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Grain boundary diffusion in nanocrystalline Nd-Fe-B permanent magnets with low-melting eutectics

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ABSTRACT

In order to combine the good thermal stability of nanocrystalline Nd-Fe-B magnets with the efficient grain boundary diffusion process (GBDP), low-melting eutectics have been mixed with Nd-Fe-B melt-spun ribbons, hot-compacted and subsequently die-upset. Transmission electron microscopy (TEM) analysis revealed the formation of 5–10 nm thick Dy-shells and a crystallography dependent diffusion into the individual solid grains on the nanoscale. Subsequent annealing at 600 °C leads to an enhanced diffusion but also some undesired Nd-O phases and induced grain growth depending on the annealing time, degree of deformation, strain rate and position within the sample. An optimized distribution of the low-melting eutectic was realized by milling the precursor powder and by using ternary alloys with reduced melting points. As a consequence a much higher effective increase in coercivity per wt%Dy was obtained compared to a homogeneous Dy-distribution which demonstrates the validity of this new approach.

1. Introduction

As the torque scales linearly with remanence, for motor applications in hybrid electric vehicles (HEVs) and generators such as wind turbines a high maximum energy product $(BH)_{max}$ has to be provided by Nd-Fe-B permanent magnets at elevated temperatures of around 150–200 °C in order to make them more efficient compared to the induction based devices [1,2]. The strong decrease of the magnetocrystalline anisotropy with higher temperature requires the incorporation of heavy rare earth (HRE) elements such as Dy or Tb into the $Nd_2Fe_{14}B$ phase in order to increase the anisotropy field H_a. As a consequence saturation polarization J_s reduces [3,4]. To face this drawback as well as the forecasted longterm criticality of the HRE elements [5] one can first reduce the grain size. Whereas with the pressless-sintering the minimum grain size is still limited to 1 μm [6,7], hot-deformation results in nanocrystalline magnets [8–10] with better thermal stability [11] and corrosion resistance [12] than their microcrystalline counterparts. Secondly one can enhance the magnetic anisotropy of the surface region of the Nd-Fe-B grains by an epitaxial Dy-rich shell [13] using the grain boundary diffusion process (GBDP) [14] in order to increase coercivity without reducing remanence [15–18]. As a modification of the GBDP one can thirdly improve the magnetic decoupling of the Nd-Fe-B grains by adding Nd + X (with X = Cu, Al etc.) to the grain boundaries [19,20]. The combination of all three approaches promises a high performance and a resource-efficient permanent magnet, but needs a reduction of the annealing temperature close to the melting point of the Nd-rich phase in order to avoid grain growth. To compensate the therefore limited diffusion one can use low-melting eutectics [19–23] instead of pure Dy or DyF_3 [24,25]. Furthermore the low deformation temperatures (700–800 °C) and short pressing times (45–450 s) of hot-deformed compared to sintered magnets (1000 °C/2-4 h), make it possible to coat the Nd-Fe-B powder with the low-melting eutectics before densification instead of coating the final magnet and still ending up with a distinct Dy shell, which is not the case for sintered magnets [26–29]. As a consequence diffusion length is reduced and the effectiveness of the diffusion process would not be restricted to the size of the sample.

A proof of principal of the powder-coating method was given in our previous publication [30] showing that the incorporation of

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DyCu increases coercivity more efficient compared to DyNiAl. Now we continue this work including high-resolution structural characterization and extend our own as well as others work [21,22] by a systematic and comprehensive study of the effect of annealing, milling and low-melting eutectics on the magnetic properties and its microstructure for each processing step hot-compaction and die-upsetting. In contrast to other reports [23], where a high increase in coercivity was achieved only at the expense of a significant reduction in remanence due to the high amount of paramagnetic material incorporated in the magnet, we focus in this work on increasing coercivity without reducing remanence e.g. in adding the eutectics most economically.

