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MATERIALS
ENGINEERING

# Fabrication and microstructural analysis of didymium–iron–boron magnet alloys with cerium additions

Zorjana Mural[a*], Märt Kolnes[a], Hosein Afshari[a], Lauri Kollo[a], Joosep Link[b], and Renno Veinthal[a]

[a] Department of Materials Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
[b] National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia

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**Abstract.** A common industrially accepted method for producing magnetic alloys with fine, α-iron-free microstructure is strip casting. Small amounts of alloys can be rapidly solidified with the method called splat quenching. In both cases the quenching rate can reach $10^6$ K/s. This work reports the results of using a method for producing small amounts of NdFeB magnetic alloys with Ce additions. The aim of the study was to determine the influence of the cooling rate on the microstructure of the cast. Implementing centrifugal casting in vacuum resulted in NdFeB alloys with the following optimal parameters: sample thickness 0.3 mm, cooling rate $10^5$ K/s, rare earth-rich phase content about 4%, thickness of dendrites 1.1 μm, arm spacing of dendrites 0.35 μm, and oxygen content not more than 650 ppm. Theoretically, it is possible to increase the alloy thickness up to 2 mm. Decreasing the cooling speed to the critical level $4 \times 10^3$ K/s completely prevented the formation of the undesired features in the microstructure of the cast.

**Key words:** magnetic alloy, didymium–iron–boron, cerium, microstructure, centrifugal induction casting, cooling rate.

## 1. INTRODUCTION

Neodymium–iron–boron (NdFeB) alloys can be processed into magnets by several different routes [1,2]. Common methods include classical powder metallurgy, comprising jet milling, orienting the refined powder, compaction, and sintering [3]. Prior to these steps the starting alloy is usually manufactured by rapid solidification: strip casting or ingot casting. In both cases the starting elemental powders or master alloys are induction melted under a protective atmosphere. If ingot casting is used, the mixture of the master alloys is melted and poured into a flat mould. In case of a relatively slow cooling, α-iron precipitation may occur during solidification [2,4]. The α-iron in NdFeB magnets hinders grain alignment and creates Nd-rich regions, which are extremely susceptible to oxidation and therefore to magnet degradation [5]. A possible way of avoiding α-iron is to increase the content of rare earth (RE) elements (Nd, Dy ~15 at%). Another route to terminate the α-iron evolvement is rapid solidification.

Today's standard industrial practice for producing starting powders for powder metallurgy processing is mainly based on strip casting. This method uses a rapidly spinning copper wheel, which contacts with the alloy melt, quenches the melt, and ribbon-shaped particles are formed. Although it has some drawbacks for investigating alloy composition and solidification kinetics, strip casting suits well for standard magnet industry. To get an initial strip cast material with acceptable homogeneity, a relatively large amount of material (up to at least 10 kg per batch) is needed for each experiment.

One route for obtaining rapidly solidified NdFeB alloys is by the method called splat quenching. In case of this method small quantities of molten alloy are directed into contact with a cooled plate. This can be done in different ways, whether by direct casting to the plate, casting between plates, or casting through holes

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[*] Corresponding author, zorjana.mural@ttu.ee

in the plate to cause rapid solidification [6,7]. One of the objectives of the present study was to further develop the splat quenching method in order to produce small quantities (in the range of 10 g) of NdFeB material with a controlled cooling rate. A commercial centrifugal casting device was used to cast the molten metal into experimental moulds. A new cooling cell was designed for the centrifugal casting unit.

Materials based on NdFeB are widely used in the fields of energy, automotive, medical, and computer equipment. In most RE ores, the content of Nd is quite small compared to cerium or lanthanum. Due to the increasing demand for RE elements applicable in the magnet industry, overcapacities of and a non-parallel increase in the demand for Ce or La are seen. Therefore new applications for Ce and La are currently researched. A potential use of Ce is its introduction into the NdFeB magnet composition. Yan et al. [8] showed that up to 25 wt% of REs could be replaced by Ce without significant decrease in magnetic properties. Nevertheless, the development of the microstructure during rapid solidification and the effect of alloying elements on magnetic properties of Ce-containing NdFeB magnets are not extensively investigated.

