The use of thermal hydrogen decrepitation to recycle Nd-Fe-B magnets from electronic waste

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Abstract
Rare earth magnets based upon neodymium-iron-boron (NdFeB) are employed in many high tech applications, including hard disk drives (HDDs).

The key elements in manufacturing NdFeB magnets are rare earth elements (REEs) such as neodymium. This element has been subject to significant supply shortfalls in the recent past. Recycling of NdFeB magnets contained within waste of electrical and electronic equipment (WEEE) could provide a secure and alternative supply of these materials.

Various recycling approaches for the recovery of sintered NdFeB magnets have been widely explored. Hydrogen decrepitation (HD) can be used as a direct reuse approach and effective method of recycling process to turn solid sintered magnets into a demagnetised powder for further processing.

In this work, sintered Nd-Fe-B magnets were processed without prior removal of the metallic protective layer using the thermal HD process as an alternative recycling method.

The gas sorption analyzer have been used to determine the quantity of the hydrogen absorbed by a samples of magnets, under controlled pressure (1, 2, 3 and 4 bar) and temperature (room, 100, 300 and 400 °C) conditions, using Sieverts’ volumetric method. The composition and morphology of the starting and the extracted/disintegrated materials were examined by ICP, XRD and SEM-EDS analysis.

Introduction
There are several pyro- and hydrometallurgical methods of Nd-Fe-B magnets recycling by: oxidation [1-3] or chlorination [1,2,5,4], extraction from liquid phase using magnesium [6,7], electrolysis in molten salts [1,7-11], reduction-diffusion route method using calcium [12] and hydrogen decrepitation [1,13-19]. Many of these are under current development.

Hydrogen decrepitation (HD) is based on the selective synthesis of neodymium hydrides though the reaction of hydrogen gas with neodymium located in the Nd-Fe-B magnet. HD process was originally designed and patented by Harris et al. (1979) as a way to break down SmCo₅ and Sm₂(Co,Fe,Cu,Zr)₁₇ alloys. It was subsequently modified by Harris et al. (1985) to disintegrate the newly developed NdFeB alloy. During the HD process, NdFeB alloy is usually exposed to hydrogen and the hydrogenation process causes a volume expansion by 5 %, which promotes the formation of intergranular and transboundary cracks, and this in turn causes the crushing of the material. The volume increase takes place in the whole volume of the magnet, causing disintegration to form bulks or powder [13-18].
During the HD process, various phase changes occur in the magnet microstructure (Figure 1). Due to the composition of the magnet, two types of reaction are distinguished [16]:

- between hydrogen and Nd-rich phase:
  \[ \text{Nd} + \text{H}_2 \rightarrow \text{NdH}_2 (\text{room temperature}) \]  
  \[ \text{NdH}_2 + \frac{1}{2} \text{H}_2 \rightarrow \text{NdH}_3 (200 \div 300^\circ C) \]

- between hydrogen and NdH$_2$Fe$_{14}$B phase (disproportionation):
  \[ \text{Nd}_2\text{Fe}_{14}B + \text{H}_2 \leftrightarrow \text{Nd}_2\text{Fe}_{14}BH_x(150 \div 200^\circ C) \]  
  \[ \text{Nd}_2\text{Fe}_{14}B + (2 \pm x)\text{H}_2 \leftrightarrow 2\text{NdH}_{2\pm x} + \alpha\text{Fe} + \text{Fe}_2\text{B}(650^\circ C) \]

Illustration A in Figure 1 shows the initial Nd$_2$Fe$_{14}$B microstructure scheme. During the HD process, reactions occur along the grain boundaries and at the triple points (B in Figure 1), because these are the preferred areas from the kinetic point of view. Depending on the process temperature, reaction 1 or/and 2 occur. Then, hydrogenation and disproportionation (reactions 3 and 4) are initiated along the grain boundary and at triple points (C in Figure 1). At triple points there is NdH$_2$ in the iron matrix with finely dispersed Fe$_2$B. Disproportionation spreads to the interior of the Nd$_2$Fe$_{14}$B phase, creating so-called pools (extensive areas to the origin of the triple points or unreacted Nd-rich areas) and connecting them necks, i.e., grain boundaries consisting of neodymium hydrides, until finally to the entire magnet [13-18].

