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Toward the reduction of Heavy Rare Earth elements in high performance NdFeB permanent magnets by the refinement of the strip cast flakes microstructure

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Abstract

NdFeB alloys for permanent magnets are produced by the strip cast process which consists in melting the raw materials in an induction furnace followed by pouring the melted alloy on a copper water cooled rotating wheel. This process allows producing NdFeB flakes with the microstructure well adapted to the further process steps of the manufacturing process of high performance sintered magnet. This study provides an evidence of the correlation between the microstructure of the starting alloys after strip casting process and the coercivity increase in NdFeB PMs. The refinement of the microstructure allows the production of fine-grained magnets with significant reduction of HRE elements (up to 39%). Thereby the potential to save overall time and costs is relevant by optimizing the microstructure of the alloys during the strip-casting step in order to ensure a homogenous distribution of the grain boundary phase in NdFeB permanent magnets.

Introduction

Rare Earth (RE) permanent magnets (PM) are critical components of electric vehicles, as well as other consumers and green technologies. Discovered in the early 1980s, NdFeB permanent magnets (PM) attain the highest performances with an energy product larger than 400 kJ/m³ making them the strongest permanent magnets commercially available.

The maximal strength can be efficiently exploited if the magnet can resist to a large opposite field without demagnetizing. The maximal field that a PM can sustain defines an extrinsic property called the coercivity that is highly microstructure and process dependant. Constant progress in the conventional powder metallurgy process, promoting grain boundaries wetting by RE-rich phases, has led to coercivity values for NdFeB PM close to 2 T [1]. For these reasons, NdFeB magnets are key components that enable further miniaturization and increase the efficiency of electrical devices for energy production and conversion [2].

The coercivity of today's magnets based on the Nd₂Fe₁₄B phase (2:14:1) drops quickly with increasing temperature. Keeping acceptable coercivity values at high temperatures (>150°C) is actually achievable by partial substitution of Light Rare Earths (LRE) such as Nd and Pr by Heavy Rare Earth (HRE) such as Dy or Tb, in the starting alloy. The Dy-containing NdFeB magnets are far more expensive than the other low coercivity grades of HRE-free types, but still affordable enough to be widely used in industry when needed. Meantime, HRE are considered particularly critical raw materials, which motivates a more moderate use in permanent magnets. This approach seriously increases the dependence on these critical raw materials in European magnet industry.

Microstructure optimization in NdFeB-based sintered magnets involving grain size reduction and grain boundary engineering has been extensively investigated in the last 20 years ([3], [4], [5], [6]) as magnetization reversal in NdFeB sintered magnets is known to start at the surface of main phase grains. Significant improvements in the conventional process have been achieved, that allowed significant increase in the coercivity of magnets by:

- (i) Grain Boundary Diffusion (GBD) of Dy or Tb around crystallographic grains of the Nd₂Fe₁₄B phase leads to the formation of a magnetically hard and protective shell. However, this approach is restricted to thin magnets (up to 5 mm), since Dy/Tb is diffused from the magnet surface. Additionally, the reduction of the HRE content by GBD is limited to approx. 2 wt.% [7].
- (ii) Grain Boundary Engineering (GBE), which allows a better control of phases at Grain Boundaries (GB) to enhance magnetic isolation between grains e.g. (i) addition of specific GB-

- phase forming elements (Al, Cu, refractories) in the initial alloy or (ii) infiltration of eutectic-forming elements through the already existing GB in the bulk magnet [8].
- (iii) Grain size reduction in polycrystalline NdFeB PM's is a well-established route to increase the coercivity without adding HRE. However, as the grain size is downsizing below $3\mu\text{m}$ the fabrication of magnets with a homogeneous microstructure and effective decoupling of the magnetic grains, allowing the development of the coercivity, becomes challenging. Nevertheless, it seems that this approach has not been commercialized due to the substantial process costs when He gas is used and due to an increased sensitivity of these micron-sized grains to oxidation. The alternative use of hydrogenation-disproportionation-desorption-recombination (HDDR) to obtain sub-micron sized particles is even more expensive [4], [6] and restricts the use of the powders to bonded magnets.

