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Complex Characteristics of Sintered Nd–Fe–B Magnets in Terms of Hydrogen Based Recycling

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Sintered Nd–Fe–B magnets, dismantled by the P.P.H.U. Polblume company from scrap hard disc drives and medical device, were thermally demagnetized and analyzed in terms of their chemical composition, structure and magnetic properties. Magnets from hard disc drives drives had a magnetic structure of two opposite poles in a plane of a magnet and were covered with a nickel coating (around 50 μm in thick), which however was often discontinuous and deeply scratched. The majority of the magnets were partially destroyed (broken or corroded). The magnet from hard disc drives were basically made of iron (65±1 wt%) and neodymium (30±2 wt%) however, they also included alloying elements such as Co (1–2.5 wt%), Dy (0–1 wt%) or Pr (0–5 wt%). The magnets from medical device consisted only of iron (65±1 wt%) and neodymium (34±1 wt%). Magnets of both kinds were textured thus their XRD patterns were amended. Diffraction patterns, typical for the $Nd_2Fe_{14}B$ (φ) phase, were achieved after mechanical crushing of the bulk magnets. A regular X-ray diffraction pattern was achieved after mechanical crushing of the magnets. The microstructure of both types of the magnets, observed by scanning electron microscopy, consisted of grey grains of a $Nd_2Fe_{14}B$ (φ) phase and a Nd-rich grain boundary phase. The magnets from hard disc drives exhibited excellent magnetic properties and anisotropy: maximum energy product above 300 kJ/m^3, remanence around 1.4 T and coercivity around 1000 kA/m, slightly varying between each magnet. Magnetic properties of medical magnet were only a little worse: maximum energy product above 200 kJ/m^3, remanence around 1.1 T and coercivity around 900 kA/m. Hydrogen disproportionation phase diagrams (temperature vs. pressure) were constructed for both kinds of the magnets, revealing possible conditions for the hydrogenation, disproportionation, desorption and recombination reaction.

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1. Introduction

It is a commonly known fact that noble and precious metals, including rare earth elements, should be recovered from the waste of electric and electronic equipment (WEEE). There is an urgent need for studies focused on recycling technologies. The rare earths metals have been recognized as critical raw materials for the UE [1, 2]. This is due to economic and environmental reasons. Recycling and recovery methods must be however designed for a particular type of electronic scrap (e-scrap) because it consists of various kinds of materials. Therefore, the present work is focused on characterization of scrap neodymium–iron–boron magnets. These so-called neodymium magnets are made of "rare earth" elements (Nd, Pr, Dy, Tb) and are available in quite a large amount in the e-scrap, however they are spread. The neodymium magnets are parts of electric motors, MRI[†] devices, detection systems, sensors, loudspeakers etc. Many of the Nd–Fe–B magnets are located in voice coil motors (VCMs) of computer hard disc drives (HDDs). There are two sintered Nd–Fe–B magnets, each 10–20 g, in the VCM of each HDD — for more details see [3]. According to Walton et al. [4], old computers are replaced by newer ones in around a five-year period. Thus, a constant inflow of scrap magnets occurs. The WEEE can be recognized as an "urban ore" and can be a source of rare earth metals that one can consider as *urban mining concept* [5]. The magnets represented more than 25% of all world applications of the rare earth metals in 2015 [6]. The market of the Nd–Fe–B magnets is about 60,000 ton per year and is expected to grow [7]. It is estimated that HDDs are the single largest products of Nd-FeB magnets in electronic goods with almost 600 million manufactured annually supplying 6000 to 12,000 tons of neodymium–iron–boron alloy [8]. Taking all of these into account, a full characteristic of scrap Nd–Fe–B magnets was carried out in hopes that this will help for further reprocessing of these materials.