**Figure 1.** Changes in the microstructure of Nd-Fe-B magnet in the HD process

An important parameter of the decrepitation process is temperature. With increasing temperature, free enthalpy value of NdH$_2$ formation increases, therefore the spontaneity of the synthesis reaction decreases. For this reason, the process temperature indirectly affects the size of the particle obtained after hydrogenation: the higher the temperature, the larger the grains of disintegrated material [13].

Due to the fact that neodymium magnets are often covered with a protective coating (metallic or plastic) that protects the magnet against corrosion, in recycling is important to
separate it from the magnet. Decrepitation allows this separation, if the following conditions are met:

- magnets contain protective coating that are not damaged; otherwise it is possible that the components of the magnet scrap will react with oxygen or moisture, what prevents the synthesis of hydrides, and thus the decrepitation process;
- hydrogen diffuses through the protective coating, which may require a long duration due to e.g. hydrogen sorption by nickel, which is often included in the coating;
- a fine neodymium magnet powder and pieces of protective coating are formed, which can be easy separated by sieving.

For example, the separation of the protective coating can be carried out by sieving (90 μm), which results in e.g. a decreasing of the nickel content to 400 ppm [18].

The decrepitation process can be an integral part of the neodymium magnet manufacturing process [15,20,21]. The hydrogenated material can be used in various ways: as a neodymium- rich concentrate or as an initial material for the manufacturing of new magnets.

**Experimental**

The aim of this work was to examine the recycling process of Nd-Fe-B magnets using HD process and to determine the optimal technological parameters: temperature and pressure. The influence of parameters was determined by examining morphology and phases changes after decrepitation. The possibility of separation the protective coating from the disintegrated magnet by sieving was also tested.

The study was conducted in the following order:

- characteristics of the initial material,
- demagnetization,
- hydrogenation/disintegration,
- characteristics of the disintegrated material,
- sieving tests.

The initial material was commercial cuboids neodymium magnets Nd-Fe-B N42 with dimensions of 25x10x2 mm covered with a metallic protective coating. The composition of the initial material was examined by ICP-MS method on an ELAN 6100 analyzer (Perkin Elmer); sample (demagnetized and crushed magnet with coating) was dissolved in hot aqua regia and examined for composition. Before the hydrogenation process, the magnets were demagnetized at 350 °C (above the Curie point) for 1 h in a slightly oxidizing atmosphere. Hydrogenation (i.e. hydrogen sorption) of neodymium magnets was carried out using the gas sorption analyzer IMI-0118 (Hiden Ioschema), whose operation is based on the Sievert volumetric method. To determine the phase changes after HD, magnets were examined by x-ray powder diffraction method on a Rigaku MiniFlex II. Morphological changes were determined by analysis on a scanning electron microscope Hitachi SU 70. The separation possibility of magnet from coating was tested by sieving of disintegrated magnets on a metallic sieve with a 3 mm square mesh.

**Results and discussion**

The chemical composition of the initial material is shown in Table 1. In addition to the typical composition of neodymium magnets (Fe, Nd and B), the initial material contained small amounts of dysprosium (0.12 wt.%), as well as nickel, copper and cobalt (in total about 3.95 wt.%), which come from a protective coating.

| wt.% | Nd  | Fe  | B   | Dy  | Ni  | Cu  | Co  | other |
|------|-----|-----|-----|-----|-----|-----|-----|-------|
|      | 7.77| 83.98| 2.14| 0.12| 0.85| 2.15| 0.95| 2.04  |

Table 1. Chemical composition of the initial material examined by ICP-MS

The composition of the protective coating is also confirmed by the cross-sectional analysis (Figure 2). The protective coating is compact, has a thickness of approx. 13 μm.
Interior of the magnet (i.e. away of the coating) has a typical neodymium magnet composition.

As a result of demagnetization in slightly oxidizing atmosphere, the protective coating has oxidized, which can be deduced after the color coating has changed (Figure 3). The disintegration was estimated arbitrary based on the appearance of the samples after decrepitation process, i.e. whether the sample completely disintegrated into powder and whether the protective coating was detached from the magnet. Based on subsequent photos (Figure 3), it can be concluded that the magnets exposed to hydrogen atmosphere at 29 and
100 °C were completely disintegrated. Other samples were only partially or slightly disintegrated. The least disintegration was observed in magnets exposed to hydrogen atmosphere at 400 °C at 1 and 2 bar pressure. These samples disintegrated into large pieces, from which the protective coating did not detached. In cases of well disintegrated samples, it is easy to see the peeled off layers of the protective coating.