All these approaches have in common that the improvements are achieved during the actual magnet manufacturing processes. For fine-grained magnets with reduced content of HRE, a well-designed and homogeneous microstructure of the strip-cast alloy is a prerequisite for an efficient complete manufacturing process. Thereby the potential to save overall time and costs is relevant by optimizing the microstructure of the alloys during the strip casting step in order to ensure a homogenous distribution of the grain boundary phase in NdFeB permanent magnets. To the best of our knowledge, studies on the microstructure optimization of the NdFeB starting alloy to improve the coercivity are limited [9]–[12].

The state-of-the-art strip-casting processes allows producing alloys with a particular microstructure well adapted to the further steps of the conventional process of manufacturing sintered NdFeB magnets [12]. It is well adapted to reach the proper cooling rate which is (i) slow enough to allow crystallization of 2:14:1 + RE-rich phase and (ii) fast enough to avoid the solidification of the $\alpha\text{-Fe}$. The microstructure of the resulting material arises from the columnar nucleation starting from the cooled copper wheel, and features micronic lamellae of the magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase separated by thin layers of mostly amorphous Nd-rich phase. The microstructural properties of the ribbons impacts the whole subsequent process steps, as they have major consequences, among others, on the grindability of the material and the phase repartition in the sintered magnets [13].

This work focuses on the reduction of HRE elements in the high performance NdFeB PM, by the refinement of the microstructure of the alloys and of the alloy composition. The proposed optimization of the NdFeB alloys can boost the development of fine-grained NdFeB PM's allowing a significant HRE reduction. The influence of the process parameters (casting conditions, cooling speed) as well as of the alloys composition on the coercivity increase is emphasized.

Experimental

Strip cast flakes with nominal composition of $(\text{Nd,Pr})_{28.5}\text{Dy}_4\text{B}_{0.92}\text{Co}_{0.9}\text{Cu}_{0.1}\text{Al}_{0.1}\text{Ga}_{0.2}\text{Fe}_{\text{bal}}$ (% weight fraction) were prepared by melting the raw materials in an alumina crucible, under argon partial pressure. Nd-Pr (with 75% - 25% wt. ratio), Dy, Fe, Al, Cu, Co, Ga with purity of 99.9 wt% and a FeB alloy consisting of 25 wt% B and 75 wt% Fe were used as starting materials. The molten alloy is poured onto a water-cooled rotating copper wheel. During the strip cast process the peripheral speed of the cooling roller was set to 1.35 m/s. The stability of the casting is ensured by the use of intermediary trays between the crucible and the wheel that regularize the alloy flow and helps to achieve good homogeneity within the batch. In this study two alloys with the same composition but with two cooling conditions (two different crucible tilting speed) have been manufactured by strip-casting. Alloy 1 was manufactured with a standard crucible tilting whereas alloy 2 with a crucible tilting speed twice higher, that allowed a partial or a complete filling respectively of the intermediate trays.

The microstructures of the strip cast flakes and the corresponding sintered magnets have been investigated by Scanning Electron Microscopy (SEM) in secondary electron (SE) and backscattered electron (BSE) modes. The mean dendritic size of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic phase was determined using two different methods:

- i) We first acquired three BSE image on polished cross section of three different flakes. We drew three lines on each image, of length L , at respectively 20, 50 and 80 % starting from the wheel side of the flake, perpendicular to the heat flow direction; for each image we counted the number of dendrites N intersected by the line and calculated the L/N ratio. The average of the L/N ratios was considered as mean dendritic size. This method (also called the intercept methods) does not allow to take into account the tridimensional character of the microstructure and is likely to overestimate the real thickness of the 2:14:1 lamellae.

