Microstructural analysis of strip cast Nd–Fe–B alloys for high \((BH)_{\text{max}}\) magnets

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High energy density magnets \(>400 \text{ kJ/m}^3\) are increasingly used in many applications. Conventional casting techniques for sintered magnets reveal the formation of a high quantity of \(\alpha\)-Fe and large Nd-rich regions. New techniques, like strip casting, produce homogeneous and fine scaled microstructures and are already used for producing high \((BH)_{\text{max}}\) magnets. The fast cooling rate during strip casting suppresses the formation of \(\alpha\)-Fe dendrites and of large Nd-rich pockets.

Directional solidification causes a formation of columnar grains containing a typical arrangement of hard magnetic Nd\(_2\)Fe\(_{14}\)B regions and Nd-rich regions. The Nd regions occur as intragranular platelets as well as intergranular phases. Intragranular lamellae show a periodicity which corresponds to a eutectoidal solidification according to the composition of the liquid and are directed parallel to the temperature gradient during solidification. The lamellae show an average width of 150 nm, a spacing of 3 \(\mu\)m, and a length up to the size of the hard magnetic grains. The fine separation of the hard magnetic and Nd phases is advantageous for the milling of the alloy after hydrogen decripitation and improves sinterability of magnets. Although the microstructure of strip cast alloys is much finer than that of ordinary cast alloys, the alignment of the powder is not deteriorated and \(B_s\) is not reduced due to a sufficient large interlamellar spacing between the Nd-rich platelets that enables the formation of single crystal powder particles after milling. © 1998 American Institute of Physics. [S0021-8979(98)18911-9]

I. INTRODUCTION

Sintered Nd–Fe–B-type permanent magnets are widely used in applications that require a high energy product/ volume ratio in order to reduce weight.\(^1\) In addition there is a rising demand for magnets with \((BH)_{\text{max}}\) higher than 400 \(\text{kJ/m}^3\). This goal can be reached by shifting the alloy composition more towards the stoichiometric Nd\(_2\)Fe\(_{14}\)B composition as well as by improving the alignment of the hard magnetic grains during compacting. In addition the distribution of phases in the starting alloy can be significantly improved. Conventional casting techniques reveal the formation of a high quantity of precipitated \(\alpha\)-Fe that deteriorates the powder alignment\(^2\) and large Nd-rich regions that are very sensitive to oxidation. The \(\alpha\)-Fe is formed according to the pseudo-binary Fe–(Nd,B) phase diagram, with Nd:B \(=2:1\), where the solidification path passes through a region (Liq. + Fe) and Fe particles are formed within the liquid.\(^3\) The formation of dendritic \(\alpha\)-Fe in cast alloys can be reduced by additives like M\(_2\)=Ti, Nb, Zr, V, Mo, or W that form M\(_2\)–Fe–B borides\(^4\) as well as by optimizing the casting technique. It has been previously shown that flat cast ingots consist of fine grains near the mold surface, columnar grains in the central portions, and coarse grains near the free surface.\(^5\) Reducing the thickness of the ingots from 8.7 to 4.4 \(\text{mm}\) resulted in an increase of the amount of columnar grains and in a decrease of dendritic \(\alpha\)-Fe in the ingot. An improvement of \(B_s\) by 5\% and \((BH)_{\text{max}}\) by 10\% of magnets produced from that ingot were attributed to a significantly reduced presence of dendritic \(\alpha\)-Fe causing a better grindability of the powder and a better grain alignment. In this article we report on the effect of strip casting on the microstructure of Nd–Fe–B magnetic material. Materials produced by strip casting are already used for high \((BH)_{\text{max}}\) magnets. This new technique allows large scale production of ingots with a homogeneous and fine scaled microstructures without a significant precipitation of \(\alpha\)-Fe. The fine dispersion of the rare earth-rich phase is important not only for high energy magnets having \((BH)_{\text{max}}\) of over 400 \(\text{kJ/m}^3\), but also for high coercivity magnets that include high Dy concentrations. In such strip cast high Dy alloys \(B_s\) and \((BH)_{\text{max}}\) are improved keeping the coercive field high because the total rare earth content can be substantially decreased without the formation of rare earth depleted regions that can deteriorate the squareness of the demagnetization curve of sintered magnets.

II. EXPERIMENT

The investigated samples with the composition (Nd,Dy)\(_{14.1}\)(Fe,Al)\(_{80}\)B\(_{5.9}\) were produced by strip casting, a technique similar to melt spinning, using a wheel speed of 1 \(\text{m/s}\). The platelike casted alloy shows a typical thickness of 250–350 \(\mu\)m and a width of several centimeters. The samples were investigated by optical microscopy with polar-
The typical microstructure of the strip cast alloy parallel to the direction of solidification observed with polarized light is shown in Fig. 1. Solidification of the melt starts at nucleation centers (C) at the wheel side of the strips. The distance between individual centers is 50–120 μm. Starting from these nucleation sites, a columnar structure of hard magnetic grains is formed due to directional solidification. The growth direction of the grains is typically the direction of the heat flow during solidification. The columns grow within a cone with an opening angle 60°–80° towards the free surface of the strips. The diameter of the individual grains perpendicular to the growth direction is 5–25 μm close to the wheel side and 25–60 μm close to the free surface side (Fig. 2), respectively.

