.2</td>
<td>1.6 ± 0.2</td>
<td>58.5 ± 0.9</td>
<td></td>
</tr>
</tbody>
</table>

The hydroxide powder exposed to distinct temperatures (883 K ≤ T ≤ 1223 K). It is observed a continuous transition which can be summarized as follows: after the treatment at 823 K, the phase with the largest amount is the hexagonal Nd$_2$O$_3$ (space group 164) and secondary phases are also identified (Fe$_2$O(BO)$_3$, NdFeO$_3$ and remaining Nd(OH)$_3$); after the treatment at 1223 K, the main phase is the cubic Nd$_2$O$_3$ (space group 206). Furthermore, both hexagonal and monoclinic Nd$_2$O$_3$ were also identified. The microstructure of the latter (material treated at 1223 K) is depicted in Fig. 3(e) where particles below 1 µm are present, although agglomerates with dimensions around 5 µm are also found.
Subproducts reactions: \( \text{Nd(OH)}_{2(\text{s})} + \text{Nd}_{2} \text{O}_{3(\text{s})} + 3\text{H}_{2}\text{O}_{(\text{l})} \)

(6b)

At last, it is worth mentioning that there are still uncertainties concerning the stability of different polymorphs of neodymium oxide (and hydroxide) since it is influenced by the presence of water, impurities, temperature and pressure [17–20]; therefore, further studies about this matter are needed.

4. Conclusions

In summary, the preparation feasibility of a Nd-enriched powder from a disproportionated NdFeB alloy chemically reacted with a \((\text{H}_{2}\text{O} + \text{H}_{2}\text{O}_{2})\) solution at room temperature was demonstrated. Nd(OH)\(_2\) is the major phase found. After a heat treatment in air a mixture of neodymium oxides is obtained. Fe concentration is about 27 times smaller than the original magnet. Although further studies in the processing variables are needed in order to reduce the contamination level of the final product, these initial results are promising in order to reveal an acid/basic-free route to extract Nd from NdFeB-based alloys.

Acknowledgments

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References