

STRUCTURE AND PROPERTIES OF Nd-Fe-B ALLOY SUBJECTED TO HDDR PROCESS

In this paper the Hydrogenation, Disproportionation, Desorption and Recombination (HDDR) route was tested, for the Nd-Fe-B master alloy, as a prospective procedure for recycling of sintered scrap neodymium magnets. The HDDR method is based on the hydrogen induced reversal phase transformation of Nd-Fe-B alloy: $\text{Nd}_2\text{Fe}_{14}\text{B} + (2\pm x) \text{H}_2 = 2\text{NdH}_{2\pm x} + \text{Fe}_2\text{B} + 12\text{Fe}$. Microstructural observations (SEM), phase constitution studies (XRD) and measurement of magnetic properties (VSM) were done to investigate the HDDR transformation progress. It was observed that disproportionation reaction starts at the grain boundaries, where the Nd-rich phase is located. Average grain size was reduced and coercive material was produced as a result of the HDDR process. Obtained results are similar to literature data.

Keyword: HDDR; magnets hydrogenation; NdFeB alloy; neodymium magnets; magnets recycling.

1. Introduction

In recent decades a tremendous technological development, especially in the field of electronic devices, is observed. Electronic equipment is widely used in both industrial and domestic appliances. As getting older, such devices are very often replaced by newer ones. Increasing amount of electronic waste is a huge problem for environment, however, it also becomes a potential source of resources. High-tech instruments, that contain valuable materials like noble metals and rare earth elements, are very interesting from the recovery point of view. The list of elements accumulated in the electronic scrap was presented in a huge report prepared on demand of United Nations Environment Programme (UNEP) [1]. It was stated that even 60 elements can be present in the electronic waste. It is believed, that neodymium magnets, besides components made of noble metals, are one of the most interesting group of electronic waste to be recycled. Their chemical composition is based on the rare earth elements [2-4], like neodymium (Nd), dysprosium (Dy) or praseodymium (Pr), which are now considered by the European Commission to be the critical ones [5]. Furthermore, development of new green technologies, such as aerogenerators or electric engines-industries, is controlled by rare earth supply [6]. Nowadays, China is almost the sole exporter of rare earth elements. Although, there is no huge risk of delivery limitation yet, it might appear soon. In the close future the access to the rare earth deposits might be an important problem for countries, which want to develop high-tech industry.

There is a Hydrogenation, Disproportionation, Desorption and Recombination process (HDDR), which is used in the magnets industry since the eighties of twenty century. This process, applying to magnets during manufacturing stages, is known to improve the Nd-Fe-B magnets coercivity by the grain

decrepitation. According to literature data [7-10] the HDDR process was briefly described in section 2 – Experimental. The HDDR method is based on reversal transformation, in which the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is disproportionated into $\text{NdH}_{2\pm x}$, Fe_2B and Fe and then, in the next step, those components recombine to form the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase again, but with much smaller grain. The HDDR route is considered to be a perspective procedure for recycling of sintered scrap magnets from hard disc drives [7-9]. Most of the literature, in the field of HDDR, is concentrated on studies done on powder form of material. In such case, samples are firstly subjected to Hydrogen Decrepitation process (HD), which is known to crush Nd-Fe-B alloys into the powder [11]. Then, the powder is processed by the HDDR route. The motivation for this work was to initially recognize an influence of the HDDR process on the bulk Nd-Fe-B alloy with a Nd-rich phase existing at the grain boundaries and consider it as useful result for recycling technique, which is planned to be developed by authors in the future.

2. Experimental

The nominal composition of the alloy was $\text{Nd}_{15}\text{Fe}_{79}\text{B}_6$. There is an excess of neodymium ($\text{Nd}/\text{Fe} = 0,19$) in respect to the stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase ($\text{Nd}/\text{Fe} = 0,14$). The Nd-rich phase is expected to exist in the alloy at the grain boundaries. The alloy was firstly subjected to annealing in vacuum at 1100°C for 48 hours to provide homogenization. Then, cuboid samples, with the weight around 5 g, were cut from the alloy and subjected processing. The experimental station was built of processing pipe, movable furnace, vacuum pumps system, gas delivery system, flow regulators, pressure gauge and temperature detector. Several HDDR processes, in various temperatures, were carried out according to [7-10] literature

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data. The HDDR process is based on reaction Eq. (1):