2. Experimental

The sintered Nd–Fe–B magnets were provided by the P.P.H.U. Polblume Zbigniew Miazga company. A magnetic field viewer film was placed into the hard disc drive magnets to reveal their magnetization. Subsequently, all of the magnets were thermally demagnetized. Visual observations were carried out in order to estimate size, shape, mass and the general look of the magnets. Coatings of the hard disc drive's magnets were examined using both light and scanning electron microscopy. Chemical composition of the magnets was investigated using two techniques: energy-dispersive spectroscopy/scanning electron microscopy (EDS/SEM) analysis done at the University, and X-ray fluorescent spectroscopy (XRF)

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†magnetic resonance imaging

analysis provided by the PANalytical company thanks to courtesy of Katarzyna Stepaniuk and Sonia Vicente Dols at PANanalytical B.V. Almelo, Netherlands. The phase structure was analyzed, for as received and crushed magnets, using X-ray diffraction (XRD) technique. Microstructural observations were carried out using SEM. Magnetic properties of hard disc drive magnets were investigated using cubic samples (1.5–1.5–1.5 mm), that were cut from the magnets, magnetized at 6 T field by a pulse field magnetizer and demagnetized using vibrating sample magnetometer (VSM). This procedure was repeated three times for each of the three orthogonal axes of the cubic sample. As a result, three demagnetizing curves were gathered for each sample, referring to the three mutually perpendicular directions of magnetization/demagnetization (one direction was perpendicular to the flat surface of the magnet and the other two were in plane directions). A medical device magnet was measured in a similar way along the two perpendicular directions. It was necessary to determine the temperature and the hydrogen pressure required for an initialization of the disproportionation reaction because the hydrogenation, disproportionation, desorption and recombination process (HDDR) process is considered as a possible method for recycling of the magnets [9]. Hydrogen disproportionation phase diagrams were constructed for both kinds of the magnets at various temperatures in a range of 500–100 °C. The HDDR reaction is based on a reversal phase transformation (disproportionation and recombination) described by the following formula:

$$Nd_2Fe_{14}B + 2H_2 \Leftrightarrow 2NdH_2 + Fe_2B + 12Fe. \quad (1)$$

Disproportionation means that the $Nd_2Fe_{14}B$ phase (main structural constituent of the magnets) decomposes into the mixture of neodymium hydride (NdH_2), iron boride (Fe_2B) and free iron (Fe). Transformation occurs under hydrogen (H_2) at elevated temperature (around 600–900 °C). The initialization of the disproportionation reaction was monitored by a drop of pressure and was examined step by step at selected temperatures.

3. Results

A drive casing must be dismantled in order to get to the magnets (several screws must be released). Finally, the magnets must be detached from a steel plate that holds them in voice coil motor. The Nd–Fe–B sintered magnets, placed in the VCMs of HDDs, are flat and "C-like" shape (arc-shaped) — Fig. 1. Dismantling procedure might partly damage the magnets (coatings might peel away or the magnets might break). If so, one could expect increased corrosion of the magnets. One could reveal bipolar magnetization of the magnets (Fig. 2) which is likely due to the way of they work [3]. Following analyses were preceded by thermal demagnetization of the magnets. The magnetic properties of the HDDs magnets are excellent, especially when measured perpendicular to the flat surface of the magnets. Demagnetizing curve (2nd quadrant) is presented in Fig. 3. The magnets exhibit strong anisotropy (M_r^{II} to M_r^T ratio is 5.6).

Fig. 1. The Nd–Fe–B magnets dismantled from HDDs. The magnets are flat and "C-like" shape.

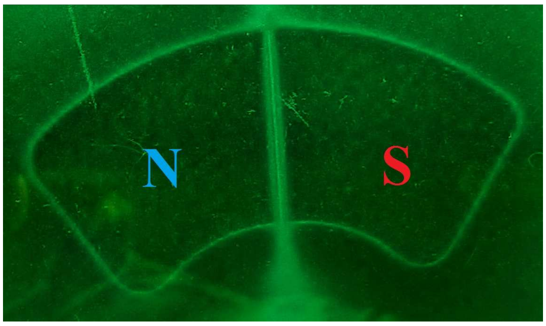

Fig. 2. The Nd–Fe–B magnets from HDDs have bipolar magnetizing.

Magnets dismantled from medical device are shown in Fig. 4. They are much bigger. The demagnetizing curves (2nd quadrant) along two directions of the medical magnet are presented in Fig. 5. One could notice strong anisotropy of the medical magnet (remanence proportion is 9).

The magnets from hard disc drives were covered with — around 50 μm thick — nickel coating (Fig. 6). The coating is expected to protect against corrosion and prevent crumbling of individual grains. However, the magnets delivered have the coating which is often broken because of dismantling procedure and storing conditions. Dealing with the coating, in terms of recycling, has been previously reported [10].

