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Titel der Einreichung:

Improving the functional recycling of rare earth permanent magnets from various waste streams

Kontaktdaten:

Name: Mario Schönfeldt, M. Eng.

Institut: Fraunhofer IWKS / Technische Universität Darmstadt

Fachrichtung: Materialwissenschaft

Adresse: Aschaffenburger Str. 121, 63457 Hanau

E-Mail: mario.schoenfeldt@iwks.fraunhofer.de

Telefon: +49 6023 32039-852

Fraunhofer
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Improving the functional recycling of rare earth permanent magnets from various waste streams

1. Introduction

Since its discovery in 1983, Nd-Fe-B is the permanent magnet (PM) material with the highest energy product at room temperature (RT). Today Nd-Fe-B is the material of choice in many key technologies like renewable energies (e.g. offshore wind turbines), electric vehicles (EV), robotics, and numerous consumer electronics. Against this background, it is supposed that the demand for high quality permanent magnets will increase significantly in the near future. According to the study Rare Earths: Outlook to 2029 the demand of rare earths (RE) will reach 55 kt RE oxides (REO) in 2024 and 68.6 kt REO in 2029 with a growth rate of 6.0 % and 4.5 % per year, respectively. RE containing magnets are projected to be responsible for 37.8 % of total RE demand in 2029. The European Raw Material Alliance (ERMA) states, that 95 % of all EV traction motors worldwide uses rare earth containing magnets. The required quantity of RE PMs in this sector will grow from 5 kt in 2019 to up to 70 kt per year by 2030. Unfortunately, the required REs, especially the heavy rare earths (HRE), are considered as highly critical and the depletion and metallurgical processes to gain the REO from ores have a big environmental footprint. Lowering the criticality and increasing the sustainability of rare earth permanent magnets are challenges which have to be solved for an environmentally friendly and carbon neutral future. These aims are in accordance with the United Nations Sustainable Development Goals and the European Green Deal. Development of more resource efficient production processes or optimization of microstructure and resulting magnetic properties are two opportunities to achieve this goal, another one is the usage of recycled material.

Currently, the research focus is dedicated to the development of different recycling procedures and many efforts were made to increase the magnetic properties and sustainability of recycled RE PMs. Today several approaches exist and are on the way to enter the RE market: (i) elemental recycling, (ii) powder metallurgical magnet-to-magnet or functional recycling, and (iii) re-melting scrap magnets and the subsequent production of sintered, hot-deformed or polymer bonded magnets. The second recycling approach aims to the production of recycled magnets directly from scrap magnet material via hydrogen decrepitation (HD) and subsequent powder metallurgical approaches. The HD recycling process chain can be carried out with standard equipment from sintered magnet production. This lowers significantly the energy consumption of the process, the amount of investment and the production costs. Furthermore, with hydrogen-based magnet-to-magnet recycling it is possible to lower the environmental impact of produced magnets by 64−96 %. However, nowadays magnet recycling on a large industrial scale still does not exist – apart from a few exceptions which showed that the process can be employed at this scale. For a viable and efficient industrial recycling process a circular economy is necessary in which a material can be recycled multiple times. To enhance such a recycling process with reproducible and specified outcomes the knowledge of the material behavior through every process step or recycling cycle is mandatory. In this regard, different material properties like chemical composition, particle size, density, microstructure, magnetic figures of merit or the degree of alignment of different Nd-Fe-B PM alloys over several recycling cycles were investigated.