Figure 3. Initial, demagnetized and disintegrated magnets; dark grey captions indicates those samples which are indicated as fully disintegrated

The results from the hydrogen sorption analyzer (Tables 2 and 3) show that the highest hydrogen uptake (2043.76 μmol·g⁻¹) was received for conditions 4 bar and room temperature, while the lowest (925.27 μmol·g⁻³) for 1 bar at 400 °C (Figure 4). At room temperature (29 °C), hydrogen uptake increases (from 1853.85 to 2043.76 μmol·g⁻¹) with increasing pressure and with decreasing process duration (from 869 min to 228 min) from 2 to 4 bar, respectively. An increase in temperature causes a decrease in the hydrogen uptake value. Maximum uptake values received at 300 and 400 °C are almost two times lower than maximum uptake values at room temperature and 4 bar conditions.

| pressure (bar) | 29  | 100 | 300 | 400 |
|---------------|-----|-----|-----|-----|
| 1             | -   | 1569.58 | 1107.16 | 925.27 |
| 2             | 1853.86 | - | 1131.42 | 1230.60 |
| 3             | 2007.31 | - | - | - |
| 4             | 2043.76 | - | - | - |

| pressure (bar) | 29  | 100 | 300 | 400 |
|---------------|-----|-----|-----|-----|
| 1             | -   | 540 | 623 | 279 |
| 2             | 869 | -   | 243 | 205 |
| 3             | 272 | -   | -   | -   |
| 4             | 228 | -   | -   | -   |

Table 2. Maximum hydrogen uptakes (μmol·g⁻¹) vs temperature and pressure

Table 3. Decrepitation duration (min) vs temperature and pressure
Figure 4. Relationships between maximum hydrogen uptakes and decrepitation duration vs temperature at 1 bar (left) and 2 bar (middle) and vs pressure at room temperature (right)

Morphological differences that have occurred in the hydrogenated samples, in relation to the initial material, are shown in Figures 5-7. The initial material (A in Figure 5) consists of evenly distributed regular grains with different chemical composition: in microscopic images, bright areas indicate higher content of neodymium, while dark - iron; this is also confirmed by mapping. In samples received at 2 bar at 300 and 400 °C (respectively B and C in Figure 5) occurred homogenization of the composition: microscopic images have less contrast (they are brighter) and mapping shows even distributions of neodymium and iron, which is clearly shown in B in Figure 5. Homogenization could be promoted by high temperature. The situation is different in the case of the samples gained at 1 bar in different temperatures (D, E and F in Figure 6): on mapping it can be seen specific necks and pools, which are rich in neodymium, resulting from the synthesis of neodymium hydrides. Areas where neodymium occurs are also poor in iron. Despite successful disintegration, the large grains with sizes that correspond to grains in the initial material can still distinguished in the disintegrated material. As mentioned earlier, samples that were decrepitated at room temperature (G, H and I in Figure 7) had the highest maximum uptake values. While in the samples gained at 2 and 3 bar (G and H in Figure 7) grains of the size corresponding to the initial material can be distinguished, in the case of the sample gained at 4 bar (I) material has been disintegrated into a finer powder. In samples H and I it is difficult to distinguish the necks, but it is easier to observe the pools, which may indicate that the hydrides synthesis reactions took place to a large extent.
Figure 5. SEM and mapping analyses of the initial material (A) and samples after decrepitation at following conditions: 300 °C and 2 bar (B), 400 °C and 2 bar (C).