We studied a NdFeB alloy where Nd and Pr were partially substituted with Ce to obtain an α-iron-free microstructure with an optimized phase composition. In this paper the relationships between the cooling rate and microstructures, chemical composition, and phase contents of Ce-containing alloys are reported.

## 2. EXPERIMENTAL

A didymium magnetic alloy (Nd and Pr were not separated during extraction) with the chemical composition $Nd_{22}Pr_{1.8}Dy_1Nb_{0.3}Al_{0.45}Ce_{8.3}B_{1.2}Fe_{bal}$ was prepared by centrifugal induction melting of mixtures of elemental powders Fe, Nd, Al and master alloys FeB, NdFe, NdPrFe, CeFe, and DyFe. In all the initial materials the oxygen content was below 600 ppm and the carbon content was below 400 ppm. A centrifugal casting unit Lifumat Met 3.3 Vac (Linn GmbH) was used for the splat quenching experiments. Starting materials were crushed and the premix was placed into a tantalum crucible. The mixture was heated under vacuum ($10^{-2}$ mBar) up to 1523 K within few minutes and held for 5–10 s. Casting was performed into an experimental copper mould when the rotating speed of 600 rpm was reached. The microstructures of the as-cast materials were identified by scanning electron microscopy (SEM). Quantitative microstructure analysis for determining phase content, dendrite thickness, and dendrite arm spacing was carried out using ImageJ software. Oxygen content was determined using an Eltra ONH-2000 spectroscope. Inductively coupled plasma optical emission spectrometry (ICP–OES) was used to characterize the chemical composition of cast alloys. Differential scanning calorimetry (DSC) was applied to obtain the melting temperature and crystallization characteristics of the material.

## 3. RESULTS AND DISCUSSION

### 3.1. Production of NdFeB alloys by rapid solidification

### *3.1.1. Design of the cooling cell*

The cooling of the NdFeB melt was first accomplished by splat quenching it onto a copper disc with a thickness of 5 mm. The face of the plate was aligned perpendicular to the direction of the melt (Fig. 1a). The thickness of the solidified material plate was approximately 4 mm. In order to decrease the thickness of the solidified NdFeB plate (hence increasing the cooling rate), a new

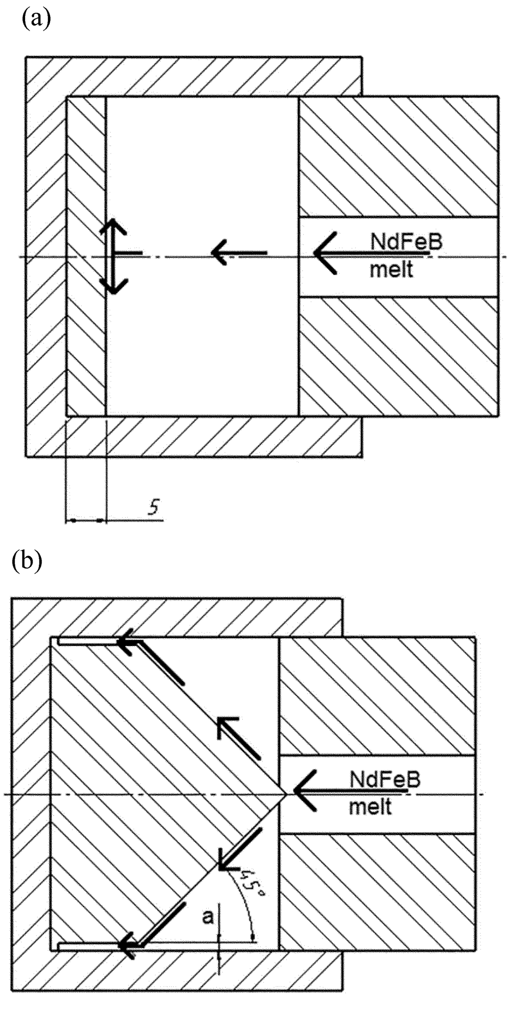

**Fig. 1.** Sketch of the centrifugal casting mould design: (a) initial version, (b) modified version. The black arrows show melt flow.