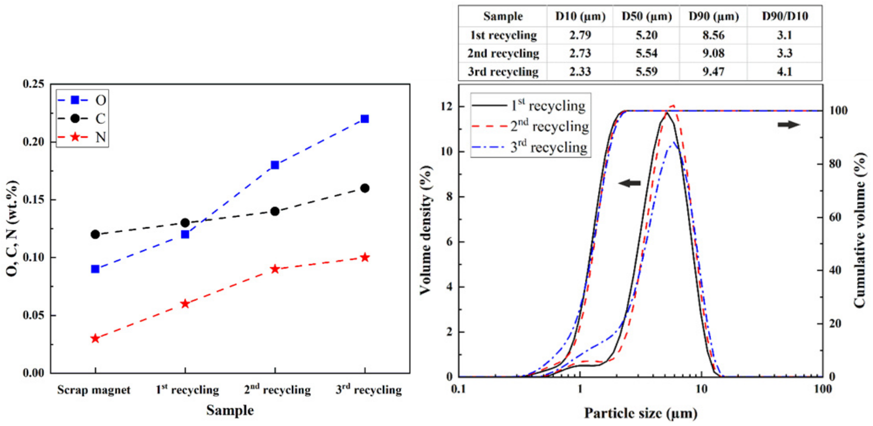
2. Experimental procedure

The starting materials for the investigation of the influence of several recycling cycles were a 10.6 kg scrap magnet used in magnetic resonance tomography (MRT) with the nominal composition of $Nd_{28.04}Dy_{0.80}Tb_{0.44}Fe_{bal}B_{1.06}Co_{1.65}Al_{0.34}Ga_{0.22}Cu_{0.18}$ (wt.%) and over 100 grain boundary diffusion (GBD) magnets (0.5 kg) from industrial magnet production with the nominal composition of $Nd_{22.5}Pr_{5.48}Tb_{1.60}Dy_{0.32}Fe_{bal}B_{0.82}Co_{0.91}Ga_{0.19}Al_{0.14}Cu_{0.11}$ (wt. %). After removing the surface coating via sand blasting the magnets were decrepitated under 5 bar hydrogen at 25 °C, followed by a heat treatment at 500 °C for 2 h and subsequent partially dehydrogenation for 3 h under vacuum and cooling to RT under argon atmosphere. The obtained coarse powder was then milled to a particle size in µm range under nitrogen with a fluidized bed jet mill to reach a particle size of approximately 5 µm D50. The obtained powder was then aligned in a transversal field press under argon atmosphere with an external magnetic field of 2.5 T and pressed to anisotropic green compacts. The green bodies were sintered in quartz glass tubes under vacuum (10^{-6} mbar) at temperatures between 1050 °C and 1100 °C followed by multiple low temperature annealing at 500 °C – 900 °C for 1 h in a tube furnace. Some of the recycled magnets were finally used again for GBD experiments with 1.5 wt.% Tb foil at 900 °C for 9 h with subsequent low temperature annealing. For the multiple recycling experiments, two 2.5 kg isotropic magnets were pressed in a cold isostatic press (CIP) with 1000 kN and 2 min pressing time, which were then sintered and annealed under vacuum in a chamber furnace. After that, the magnets were again hydrogen decrepitated, milled, pressed and sintered under the same conditions described above. For the compensation of Nd-losses and buildup of impurities during the recycling procedure, different amounts of fresh Nd hydride with a particle size (D50) of 3.5 µm were mixed with the recovered powder under argon at a 3D tumbling mixer.

3. Results and discussion

3.1 Multiple recycling of MRT magnets

Non-metallic impurities are known to have a strong impact on the sintering behavior and magnetic properties of magnets. Figure 1 illustrates the measured O, C and N content of the starting material and recycled magnets after each cycle. The starting material has an oxygen content of 0.09 wt.% which increased to 0.22 wt.% after three recycling cycles. Although all synthesis or recycling processes are done under vacuum or argon, oxygen pickup cannot be avoided completely. The carbon content also increases from 0.12 to 0.16 wt.%. The evolution of nitrogen content as a function of recycling cycles, shown in Figure 1, has not been investigated in the literature, yet. However, this is important from a technical point of view, since N_2 is used as the milling gas for industrial magnet production. The nitrogen content also increases through the multiple milling procedures from 0.03 to 0.10 wt.%. This increase with every recycling cycle can lead to a reduction in magnetic properties and sinterability of RE magnets. Despite of increasing amounts of impurities, the absolute content of oxygen, carbon and nitrogen after three cycles is still comparable to primary magnets for the used starting material and technical equipment.



Sample	D10 (µm)	D50 (µm)	D90 (µm)	D90/D10
1st recycling	2.79	5.20	8.56	3.1
2nd recycling	2.73	5.54	9.08	3.3
3rd recycling	2.33	5.59	9.47	4.1

Figure 1: Content of impurities O, C and N (left) and particle size distribution (right) with respect to the recycling cycles. Multiple recycling leads to an increase of impurities and particle size with every recycling cycle.

In addition to the composition and impurities, the particle size distribution of sintering powder, resulting microstructure and grain size is known to have a substantial impact on the magnetic properties. Furthermore, particle size distribution strongly influences the sintering temperature and therefore the amount of energy required for magnet production and recycling. Figure 1 depicts the particle size distributions of sintering powder from each recycling cycle after hydrogen decrepitation (HD) and milling. The average particle size D50 increases from 5.20 µm after first milling to 5.59 µm after the third recycling cycle, while the D90 value also increases. Simultaneously the content of fine particles increases, which is indicated by the D10 values and also shown in the graph in Figure 1 as a growing shoulder. The ratio of D90 and D10 can be used as a figure of merit for a narrow particle size distribution. With increasing amounts of fine particles, the D90/D10-value also increases from 3.1 to 4.1 after three recycling cycles. Reasons for this can be grain growth during multiple sintering, which leads to a coarser microstructure, and oxygen pickup through the recycling cycles. Oxidized 2-14-1 matrix phase or grain boundary phase can influence the hydrogen pick-up during HD processing and would also contribute to a coarser powder after milling.

In Figure 2 the sample z inverse pole figure (z-IPF) maps are plotted. Here, each pixel is color coded according to its orientation with respect to the sample z axis, i.e. alignment direction. Qualitatively, from the decreasing amount of red colored grains compared to the scrap magnet, the reduced degree of orientation in the recycled magnets can be observed. While qualitatively the degree of alignment can be observed from Figure 2, the change according to the number of recycling cycles is not that obvious and needs to be investigated quantitatively by advanced data analysis. In this regard, the list of Euler angles for each indexed pixel, as measured by EBSD, is exported and further analyzed within an external algorithm. The degree of alignment decreases from 89.8 % (1st cycle) to 87.2 % (2nd cycle). The addition of 2 wt.% Nd hydride leads to an improvement to 90.8 % and 88.5 % respectively.

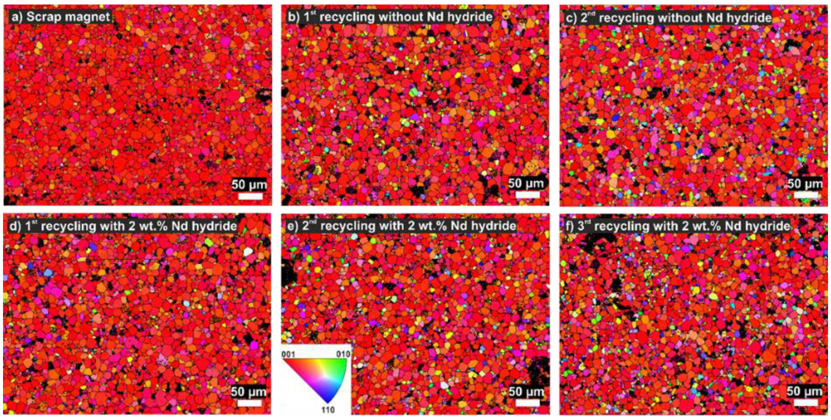


Figure 2: IPF-z maps of the scrap magnet (a), the recycled magnets without Nd hydride addition (b - c) and with Nd hydride addition (d – f). Deviations from red colored grains indicates a misalignment to the sample z axis (magnetization direction). The amount of misaligned grains increases with increasing number of recycling cycles.