ii) To overcome this issue a second method was developed and use for comparison. Using BSE images of polished cross sections of several flakes, an image processing script has been developed to reliably discriminate the two phases ($\text{Nd}_2\text{Fe}_{14}\text{B}$ and Nd-rich respectively) and then, automatically and locally determine the thickness of each lamella. This yields a raw statistical distribution of the lamella thickness at a given distance from the copper wheel and a graphical display of the spacing. The raw values obtained from parallel cross-sections have to be corrected depending on the intersection angle θ of the lamellae with the cross-section plane. This angle is therefore extracted from transversal cross-sections spanning the two-phased structure of the ribbon over its whole thickness. However, the real angle of each lamella is not the one which is directly measured on the picture because of the randomness of the azimuthal angle ϕ , and is also corrected accordingly. This method will be called the image analysis method.

The thickness of the flakes was estimated after the manually measurement of 100 different flakes of the same batch.

After hydrogen decrepitation (HD) process the flakes have been pulverized into fine powders of 3.5 μm mean grain size by jet milling under nitrogen. The powders were isostatically compacted and aligned in a magnetic field, vacuum sintered and annealed at optimum temperature. The densities of the magnets were measured by Archimedes methods. The magnetic properties were measured by a hysteresigraph after the saturation under 8T magnetic field.

Results and discussion

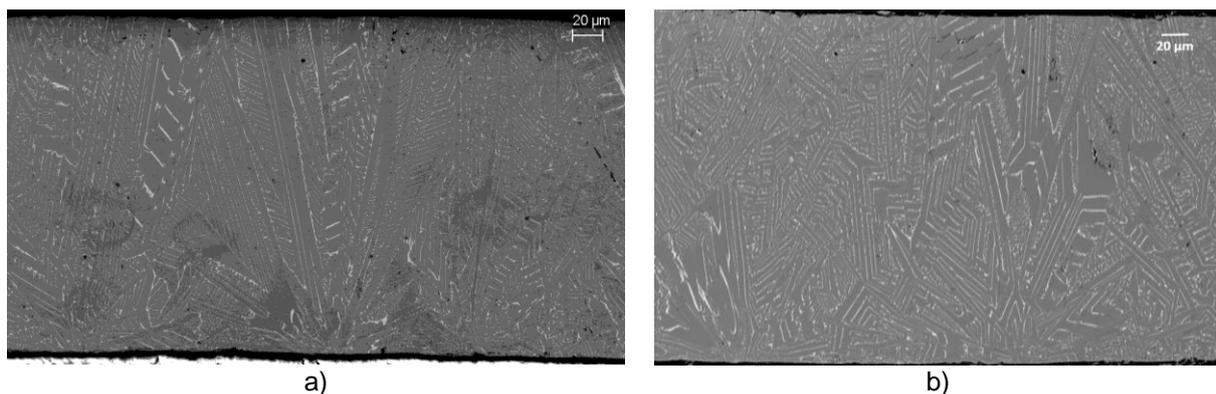
The thickness of the obtained strip cast flakes is given in Table 1 together with the measured mean dendritic size of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic phase by the two methods described above. The cooling conditions clearly influence the flakes thickness and the mean dendritic size. The flakes thickness increases with the increase the crucible tilting speed. This is consistent with the decrease of the cooling speed of the alloys, while the crucible tilting is higher allowing a higher quantity of melted alloy to be present in the intermediary trays and thus to decrease the cooling speed of the melted alloy. The same trend is observed in the Nd-rich lamellae spacing: when the molten alloy is poured in the intermediary trays and subsequently on the copper wheel, the molten alloy is at a temperature close to the melting temperature of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase (1450°C) which is the first phase to solidify on the water-cooled wheel. As the quantity of the molten alloy is higher, this keeps a higher temperature of the molten alloy and the quantity of the solidified $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is higher.

	Mean flakes thickness	Mean Nd-rich lamellae	
		Intercept methods	Image analysis
Alloy 1	263 \pm 57 μm	3.9 μm	2.35 μm
Alloy 2	369 \pm 52 μm	4.5 μm	2.90 μm

Table 1. Measured mean flakes thickness and 2:14:1 lamellae for the two alloys.