The mass of the examined HDDs magnets varies between 10 and 20 g, depending on their size, which is iden-

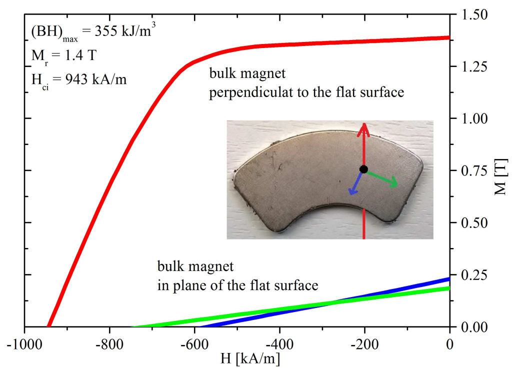

Fig. 3. Demagnetizing curve (2nd quadrant) for HDDs magnets.

Fig. 4. Magnets dismantled from medical device.

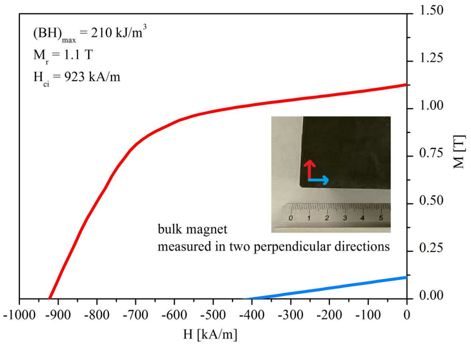

Fig. 5. Demagnetizing curve (2nd quadrant) for medical device magnet.

tical to the results reported by Walton et al. [4]. The chemical composition of the magnets is dominated by iron (65±1 wt%) and neodymium (30±2 wt%). However, different concentrations of alloying elements, such as Co (1–2 wt%), Dy (0–1 wt%) or Pr (0–5 wt%), might be found in the magnets. These additives are used in order to improve magnetic properties of the magnets, e.g. enhancing coercivity or increasing operating temperature [11]. One could refer to the market review, provided by Walton [12], which shows that the chemical composition of the scrap magnets varies with the year of production and is not reproducible even by a one supplier.

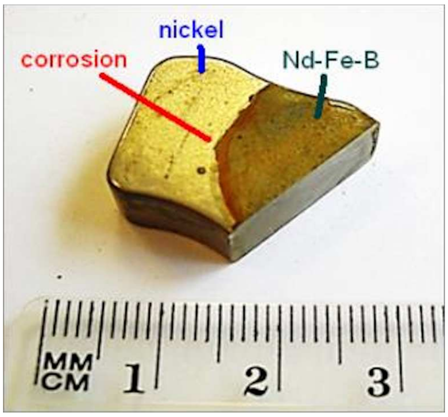

Fig. 6. The hard disc drive magnets are covered with a protective nickel (sometimes Ni/Cu) coating. The coating of scrap magnets is often discontinuous, enhancing corrosion of the magnets.

The microstructures of the magnet from hard disc drive and of the magnet from medical device are shown in Fig. 7 and Fig. 8, respectively. Both structures are similar and consist of grey grains of the hard magnetic $Nd_2Fe_{14}B$ (φ) phase and the bright paramagnetic Nd-rich grain boundary phase (dark areas indicate pores). This dual-phase structure is essential for achieving good magnetic properties. The paramagnetic grain boundary phase is expected to magnetically isolate the hard magnetic grains, hindering the demagnetization of the magnet.

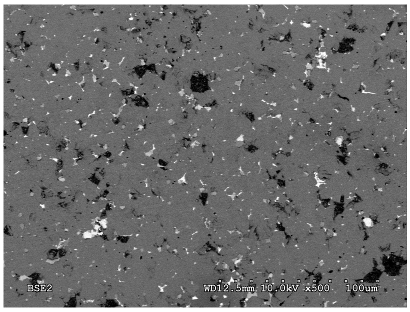

Fig. 7. Microstructure of the magnet dismantled from hard disc drive. Bright Nd-rich grain boundary phase is visible between the grey grains of $Nd_2Fe_{14}B$ (φ) phase. Black areas indicate pores left after crumbling of grains.

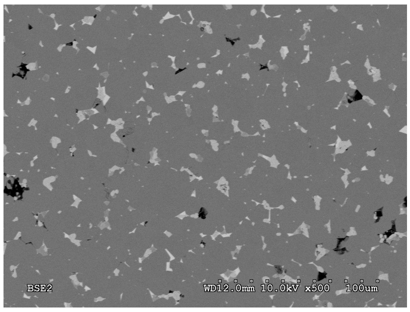

Fig. 8. As in Fig. 7 but for the magnet dismantled from medical device.