3.2 Microstructure evolution through functional recycling of GBD magnets

For applications at elevated temperatures (like electric motors) high coercive magnets are necessary. A common method to increase the temperature stability is the usage of heavy rare earths like Dy or Tb due to their higher magneto crystalline anisotropy. HRE are highly critical and due to their high prices, a cost driver of permanent magnet (PM) production. To reduce the necessary content of HRE the Grain Boundary Diffusion Process (GBD) was developed by Park et al in 2000 and recently successfully implemented into industrial magnet production. This process results into a core shell structure with optimized HRE content and microstructure. The formation of a $(Nd,HRE)_2Fe_{14}B$ shell at the outer region of the $Nd_2Fe_{14}B$ grains leads to a magnetic hardening effect. The formation of reversed domains and demagnetization process starts at the edges and corners of the 2-14-1 grains which can be successfully hindered through the formation of the HRE-shells. At the same time, the HRE elements are only at the position where they are needed, the outer regions of the grains, which leads to a reduction of the necessary HRE content of the whole magnet. In this work, for the first time, commercially available GBD magnets were recycled with the functional recycling approach to answer the question how the powder metallurgical recycling process will influence the core shell microstructure and magnetic properties of recycled magnets.

The microstructure (see Fig. 3 and Fig. 4) of the Nd-Fe-B scrap magnet consists of the typical $Nd_2Fe_{14}B$ matrix grains (dark) which are surrounded by rare earth rich grain boundary phases and triple junctions (bright). At the outer regions of the grains heavy rare earth rich Tb-shells are visible. The recycled magnet shows a homogenous microstructure of $Nd_2Fe_{14}B$ grains and rare earth rich phases with no cracks or pores. It is notable that no core shell structures are visible at the BSE images of powder samples and the recycled magnet (Fig. 3b-d), which indicates that the shells disappear through the functional recycling process. The marked areas within the EDS line scans in Figure 3 mark the regions with a Tb enrichment. The $Nd_2Fe_{14}B$ grains of the scrap magnet show a narrow Tb-shell of approximately 0.5 µm thickness. At the same position with increase of Tb content a decrease of Pr and Nd can be observed which indicate the partial substitution of Pr and Nd with Tb through the formation of $(Nd,Pr,Tb)_2Fe_{14}B$ shells. Also, at both powder samples Tb enrichments at the edges of grains with thickness of 0.5 – 0.8 µm can be measured. The large number of cracks and imperfections between the individual grains makes an accurate measurement more difficult. Compared to these samples, the recycled magnet shows larger Tb enrichments with 4 µm thickness. The reason for this broadening of Tb shells could be the heat treatment processes during functional recycling. The material is heated at 500 °C for 3 h at HD process and 1100 °C for 4 h followed by 700 °C for 1 h and 500 °C for 1 h at sintering and annealing.

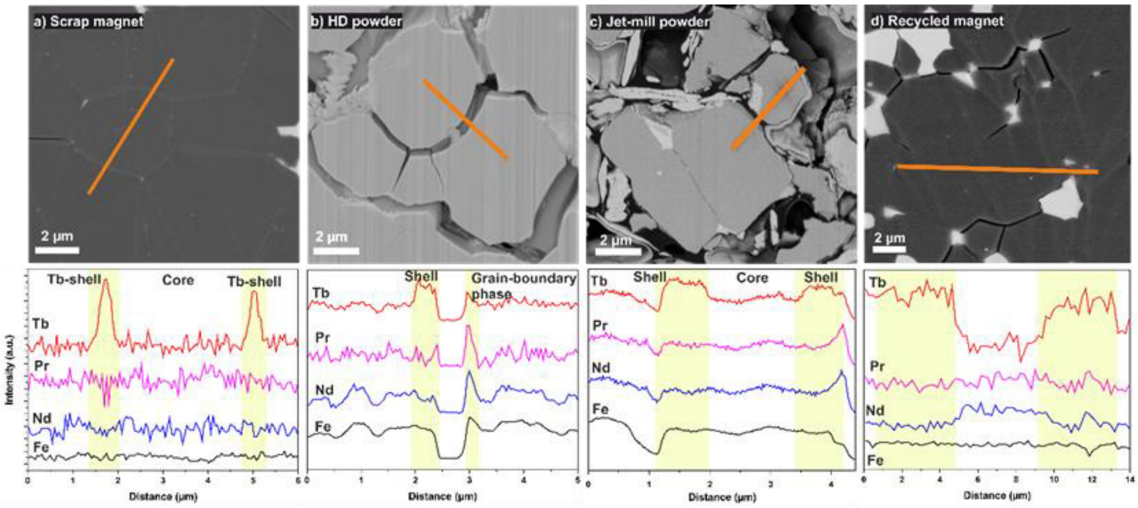


Figure 3: SEM BSE images and EDS line scans of of scrap magnet (a), HD powder (b), jet-mill powder (c) and recycled magnet (d). While at the GBD scrap magnet a narrow Tb-core-shell structure with 0.5 µm can be observed, the other samples show less clear core-shell formation but broader Tb enrichments at the outer regions of the grains.