cooling cell was designed. This cell had a cone-shaped insert, which first directs the melt towards the outer walls at an angle of 45° (see Fig. 1b). The melt was collected at the thin gap between the inner copper insert and the outer copper cylinder. The gap thickness $a$ was varied between 0.3 and 0.9 mm.

### *3.1.2. Estimation of the cooling rate*

For estimating the cooling capability of the newly designed cooling cells in centrifugal casting, first the cooling rates of the cast NdFeB alloys were calculated. The heat flux calculations were performed using the unsteady heat conduction formula [9] for plate geometry. First, the time needed for the middle of the plate to reach the crystallization temperature was calculated using the following formula:

$$t = \frac{F_0 \rho C_p x_m^2}{k}, \tag{1}$$

where $t$ represents time and $x$ is the distance from the surface to the centre, $C_p$ is specific heat, $\rho$ is density, $k$ is thermal conductivity, and $F_0$ is the dimensionless Fourier number obtained from the plot in Fig. 2.

Temperature is a function of time after the temperature of two surfaces has been rapidly increased to $T_0$, which is the temperature at which the crystallization stage is completed. In our calculations, 973 K was used as $T_0$. Temperature $T_i$ is the initial temperature of the mid-plane of the plate. The cooling rate $\varepsilon$ for each sample was calculated using the following formula:

$$\varepsilon = \frac{\Delta T}{t}, \tag{2}$$

where $\Delta T$ is the temperature change between 1523 K and 973 K and $t$ is time [9].

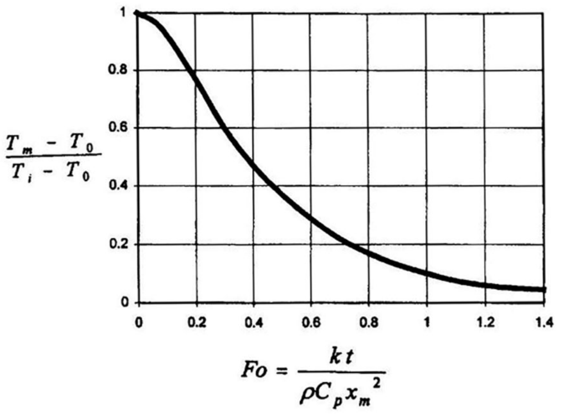

**Fig. 2.** Plot for calculating the temperature $T_m$ at the centre of a plate [9].

**Table 1.** Experimentally determined thermal specification of the NdFeB alloy

| Density $\rho$, g/cm$^3$ | Thermal conductivity $k$, W/m K | Melting point $T_{melt}$, K | Specific heat $c$, J/kg K | $T_0$, K |
|---|---|---|---|---|
| 6.7 | 9.0 | 1469 | 521 | 973 |

**Table 2.** Cooling rates and batch sizes per cast

| Sample | Sample thickness, mm | Cooling rate, K/s | Batch size, g |
|---|---|---|---|
| A40 | 4.0 | $1 \times 10^3$ | 6.0 |
| B03 | 0.3 | $2 \times 10^5$ | 0.5 |
| B06 | 0.6 | $5 \times 10^4$ | 1.0 |
| B09 | 0.9 | $2 \times 10^4$ | 1.6 |

For the calculation of the cooling rate, a control volume inside the mould was chosen. It had a plate with the surface area of 1 cm$^2$ and different thicknesses in different moulds.