The transformation occurs reversibly in the temperature range of 700-900°C under hydrogen pressure. In the first technically stage, called “Hydrogen Disproportionation”, the alloy is annealed under hydrogen atmosphere. During this stage the Nd₂Fe₁₄B phase absorbs hydrogen and disproportionates into neodymium hydride, iron boride and free iron. In the second stage, called “Desorption and Recombination”, the hydrogen is evacuated from the processing chamber and accumulated hydrogen is desorbed from the material. It was shown, that the desorption of the hydrogen from the Nd-Fe-B alloy runs stepwise [12]. During this step recombination reactions starts. All the three compounds (NdH_{2±x}, Fe₂B and Fe) react with each other and form the Nd₂Fe₁₄B phase again. The recombined Nd₂Fe₁₄B phase has much more smaller grain, then it had before the HDDR process. The technical scheme of the HDDR process is shown in Fig. 1. After processing, microstructure observations (SEM – SU-70), phase constitution studies (XRD – Rigaku Miniflex II Diffractometer with Cu Kα) and magnetic properties measurements (VSM – Lakeshore 7410) were carried out to investigate changes in the alloy.

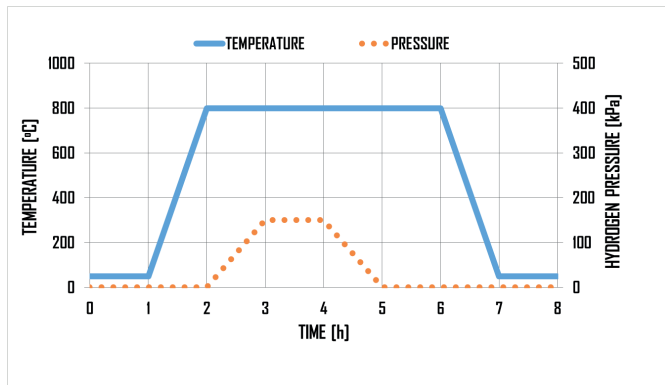


Fig. 1. Scheme of the HDDR process

3. Results and discussion

3.1. Initial state

Microstructure of the alloy in the initial state is presented in Fig. 2-left. One could see grains of the Nd₂Fe₁₄B phase (grey) and the Nd-rich phase at the grain boundaries (bright). Corresponding XRD pattern is shown in Fig. 2-right. Magnetization curve and magnetic properties are presented in fig. 2-bottom. One could state, they are typical for soft magnets, what is a result of large grain structure of the alloy in the initial state.

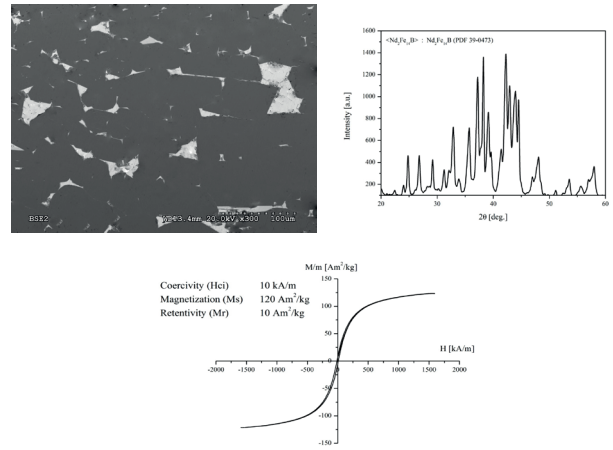


Fig. 2. Microstructure of the Nd-Fe-B alloy in the initial state - left, corresponding XRD pattern – right, and correlated magnetization curve – bottom

3.2. Disproportionation stage

Effect of the disproportionation reaction can be even seen in a macroscale (Fig. 3), where the reaction front is visible. One could see, that the external area of the sample is in reaction stadium, while the internal part of the sample is still untouched. When looking in a microscale, it might be noticed that the reaction propagates through the grain boundaries. It is due to the hydrogen easy diffusion route and strong neodymium affinity to hydrogen. Several pictures of the reaction progress are presented in Fig. 4. Similar model of the reaction was presented in literature schemes [13].

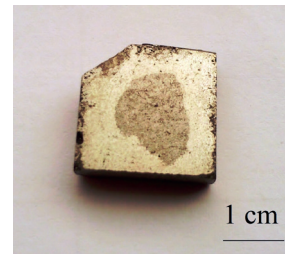


Fig. 3. Macrostructure of the sample during disproportionation reaction

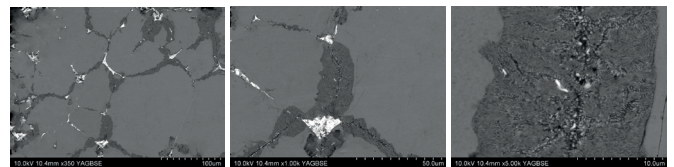


Fig. 4. Microstructure of the alloy in the first stage of the reaction

Finally, the reaction leads to the lamellar microstructure, which could be seen in Fig. 5-top. White strips are known to be the rod-like Nd hydride phase and black strips are Fe phase [14]. However, further heating might lead to evolution of the microstructure and decay of the lamellar microstructure. The XRD pattern, in the disproportionation stage, is shown in Fig. 5-left. One could notice the presence of NdH_x , Fe_2B and Fe. Obtained microstructure and phase constitution pattern are the same like indicated in literature [14]. In disproportionated state the alloy has soft magnetic properties, which is confirmed by magnetization curve presented in Fig. 5-right.