A renewed GBD process with 1.5 wt.% Tb at the recycled magnets leads again to the formation of a core-shell structure (see Fig. 4). The thickness of the Tb-shells near the surface is 0.5 – 0.6 µm which is comparable to the GBD scrap magnets (0.5 µm). At the EDS line scans the reduction of Nd through Tb substitution and formation of $(Nd,Tb)_2Fe_{14}B$ shells is also clear visible.

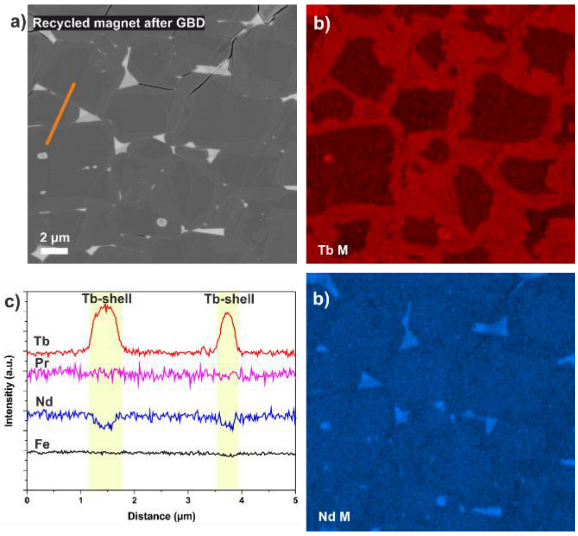


Figure 4: SEM BSE image (a) and EDS mappings (b) of a recycled magnet after a renewed GBD process. A new formation of Tb-shells is clear visible. The thickness of Tb-shells is determined with EDS line scans (c) to 0.5 - 0.6 µm.

Figure 5 shows the magnetic properties of GBD scrap magnet, recycled magnet and recycled magnet after the renewed GBD in dependance of the temperature. In case of scrap magnet and recycled magnet rectangular demagnetization curves with a squareness of 96 % can be observed. Through the Tb-GBD at the recycled magnets the curves loose some of their rectangularity. This is due to an inhomogeneous distribution of Tb from the surface of the magnet to the center. The starting material shows a remanence B_r of 1.38 T, coercivity H_{cJ} of 2143 kA/m and energy product $(BH)_{max}$ of 364 kJ/m^3. The recycled magnet shows a sightly decreased remanence of 1.31 T and $(BH)_{max}$ of 328 kJ/m^3 which can be related to a different pressing method and degree of alignment. In case of H_{cJ} a larger decrease of 21 % to 1703 kA/m can be observed. This large drop in coercivity is caused by the changes in microstructure. The formation of a $(Nd,HRE)_2Fe_{14}B$ shell with higher magneto-crystalline anisotropy leads to a magnetic hardening effect an increases the resistance against the formation of reversed domains. Without the shells the demagnetization starts at lower magnetic fields and leads to a reduced coercivity of the recycled magnets. After the renewed GBD process the temperature stability and coercivity of recycled magnets can be fully restored and shows values of 1780 kA/m (50°C) and -0.14 % (α) and -0.52 % (β).

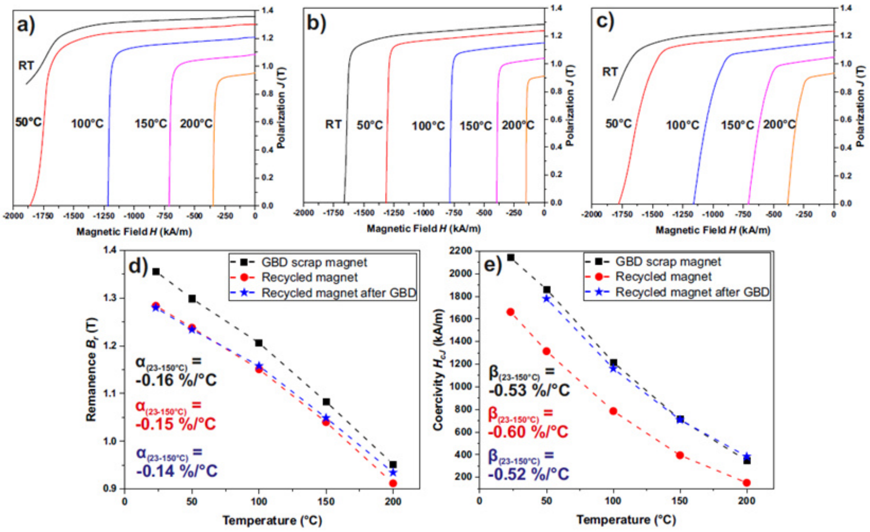


Figure 5: Demagnetization curves of original GBD magnet (a), recycled magnet (b) and recycled magnet after renewed GBD with 1.5 wt.% Tb (c), and remanence (d) and coercivity (e) of all three magnets in dependance of applied temperature. After the renewed GBD the coercivity of recycled magnets can be fully restored.