Figure 6. SEM and mapping analyses of samples after decrepitation at following conditions: 100 °C and 1 bar (D), 300 °C and 1 bar (E) and 400 °C and 1 bar (F).
Phase changes of the magnets after decrepitation were presented in XRD spectrograms (Figures 8-16). Most probably, the reflections at 50 and 52 deg are due to the presence of the α-Fe phase, but are not included; only phases containing neodymium are marked in spectrograms. The XRD pattern of the initial material (Figure 8) consists only of the reflections from the Nd$_2$Fe$_{14}$B phase, while after HD, reflections from the synthesized neodymium hydrides appear: NdH$_2$, NdH$_{2.27}$ and NdH$_3$. Reflections from the following hydrides are on each spectrograms (Figures 9-16): NdH$_2$ at approx. 28 and 69 deg, NdH$_{2.27}$ at 28.5 deg and NdH$_3$ at 37.5, 57 and 60.5 deg. Furthermore, in the samples that are obtained as a result of decrepitation at $100^\circ$C (Figure 11) and room temperature and high pressure (Figures 14-16), there are additional reflections from NdH$_{2.27}$ also at 47 and 56 deg. Hence it can be concluded that not only the temperature but also the pressure increase promotes occurring of disproportionation reactions.
Figure 9. XRD patterns of sample obtained at 300 °C and 2 bar

Figure 10. XRD patterns of sample obtained at 400 °C and 2 bar

Figure 11. XRD patterns of sample obtained at 100 °C and 1 bar

Figure 12. XRD patterns of sample obtained at 300 °C and 1 bar
Figure 13. XRD patterns of sample obtained at 400 °C and 1 bar

Figure 14. XRD patterns of sample obtained at room temperature and 2 bar

Figure 15. XRD patterns of sample obtained at room temperature and 3 bar

Figure 16. XRD patterns of sample obtained at room temperature and 4 bar
Sieving tests were performed on fully disintegrated samples. Results of these tests are shown in Figure 17. Best results of coating separation were gained for samples 29 °C, 2 bar and also 100 °C, 1 bar, because the separated pieces of the coating are compact and large. Despite this, in each case, small pieces of coating still remain in the samples. However, the sieving tests demonstrate that it is possible to separate the protective coating from magnet after decrepitation, and the effectiveness of this operation will depend on the chosen mesh.
Figure 17. Results of sieving tests; the coating flakes are marked with circles.
Figure 18 is a presentation of SEM images of the sieved materials (under the mesh). These are fine powders, for which the average particle diameter is in the range 10.30-15.60 μm (Table 4), depending on the material. In this regard, these particles are not homogeneous, what can be derived from the values of the standard deviations (Table 4). Their chemical composition (Table 5) is characterized by a low level of nickel (0.11-0.34 wt.%), which confirms the effectiveness of separating the magnets after decrepitation from protective coating.

Table 4. Average particle diameters (and standard deviations) of the sieved material; average particle diameters based on SEM images (calculations were carried out using the ImageJ software)

| sieved material | 29 °C; 2 bar | 100 °C; 1 bar | 29 °C; 3 bar | 29 °C; 4 bar |
|-----------------|--------------|--------------|--------------|--------------|
| average particle diameter (μm) | 14.75 | 15.60 | 11.30 | 12.29 |
| standard deviation of average particle diameter (μm) | 7.11 | 5.42 | 4.35 | 5.37 |

Table 5. Chemical composition of the sieved material examined by ICP-MS (without hydrogen)

| sieved material | Nd | Fe | B | Ni | other |
|-----------------|----|----|---|----|-------|
| wt.%            | 7.68 | 53.53 | 34.16 | 0.14 | 4.49 |
|                 | 10.71 | 57.55 | 27.13 | 0.11 | 4.50 |
|                 | 8.69 | 54.77 | 31.66 | 0.15 | 4.73 |
|                 | 11.61 | 62.95 | 20.60 | 0.34 | 4.50 |

Conclusions:
Complete disintegration of neodymium magnets under hydrogen atmosphere occurs at a relatively low temperature (<100 °C) and high pressure (2-4 bar). Hydrogen uptake increases with increasing pressure and decreases with increasing temperature. Increased pressure and temperature reduce the process duration.

During the HD process, a number of phase transformations occur in neodymium magnets. The characteristic areas in material are formed at the grain boundaries ("necks") and triple points ("pools") resulting from synthesizing neodymium hydrides. XRD analyzes show that the presence of neodymium hydrides was recorded in each case, regardless of the process parameters.

The decrepitation process can be used as a method of separating the magnet from the protective coating, which is a contaminant. High pressure during HD process is not recommended when using a sieving method for coating separation, so the best conditions for decrepitation, in this regard, according to the above tests; are a temperature 29-100 °C and pressure 1-2 bar.

The choice of technological parameters is a compromise between, the extent of disintegration, the process duration, and the size and number of pieces of coating, which can be easily and efficiently separated by sieving.

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