The columnar grains consist of a hard magnetic phase, which is proven by the existence of the magnetic domain pattern in that structure. The orientation of the domain walls visible with polarized light indicates that the growth direction of these columns within the cone does not correspond with either ⟨100⟩, the easy growth axis of the tetragonal 2:14:1 structure, or ⟨001⟩. A columnar dendritic 2:14:1 structure with a growth direction parallel to ⟨001⟩ was previously observed in splat cooled Nd₁₃Fe₇₇B₈ magnets. A preferred c axis texture normal to the ribbon plane was also observed in melt spun Nd₁₀Fe₇₅B₈ ribbons. Close to the wheel side between the nucleation sites, smaller elongated grains are formed with a growth direction more parallel to the surface. In these grains the domain walls tend to be oriented perpendicular to the surface, indicating a preferred ⟨100⟩ growth direction of the magnetic grains in that region. Within the large dendritic columns of the 2:14:1 phase a thin plateletlike structure is formed parallel to the growth direction. The occurrence of this intragranular layered structure does not usually influence the domain structure of the hard magnetic grains (compare Fig. 1). Figure 3 shows a SEM backscattered electron micrograph of a strip cast sample perpendicular to the wheel side. The hard magnetic grains appear as dark areas. Thin bright regions which occur with a certain periodicity within the hard magnetic grains and at grain boundaries consist of the Nd-rich phase. There is no indication for the formation of dendritic α-Fe or a significant amount of additional phases like Nd₁₃Fe₄B₄ formed during solidification. The lamellar arrangement of the two phases that are oriented parallel to the temperature gradient is characteristic for a eutectoidal solidification. The interlamellar spacing between the Nd-rich platelets is about 3 μm and is controlled by the temperature gradient during solidification as well as the composition of the liquid.

The orientation relationship between the Nd-rich intragranular platelets and hard magnetic matrix grains was further investigated by TEM. Figure 4 shows the typical microstructure of a columnar 2:14:1 grain in the center of a strip viewed perpendicular to the direction of solidification. Hard magnetic grains are separated by intragranular Nd-rich lamellae with a thickness of 60–150 nm. Within a grain all hard magnetic regions show the same crystallographic orientation. Close to grain boundaries the Nd-rich intragranular regions are also found with more irregular shapes.

At grain boundaries and especially at grain boundary junctions, intergranular Nd-rich phases are found. Selected area electron diffraction (SAD) confirms that the Nd-rich platelets as well as the intergranular Nd-rich phases mainly occur as fcc Nd and less frequently as Nd oxide. X-ray spectra show that there is usually a significant amount of Fe

FIG. 1. Optical micrograph of the cross section of strip cast (Nd,Dy)₁₄₄(Fe,Al)₆₀B₈₉ showing the columnar growth of hard magnetic grains starting at nucleation centers (C) and the magnetic domains structure inside the columnar grains.

FIG. 2. Optical micrograph taken parallel to the surface of the strips near the free surface side.

FIG. 3. SEM micrograph of the polished cross section of the strip cast alloy showing the distribution of hard magnetic phase (dark) and Nd-rich phase (bright) in backscattered mode.
dissolved within the Nd-rich phases. During the TEM investigation no $\alpha$-Fe or Nd$_{1+4}Fe_4B_4$ was detected. The analysis of various diffraction patterns revealed that most of the lamellae are formed parallel to the $\{1,1,-1\}$ plane of the tetragonal Nd$_2Fe_14B$ phase and of the fcc Nd-rich lamella.

Good magnetic properties require a homogeneous distribution of all phases and dopant elements throughout the cast material. Traditional casting techniques can cause a segregation of individual phases depending, e.g., on the geometry of the casting mold, composition, or cooling rate, and therefore lead to strong inhomogeneities of the microstructure and the chemical composition.\textsuperscript{2,5,10} The strip casting technique enables a fine separation of hard magnetic and rare earth-rich phases in the cast alloys. The merits of using strip cast alloys as a starting material for high performance Nd–Fe–B magnets are as follows:

1. The rapid solidification process prevents the formation of large dendritic $\alpha$-Fe grains in the cast alloy without the need of isothermal annealing even if the total rare earth content is reduced in order to produce high $(BH)_{max}$ magnets. The sufficiently large interlamellar spacing of about 3 $\mu$m between the Nd-rich platelets in the columnar Nd$_2Fe_{14}B$ grains is crucial in order to enable the formation of single crystal powder particles after HD treatment and jet milling necessary for optimum alignment of the particles and for high $Br$ in the magnets.

2. The homogeneous fine scale microstructure, containing a high amount of thin rare earth-rich platelets, leads to a high density of fine pre-cracks after hydrogen decrepitation. That and the lack of large dendritic $\alpha$-Fe grains improves the crushability of strip cast alloys significantly.

3. The good dispersion of rare earth-rich phases in the strip cast alloys leads to an optimum distribution of liquid phase during sintering and enables the production of high density magnets with high coercive fields even at lower sintering temperatures. The total rare earth content can be decreased by using strip casting without the formation of rare earth depleted zones in the magnets. That is essential for high $(BH)_{max}$ magnets but also in the case of magnets with high Dy content in order to improve the remanence and $(BH)_{max}$ while keeping high $H_c$.