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Mario Schönfeldt | 17.11.2023 | Karlsruhe | Symposium "Energie-Campus“
Ideenwettbewerb „Energie und Umwelt – Meine Idee für morgen“

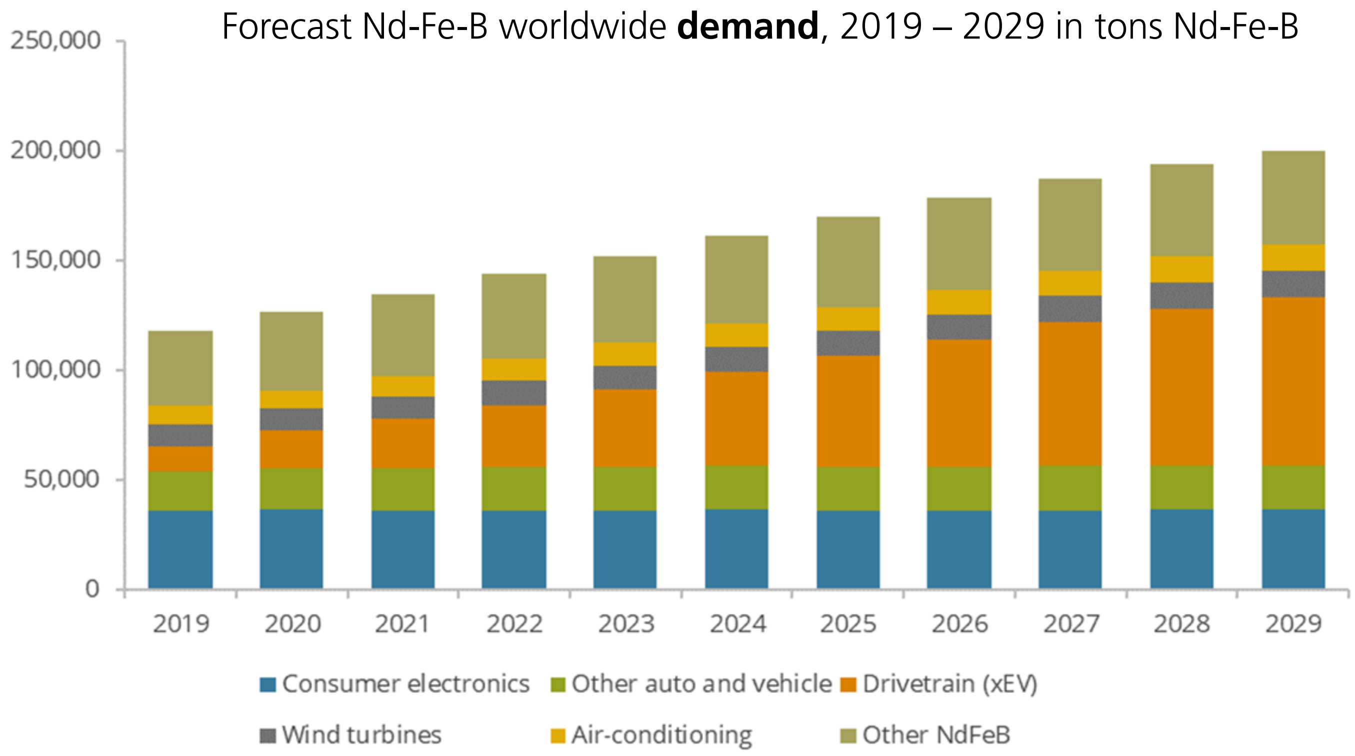
Improving the functional recycling of rare earth permanent magnets from various waste streams

Motivation

Demand and applications

Demand for high performance magnets

- Nd-Fe-B market will be driven by the increased demand in the drivetrain for e-mobility
- Global demand for Nd-Fe-B will be growing from 140 kt to 200 kt from 2021 till 2029



1.5 - 2.5 g Nd-Fe-B

1 - 1.5 kg Nd-Fe-B

1 - 3 t Nd-Fe-B

Up to 6 t Nd-Fe-B

Roskill Rare-Earth Report 2020.
Pictures: www.computerweekly.com, www.bls.gov, www.premierimaging.org, www.bam.de.

Motivation

Criticality of rare earth elements (REE)

Ecological and economical burdens through REE mining and primary production

- Production of **1 ton RE oxide** causes **1.4 tons radioactive waste**, **1,000 tons wastewater** and **2,000 tons waste material**
- Monopoly position of China controls the global market price

Seltene Erden aus China

Naturzerstörung für unsere Windräder

Die chichesische Regierung hat Bestrebungen geäußert, gegen die fatalen Auswirkungen des Abbaus von Seltenen Erden auf die Natur vorzugehen. © picture alliance / dpa / Chinafotopress / Weng Huan

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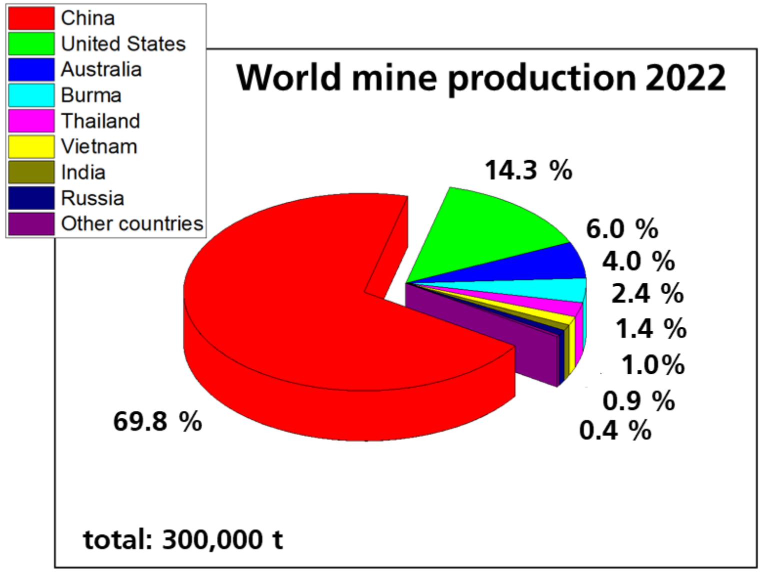
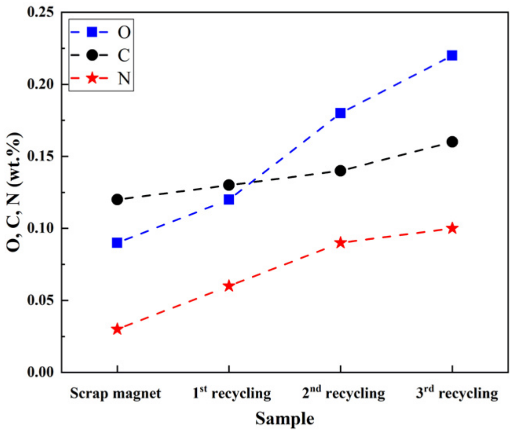