Experimentally obtained information concerning thermal properties of the alloys and density are reported in Table 1. The cooling rate for the alloy quenched onto the disc was determined to be $10^3$ K/s. The sample thickness is about 4 mm. Batch size is 5–6 g/cast.

Quenching rates for the modified cooling unit, calculated applying the above-described procedure, were estimated as $2 \times 10^5$, $5 \times 10^4$, and $2 \times 10^4$ K/s, respectively (see Table 2). As all the samples had identical chemical composition, the alloys' designations A40 and B03–B09 follow the version of the cooling unit design.

The batch size for alloys cast into the modified mould varied between 0.5 and 1.6 g in a 5 g sample. According to experimental results, the cooling rate should be higher than $10^3$ K/s to achieve an α-iron-free alloy. Sample thickness can be calculated using this value in Eqs (1) and (2). This allows predicting that it is possible to go up to 2 mm thick casts to obtain an α-iron-free microstructure and increase the batch size up to 7–8 g in a 10 g sample.

## 3.2. Development of the RE–Ce alloy

### *3.2.1. Stability of the alloy composition*

The chemical composition and distribution of the alloying elements were studied to verify the uniformity, possible changes in the chemical composition during casting, and sensitivity to oxygen contamination. Firstly, the premixed starting powders were crushed and held in air for one week in order to initiate partial oxidation of RE elements. The experiments showed low sensitivity of splat quenching towards oxidation. The oxides were

**Table 3.** Example of boron loss during melting and casting

| | B content in starting mixture, wt% | B content in cast alloy, wt% | B loss, wt% |
|---|---|---|---|
| A40 | 0.60 | 0.26 | 58.00 |
| A40 | 1.80 | 0.71 | 61.00 |
| Average loss | | | 59.50 |

found to be removed with the slag, and the oxygen content of the resulting alloy was less than 700 ppm. The difference between the calculated and measured content of RE and other elements did not exceed 1.5%.

Secondly, the stability of boron during casting was estimated. A significant loss of the boron content was observed after casting. Table 3 shows the boron content in the starting mixtures and cast alloys. The average boron loss was about 60%. It can be due to the reactions between boron, oxygen, and nitrogen impurities and the consequent removal of the compounds with the slag. Boron loss was taken into account when designing the alloy composition so that the final cast alloy has 1.2 wt% of boron.

### *3.2.2. Effect of the cooling rate on the alloy microstructure*

The microstructure of sample A40 with the estimated cooling rate of $10^3$ K/s is shown in Fig. 3.

A considerable amount of α-iron was observed starting from around 100 μm from the contact surface (area b in Fig. 3). This is due to the relatively slow solidification of the melt. From standard strip casting, the cooling rate is known to dramatically influence the microstructure and magnetic properties of the alloys [10].

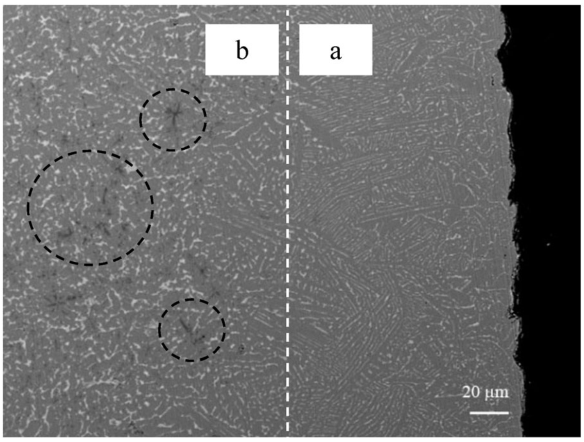

**Fig. 3.** Micrograph of the cast ingot with the formed α-iron: (a) rapidly cooling area that was in contact with the mould; (b) more slowly cooled area. Dashed circles show α-iron areas.