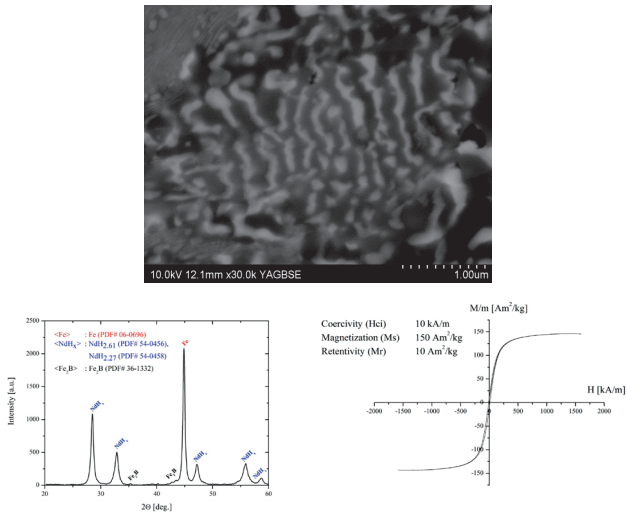


Fig. 5. Microstructure of the alloy in disproportionated state – top, corresponding XRD pattern- middle, and correlated magnetization curve – left

3.3. Recombination stage

The microstructure, in recombined state, is presented in Fig. 6-top. Submicron grains of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase (grey) can be observed and the Nd-rich phase (bright), located at the grain boundaries, can be noticed. The strong grain refinement is achieved as a result of the HDDR process. XRD pattern, for the recombined alloy, is presented in Fig. 6-left, where one could clearly see the presence of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase again. However, there are some differences in the diffraction pattern, in reference to the spectrum obtained in initial state. Firstly, iron peak (Fe) is present, which means, that either the temperature or desorption time (or both) were not long enough to provide full recombination. On the other hand, the alloy might be overheated and it would not possess nano-grains. Secondly, neodymium (Nd_2O_3) and iron (Fe_3O_4) oxides appeared after the recombination stage. There is an excess of neodymium in the alloy, which increases tendency to oxidation. The most likely reason of oxidation is the fact that in our experiments the processing chamber was opened in the middle of the process to investigate the reaction progress. Recent study on HDDR reveals, that oxidation can be avoided when the

entire processing is carried out in one chamber [15]. In such situation formation of Nd_2O_3 is inhibited. The alloy examined in our studies has hard magnetic properties after recombination. Wide hysteresis loop, with the coercivity above 500 kA/m, is presented in Fig. 6-right. According to the pinning theory, magnetic coercivity can be increased due to the grain refinement [14,16]. The coercivity increases, if the grain is fine enough to be a single domain. Critical single domain size for the $\text{Nd}_2\text{Fe}_{14}\text{B}$ is 0,24 μm . Furthermore, separation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, due to the presence of the Nd-rich phase between them, results in magnetic isolation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains and provides high coercivity of the material [14,16]. Moreover, in our experiments the commercial Nd-Fe-B alloy was examined. However, the HDD sintered magnets contain additions of other elements, as well. In such a case, some modifications in the HDDR process should be introduced to co-process different magnets. Increasing of hydrogen pressure, which provides full disproportionation of co-processed different magnets, is mentioned in [15] and allows for producing highly coercive materials.

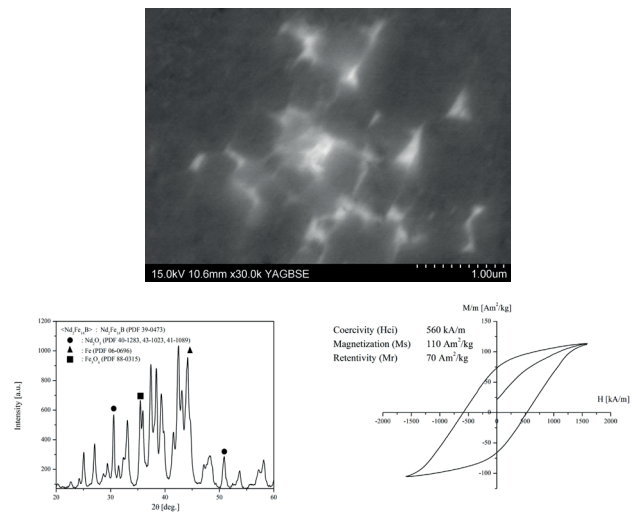


Fig. 6. Microstructure of the alloy after recombination – top, corresponding XRD pattern – right, and correlated magnetic hysteresis loop - right