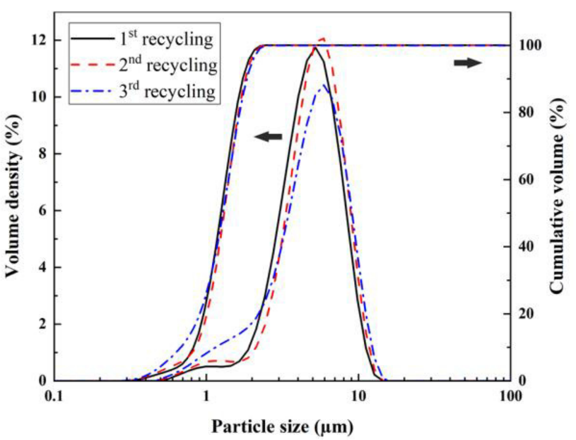
Own illustration according data from U.S. Geological Survey, Mineral Commodity Summaries, January 2023.
www.deutschlandfunkkultur.de.
www.wiwo.de.

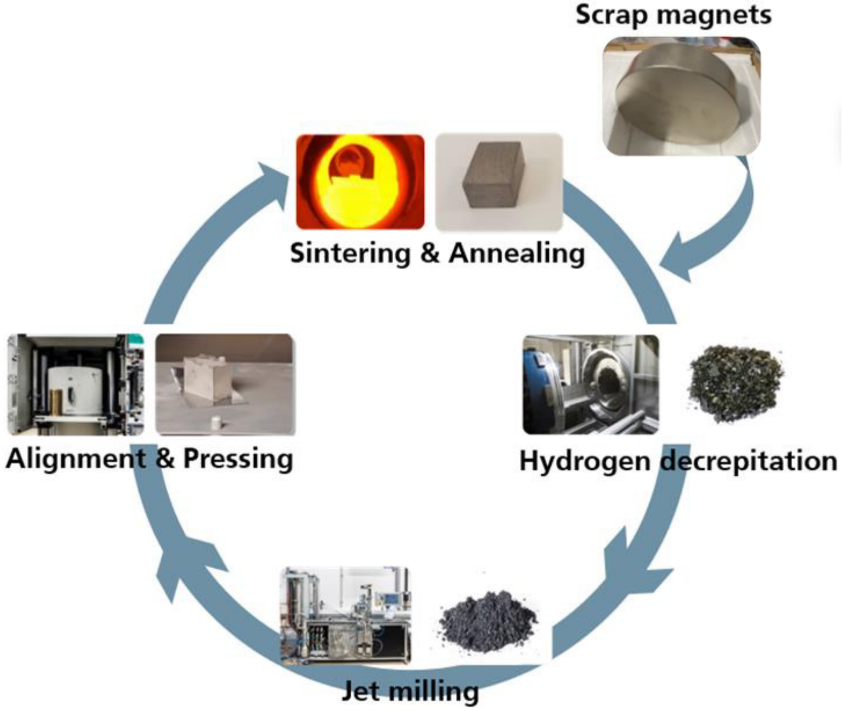
Results

Multiple recycling of MRT magnets

- Multiple functional recycling of 10 kg scrap magnets from magnetic resonance tomography (MRT)
- Increase of impurity content or particle size can be observed
- Degree of alignment and resulting magnetic properties decreases with increasing number of recycling cycles
- Multiple recycled magnets can reach the same density like original scrap magnet
- Three times recycled magnets are comparable to primary magnets