X-ray diffraction spectra have been analysed with the Rietveld refinement. The proportion of the 2:14:1 and of the Nd-rich phases are quite similar for the two alloys (96 % for the magnetic 2:14:1 phase and 4 % for the Nd-rich phase).

The typical microstructures of the strip cast flakes, in cross section and perpendicular to the cooling direction are presented in the SEM-BSE images of the Figure 1. The grey phases represents the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic phases and the white ones the Nd-rich phases. No significant difference can be noticed in the microstructure of the flakes for the two cooling conditions.



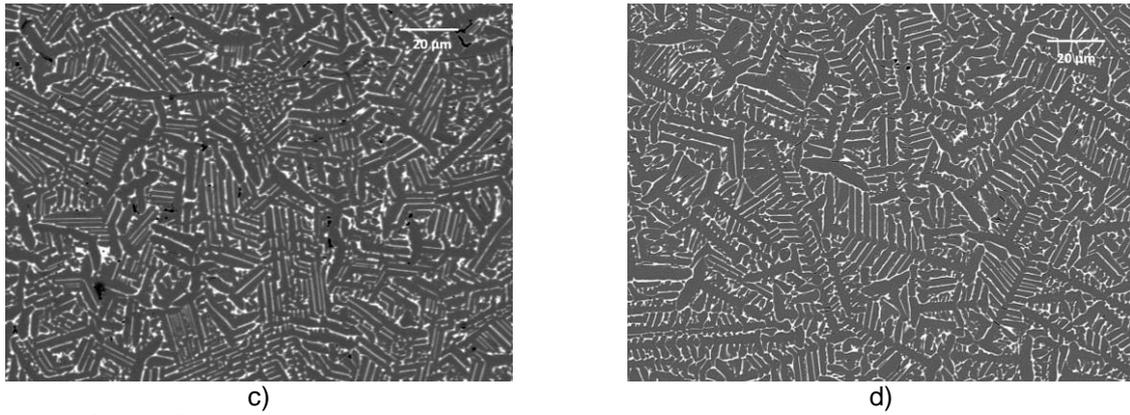


Figure 1. SEM-BSE images of the cross section of the a) alloy 1 and b) alloy 2 and perpendicular to the cooling direction for the c) alloy 1 and d) alloy 2.

Figure 2 shows the EDX map of the different elements in the alloy 1. As expected the additional elements, like Cu or Ga form binary Nd-M or ternary Nd-Fe-M (with M = Cu and Ga) phases in the Nd-rich regions [14]. Dy is distributed uniformly in the alloy.