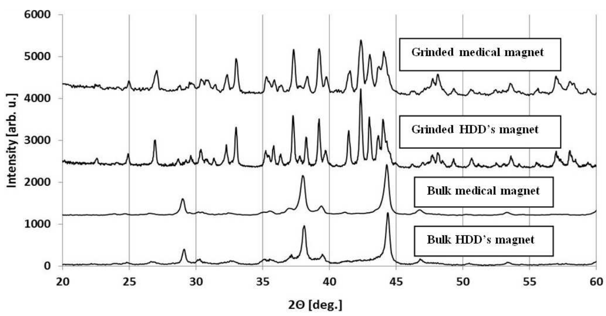

Fig. 9. Phase structure of the magnets. The bulk, as received, magnets exhibit textured structure (at the bottom). The typical XRD pattern for the Nd–Fe–B magnets might be obtained for grinded powders.

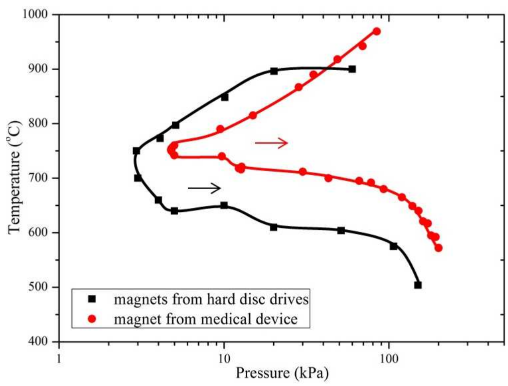

Fig. 10. Hydrogen disproportionation phase diagram for the magnets. Temperature and hydrogen pressure required for the disproportionation reaction are available on the right side of the diagram (indicated by arrows).

The XRD patterns observed for both types of magnets "in raw state" indicate textured structure (Fig. 9, bottom). The typical pattern for the Nd–Fe–B magnet might be achieved after pulverization of the magnets (Fig. 9, top).

The hydrogen disproportionation phase diagrams, indicating the hydrogen pressure required at selected temperatures for the initialization of the disproportionation reaction, are plotted for both kind of the magnets in Fig. 10. Arrows show that the disproportionation proceeds for the parameters available on the right side of the curves. As one could see, a higher pressure is required for the medical device magnet than for the hard disc drives one in order to initialize the disproportionation at the same temperature.

4. Summary

The holistic characterization of the Nd–Fe–B sintered magnets, dismantled from scrap hard disc drives and medical device, was provided. The magnets from hard disc drives have 10–20 g and are covered with Ni coating. These results are with good agreement to the work of Walton et al. [4]. The medical device magnets are larger but free of coating. Chemical composition of all the magnets is based on iron (65 wt%) and neodymium (30–34 wt%). Hard disc drive magnets contain also small amount of alloying elements (Co, Dy, Pr). Two magnetic poles might be recognized at the surface of the hard disc drives magnets. Magnetic properties of the magnets are excellent, especially when measured perpendicular to their flat surface $(\boldsymbol{BH})_{\max}$ above 300 kJ/m^3. Magnet from medical device exhibits not much less $(\boldsymbol{BH})_{\max}$ above 200 kJ/m^3.

The magnets from hard disc drives have bipolar magnetizing and exhibit excellent magnetic properties, especially when measured perpendicular to their flat surface (strong anisotropy is observed).

Such investigations are believed to be useful for further recycling of the scrap magnets and developing of recovery technologies. For example, for the past few years Hitachi Ltd. has developed a technology allowing for dismantling and recycling of rare earth magnets from HDDs and compressors of air conditioners [13]. The machine is able to deal with approximately 100 HDDs per hour comparing with 12 HDDs dismantled manually by one person in the same time [14]. On the other hand, it was recognized as a difficult to scale up the HDDR process due to endothermic nature of the recombination reaction which alerts the kinetics of the reaction (significant variations in magnetic properties were observed after processing of 400 g batches of Nd–Fe–B material [15]). Besides, also differences in chemical composition of the magnets, tendency to oxidation and residuals of nickel coating present in recycled material seem to be challenges for recycling.

Acknowledgments

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