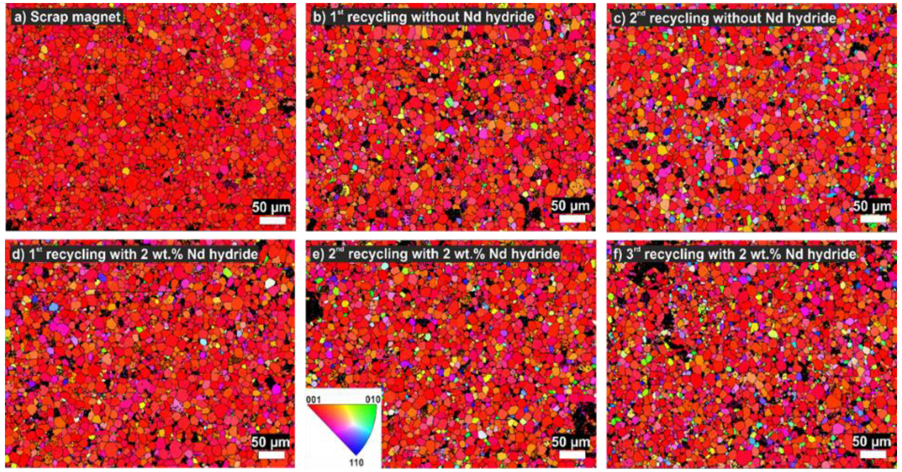

Scrap magnets

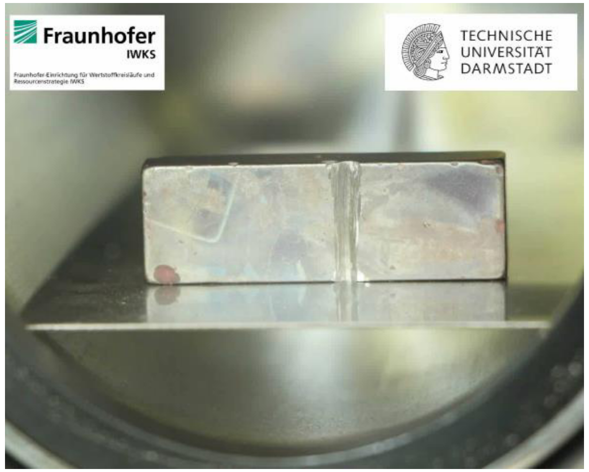
Sintering & Annealing

Alignment & Pressing

Hydrogen decrepitation

Jet milling



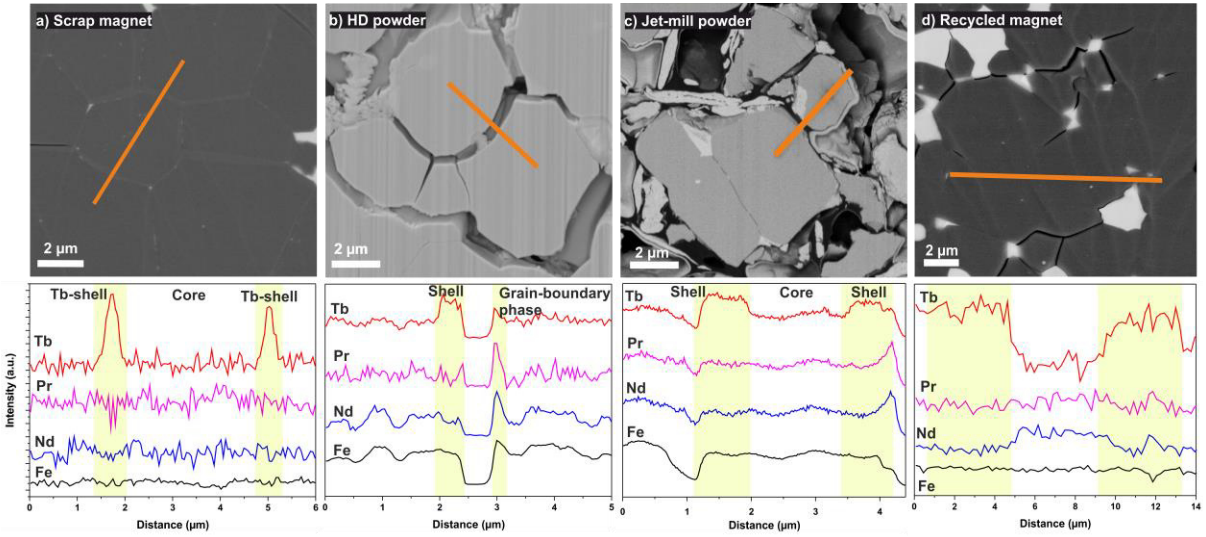


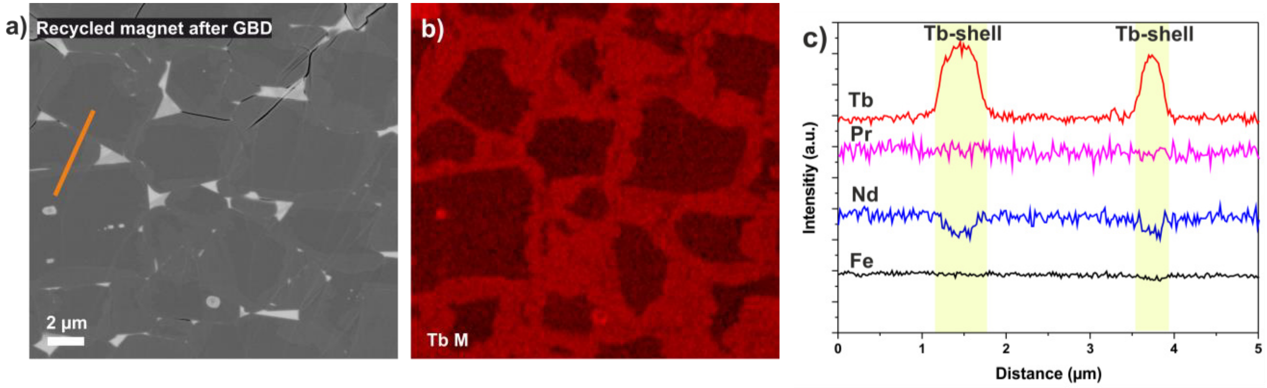
M. Schönfeldt et al., Journal of Alloys and Compounds, 939 (2023) 168709.