3.4. Additional observations

It was observed, that the samples subjected to the HDDR process at lower temperature (650) were crushed into the powder and were very brittle, but they still underwent the HDDR process. It is likely due to the concurrent process – HD – which results in crushing of the Nd-Fe-B alloys [11]. Moreover, it should be mentioned, that decrepitating process undergoes in two stages. Firstly, during so-called HD, $\text{Nd}_2\text{Fe}_{14}\text{BH}_{2.5-2.9}$ and $\text{NdH}_{2.2-4}$ are formed in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Nd-rich phase, respectively. Secondly, when disproportionation starts, $\text{Nd}_2\text{Fe}_{14}\text{BH}_{2.5-2.9}$ decrepitates into $\text{NdH}_{2\pm x}$, Fe_2B and Fe. However, pulverization during the HD can be avoided by heating up to the processing temperature without hydrogen.

4. Conclusions and summary

Experiments, presented in this paper, show that the disproportionation reaction starts at the grain boundaries, where the Nd-rich phase is located. Similar model of the reaction was presented in schemes in [13]. Microstructural observations and structure measurements are similar to the results presented in [10, 14]. Average grain size was reduced as a result of the HDDR process. Coercive material was produced after the HDDR treatment, which was due to the grain refinement and magnetic separation of the Nd₂Fe₁₄B grains [14,16].

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REFERENCES

- [1] M. Schlupe, Ch. Hagelueken, R. Kuehr, F. Magalini, C. Maurer, Ch. Meskers, E. Mueller, F. Wang, Recycling From E-Waste To Resources - United Nations Environment Programme, Oktoberdruck AG Berlin 2009.
- [2] J.M.D. Coey, IEEE T Magn. **47**, 4671 (2011).
- [3] J.M.D. Coey, Rare-Earth Iron Permanent Magnets, Oxford 2006.
- [4] S. Pandian, V. Chandrasekaran, G. Markandeyulu, K.J.L. Iyer, K.V.S. Rama Rao, J. Appl. Phys. **92**, 6082 (2002).
- [5] http://ec.europa.eu/enterprise/policies/rawmaterials/documents/index_en.htm
- [6] K. Binnemans, P.T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton, M. Buchert, J. Clean. Prod. **51**, 1 (2013).
- [7] B.F.A. Da Silva, S.R. Janasi, H. Takiishi, D. Rodrigues, M.F. De Campos, Hybrid Bonded Rare-Earth Magnets Produced with Strontium Ferrite and Recycled NdFeB Powders, in: Proceedings of the 22nd International Workshop on Rare-Earth Permanent Magnets and their Applications 2012.
- [8] K. Güth, T.G. Woodcock, L. Schultz, O. Gutfleisch, Recycling of sintered Nd-Fe-B magnets by the d-HDDR route, in: Proceedings of the 22nd International Workshop on Rare-Earth Permanent Magnets and their Applications 2012.
- [9] A. Walton, A.I. Bevan, V.S.J. Mann, J.D. Speight, I.R. Harris, A.J. Williams, H. Yi, The Use of Hydrogen to Separate and Recycle NdFeB Magnets from Electronic Waste, in: Proceedings of the 22nd International Workshop on Rare-Earth Permanent Magnets and their Applications 2012.
- [10] G.C. Hadjipanayis, Bonded Magnets. Proceedings of the NATO Advanced Research Workshop on Science and Technology of bonded magnets, Springer Netherlands, 2003.
- [11] O. Gutfleisch, I.R. Harris, J. Phys. D: Appl. Phys. **29**, 2255 (1996).
- [12] A.J. Williams, P.J. McGuinness, I.R. Harris, J. Less-Common Met. **171**, 149 (1991)
- [13] M. Itakura, N. Kuwano, K. Yamaguchi, T. Yoneki, K. Oki, R. Nakayama, N. Komada, T. Takeshita, Mater. Trans. JIM **1**, 95 (1998).
- [14] O. Gutfleisch, J. Phys. D: Appl. Phys. **33**, 157 (2000).
- [15] R.S. Sheridan, A.J. Williams, I.R. Harris, A. Walton, J. Magn. Mater. **350**, 114 (2014).
- [16] Y. Shinba, T.J. Konno, K. Ishikawa, K. Hiraga, M. Sagawa, J. Appl. Phys. **97**, 053504 (2005).

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