Clearly, for cerium alloyed neodymium magnets under-quenching occurs when a cooling rate below $10^3$ K/s is used. Under-quenching refers to the critical point of cooling speed at which α-iron dendrites start to occur. This shows that magnet alloys applicable for standard powder metallurgy processing can be processed only in thin layered forms.

Micrographs of cast alloys B03, B06, and B09 are presented in Fig. 4. No α-iron was observed.

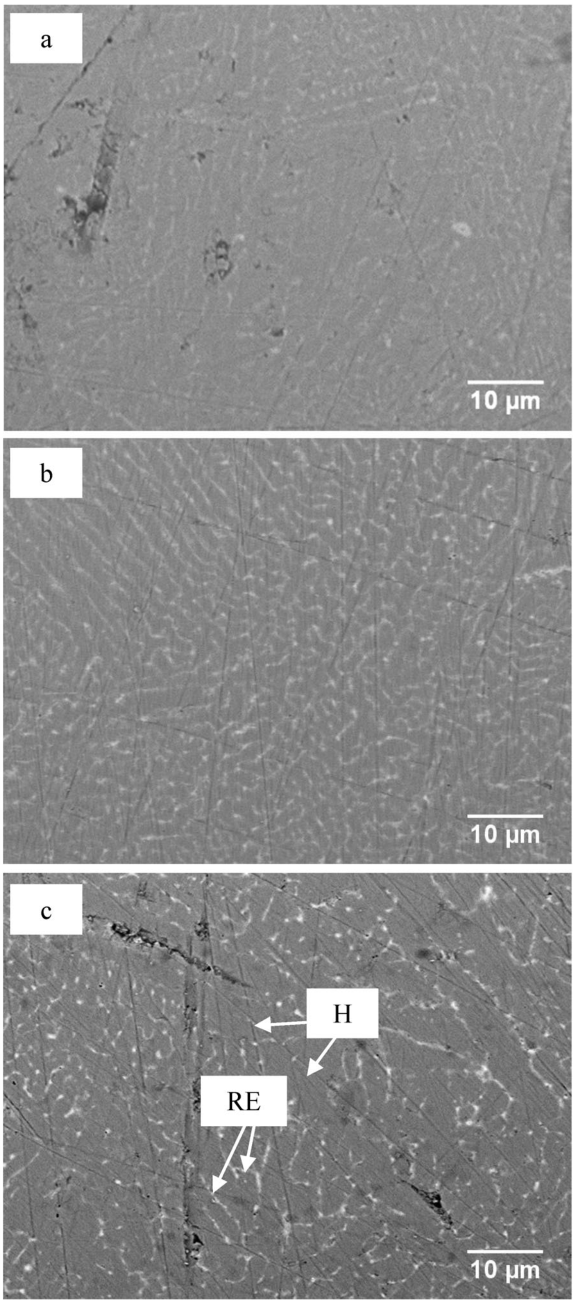

**Fig. 4.** Microstructures of the alloys: (a) B03, (b) B06, and (c) B09. H – hard phase, RE – rare earth-rich phase.

The thicknesses of the dendrites (hard phase thickness) and dendrite arms (RE-rich phase thickness) between them are presented in Table 4, where also the contents of the phases are shown for comparison. It is clearly seen that the higher the quenching rate, the finer the microstructure features and the more homogeneous the mixture of phases. The difference between the thicknesses of the dendrites of samples B09 and B03 is more than 60% and between dendrite arm spacings about 25%. Figure 5 re-plots the data presented in Table 4 to show the correlation between the cooling rate, thickness of dendrites, and arm spacing of dendrites.