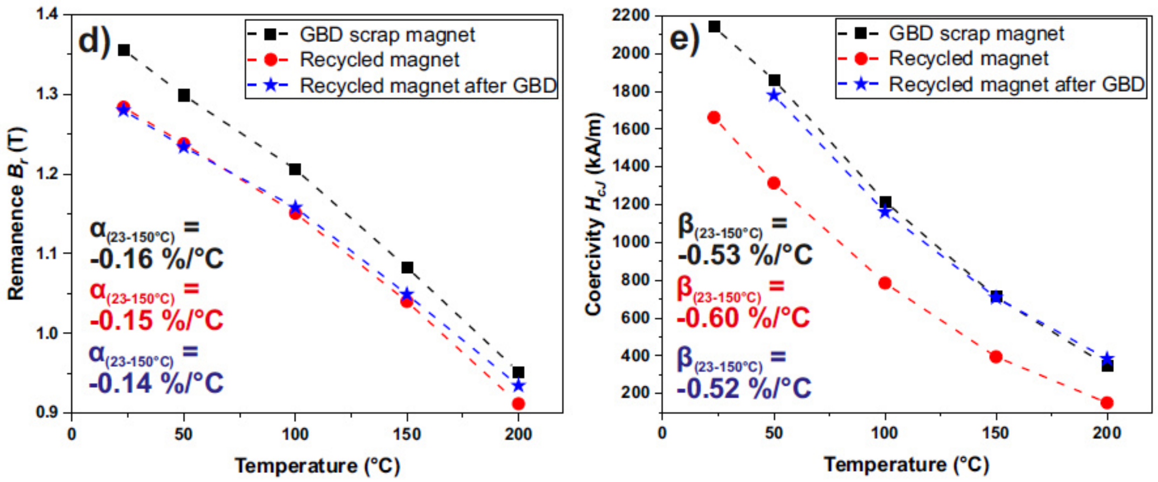
Results

Functional recycling of HRE-lean GBD magnets

- Recycling of over 100 grain boundary diffusion (GBD) magnets (0.5 kg) from industrial magnet production
- Destruction of beneficial microstructure through heat treatment processes during recycling
- Recycled magnets show same rectangular demagnetization curves with squareness of 96 %, but a larger decrease in coercivity of 21 %
- Coercivity and temperature coefficients of recycled magnets can be fully restored by a renewed GBD



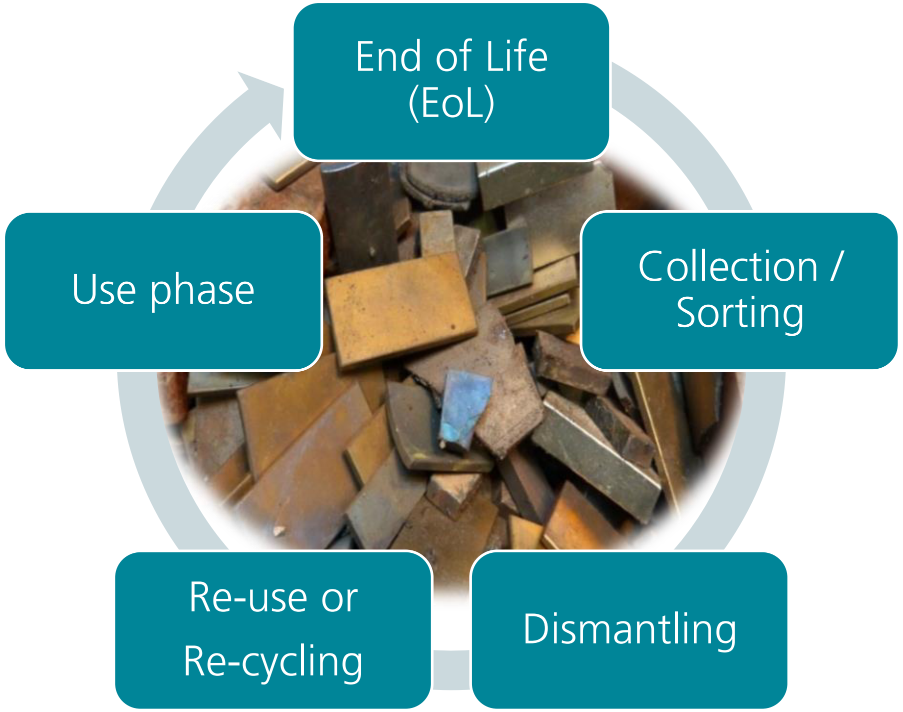




M. Schönfeldt et al., Acta Materialia (2023), submitted.

Summary and conclusion

- Magnets from **different waste streams** were recycled by functional recycling approach in hydrogen atmosphere
- Through adjustment of process parameters **negative effects** and **quality impairments** can be **prevented**
- **Recycled magnets** can achieve **similar properties** like primary ones with **improved sustainability** in terms of ecology and economy with **less supply risk**
- Improved understanding of material behavior through the recycling process will **support the implementation of an industrial recycling of RE permanent magnets in Europe**

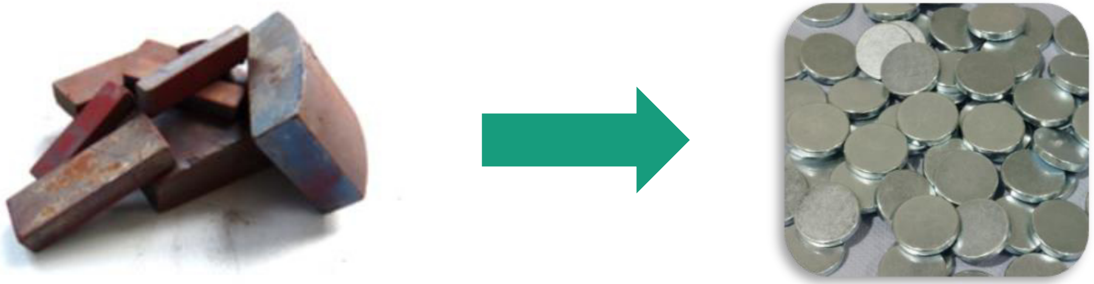

End of Life (EoL)

Collection / Sorting

Dismantling

Re-use or Re-cycling

Use phase



Thank you for your attention!

Mario Schönfeldt
Magnetic Materials
Phone: +49 6023 32039-852
mario.schoenfeldt@iwks.fraunhofer.de

Fraunhofer IWKS
Aschaffenburger Str. 121
63457 Hanau - Germany
www.iwks.fraunhofer.de