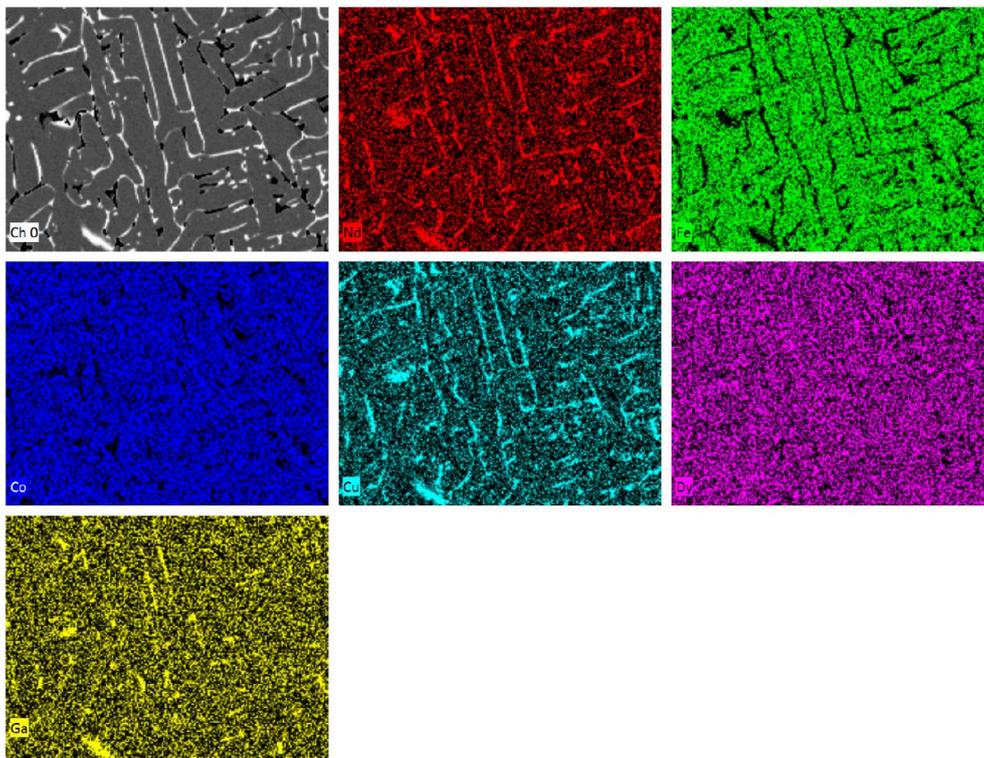


Figure 2. EDX map for alloy 1.

The demagnetization curves at room temperature and 150°C of magnets fabricated with the two alloys are plotted in Figure 3. The measurement of the coercivity at room temperature is not possible with the hysteresigraph due to the magnetic saturation of the used magnetic poles; it is thus convenient to compare the coercivities at 150°C. While the remanence is slightly the same for the two magnets, coercivities are quite different: 8.86 kOe (554 kA/m) for the magnet 1 against 7.49 kOe (705 kA/m) for the magnet 2.

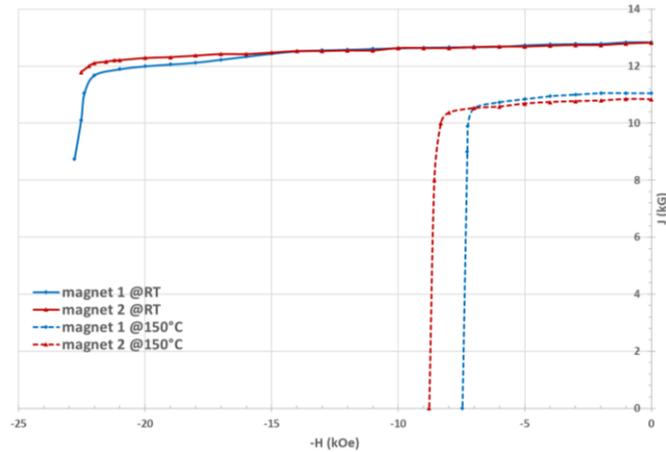


Figure 3. Demagnetization curves at room and 150°C temperature for magnet 1 and magnet 2 respectively.

This difference can be attributed either to microstructural features of the magnets or to differences in the magnets composition.

The microstructure of the magnets have been investigated by SEM analysis. **Figure 4** shows the SEM-BSE cross section images of the two magnets.