For comparison, strip casting provides a uniform and α-iron-free dendritic microstructure of the strips with the thickness of 0.2–0.3 mm, hard phase thickness of 4–6 μm, and RE-rich phase thickness up to 0.5 μm [11,12]. In case of Ce-containing alloys, α-iron dendrites form more easily due to the lower melting point of the CeFeB phase [13]. Gao et al. [14] showed that when the drop tube technique is used most small drops of NdFeB alloy are free from the α-iron phase because of the high undercooling prior to solidification. However, the droplet size should stay below 0.6 mm for the alloys with lower RE content and below 2 mm for the alloys that are rich in RE. These authors also claim that lower cooling rates result in a coarse microstructure. Our results are in a good agreement with those provided by Gao et al. [14] for the Ce-free alloy.

**Table 4.** Microstructure of the melts

| Sample | RE-rich phase, % | Hard phase, % | Dendrite thickness, μm | Dendrite arm spacing, μm |
|---|---|---|---|---|
| B03 | 3.90 | 96.10 | 1.08 | 0.35 |
| B06 | 6.70 | 93.30 | 1.36 | 0.37 |
| B09 | 12.50 | 87.50 | 1.78 | 0.43 |

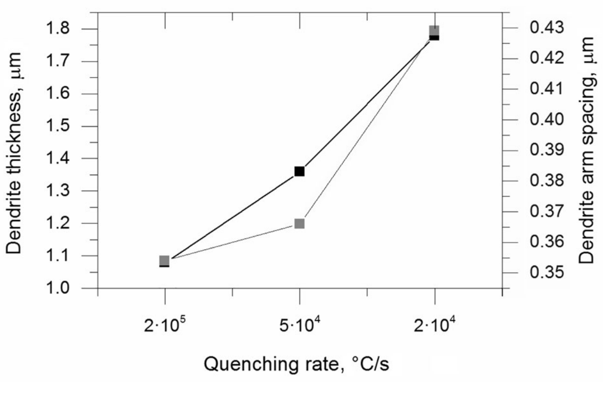

**Fig. 5.** Correlation of quenching rate and parameters of microstructure.

## 4. CONCLUSIONS

Magnetic NdFeB alloys were prepared by centrifugal induction casting to study the influence of quenching rate on the microstructure of the castings. By implementing this method it is possible to achieve a cooling rate up to $10^5$ K/s and obtain an alloy with a fine microstructure free from α-iron with a smaller Nd-rich phase that is distributed more homogeneously. However, the batch size in this case is only 0.5 g per melt. Increasing the cast thickness up to 0.9 mm gives a maximum of 1.6 g. Theoretically, it is possible to increase the amount of the molten alloy flown into the mould up to 8 g per cast. In this case the gap between the inner insert and the outer cylinder should be 2 mm. Generally, to eliminate the formation of α-iron the cooling speed should be higher than $1 \times 10^3$ K/s.

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# Tseeriumiga NdFeB magnetsulamite valmistamine

Zorjana Mural, Märt Kolnes, Hosein Afshari, Lauri Kollo, Joosep Link ja Renno Veinthal

Levinuimaks magnetsulamite valmistamise meetodiks on tänapäeval ribavalu. Antud meetodiga toodetud sulamid ei sisalda mikrostruktuuris α-rauda ja on peene struktuuriga tänu suurtele allajahutamiskiirustele. Väikese koguse sulami eksperimentaalseks valmistamiseks saab pidevprotsessi (ribavalu) asendada tsüklilisega, mida inglise keeles tähistab mõiste *splat quenching*. Antud juhul tardub väike kogus kokkupuutel jahutatud vormipinnaga. Mõlema meetodi puhul saavutatakse jahtumiskiirus kuni $10^6$ K/s. Artiklis on kirjeldatud tsentrifugaalvalumeetodit, mis võimaldab väikestes kogustes NdFeB magnetsulamite valmistamist. Töö eesmärgiks oli uurida jahtumiskiiruse mõju magnetsulami mikrostruktuurile. Töö tulemusena saadi optimaalsete parameetritega NdFeB sulam: jahtumiskiirus $10^5$ K/s, lamelli paksus 0,3 mm ja hapnikusisaldus alla 650 ppm.