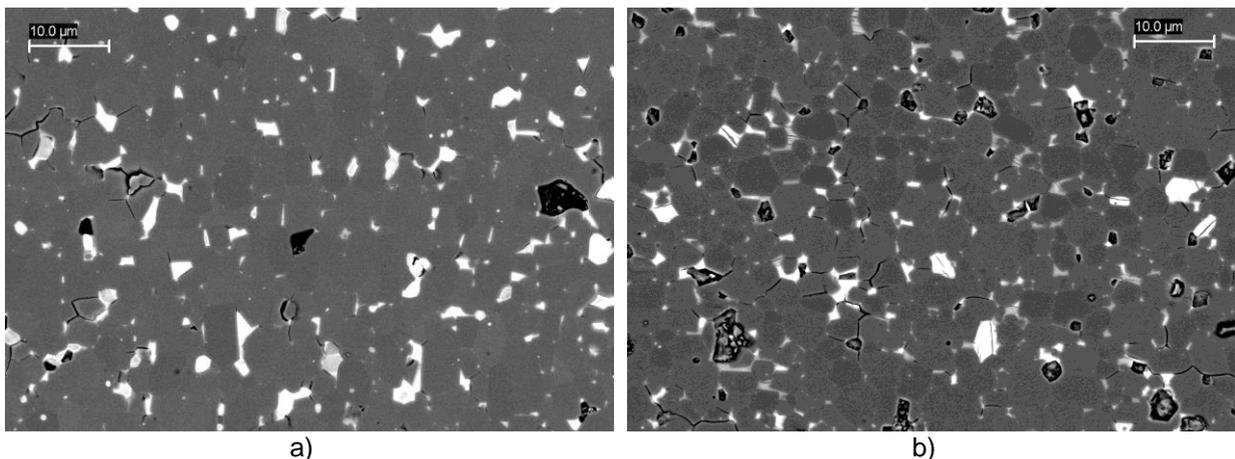


Figure 4. SEM-BSE cross section image of the magnets manufactured with the a) alloy 1 and b) alloy 2.

A first observation is that for the same heat treatment, a grain boundary is hardly observed between the grains in magnet 1 (Figure 4a) but triple junctions are present. In contrast, in magnet 2, a grain boundary is easily observed and is continuously connected to the triple junctions, as shown in Figure 4b. Judging from the SEM contrast, several grain boundary phases coexist. In SEM images, the RE-rich phase is observed as a bright area and the Fe-rich one as a dark area.

The mean magnetic grain sizes in the two magnets have been estimated by the intercept method on three different images on the same magnet. In the magnet with the alloy 1 it has been estimated to 3.3 μm whereas for magnet with the alloy 2 it was estimated at 2.9 μm. This is certainly only a rough estimation, as the mean grain size of the initial powders was of 3.5 μm for the two alloys, but it gives an indication of the differences in the microstructural features of the two magnets and suggest that grain growth occurs in magnets with alloy 1.

The chemical composition of the magnets have been measured by Inductively Coupling Plasma (ICP) for the B content and X-Ray Fluorescence (XRF) for the other elements. Even if the starting alloys compositions have been the same, some differences in the final composition occurs especially in the B and Fe content, as the raw material FeB doesn't have a homogeneous composition.

The main difference in the composition of the two magnets is the B content: 0.94 wt.% for magnet 1 and 0.88 wt.% for magnet 2. This could explain the difference in the coercivity, as the excess of B and Nd, regarding the stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, form two kind of compounds: the boride NdFe_4B_4 non-magnetic phase and the low melting RE-rich phase at grain boundaries. Higher content of B led to

higher amount of boride phase at the expense of the RE-rich phase formation, which is liable for the improvement of the coercivity [15].

The magnetic performances of these magnets have been compared to a state of the art commercial grade the VD 863TP from Vacuumschmelze [16]. This magnets contains 6.6 wt.% of Dy and presents the same magnetic properties as the magnet from the alloy 2, which contains only 4 wt.% of Dy.

Conclusion

Two NdFeB alloys with different cooling conditions have been produced at pilot scale (15 kg/batch). High performance NdFeB permanent magnets have been produced with these alloys by the conventional powder metallurgy route. The influence of the process parameters on the microstructural features of the alloys have been emphasized by the measure of the flakes thickness and the 2:14:1 dendritic size. The control of the strip cast process step is essential to obtain fine and homogeneous particle size distribution of the powders after the milling step and subsequently an homogeneous microstructure of the magnets.

The role of the boron content in the composition of the magnets have been highlighted. The quantity of the boride and RE-rich phases are influenced by the boron content. As the coercivity is related to the quantity, the magnetic state and the distribution of the RE-rich phase around the magnetic grains, it is hence influenced by the boron content in the magnets. Magnets with high coercivity (> 705 kA/m) at 150°C using 4 wt.% of HRE elements could be produced. Compared to the state of the art commercial grade containing 6.6 wt.% of Dy a reduction by almost 40% has been achieved.

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