2. Experimental

$Dy_{70}Cu_{30}$, $Dy_{20}Nd_{50}Cu_{30}$ and $Tb_{20}Nd_{50}Cu_{30}$ eutectics (the following denoted as DyCu, DyNdCu, and TbNdCu, respectively) have been arc-melted and subsequently melt-spun at a wheel speed of 30 m/s to obtain fine crystalline ribbons with optimized homogeneity. The ground-up powders were sieved with mesh size of 250 μm and mixed together with Dy-free MQU-F melt-spun ribbons (Molycorp Magnequench) with composition of $Nd_{13.6}Fe_{73.6}Co_{6.6}Ga_{0.6}B_{5.6}$. For refinement the mixed powders were milled in a planetary ball mill (Fritsch Pulverisette P6) under heptane for 10 min using a ball-to-powder-ratio of 3:1 and a speed of 250 rpm. In order to compare the effective increase in coercivity per wt%Dy ($\Delta\mu_0 H_c^{eff}$) of the GBDP with those of a homogenous Dy-distribution MQU-G powder with similar composition compared to MQU-F but with 3.85 wt%Dy was used ($Nd_{12.2}Dy_{1.6}Fe_{73.2}Co_{7.1}$-$Ga_{0.6}B_{5.3}$). Hot-compaction at 725 °C and 100 MPa for 2 min under vacuum leads to fully dense nanocrystalline cylinders for all powders. Die-upsetting was conducted in argon at 750 °C. The degree of deformation $\phi = \ln(h_{start}/h_{end})$ with h_{start} and h_{end} representing the sample height before and after die-upsetting, respectively, was varied from 0.7 to 1.4 using a strain rate of 0.002 s^{-1} (standard) or 0.02 s^{-1} (fast). The samples were annealed in sealed quartz tubes in Ar at optimal temperature of 600 °C [31] and subsequently quenched. A schematic overview of the preparation process and the varied parameters is given in Fig. 1.

Magnetic properties have been characterized in a pulse magnetometer (Metis Instruments) in fields up to 7 T. To study phase distribution backscattered electron (BSE) images and energy dispersive X-ray (EDX) elemental maps have been taken with a scanning electron microscope (SEM) Jeol 7600F operating at 20 kV. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM), EDX and high-resolution TEM (HR-TEM) analyses were carried out at a FEI Tecnai F20-ST at 200 kV and a FEI Titan 80–300 at 300 kV. TEM lamellas have been prepared by focused ion beam (FIB) in a FEI Strata 400S microscope using 30 keV Ga-ions. Thermal analysis was conducted by differential scanning calorimetry (DSC) in a STA 429 Netzsch device and carrier gas hot extraction in a Leco O/N TC-436DR and a Leco 838 Analyser.

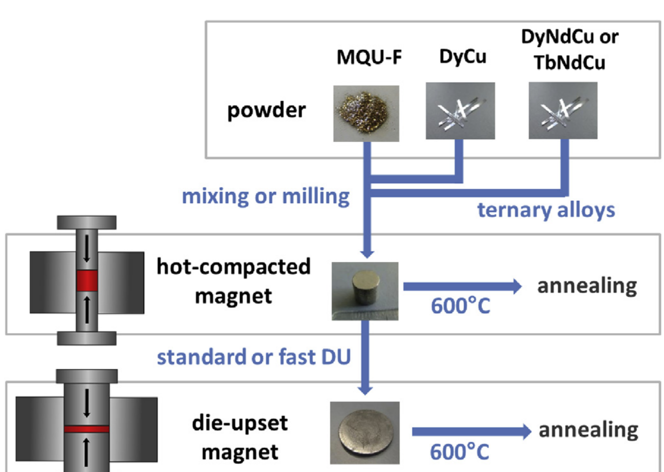

Fig. 1. Schematic overview of the preparation process.

3. Results and discussion

3.1. Magnetic properties

Fig. 2 shows the demagnetizing branches of hot-compacted and die-upset magnets with 1.1 wt%Dy (1.3 wt%DyCu). One can see, that already after hot-compaction coercivity is increased with respect to the Dy-free MQU-F reference sample due to the addition of DyCu. Annealing at 600 °C further enhances coercivity without reducing remanence for both, hot-compacted and die-upset magnets, respectively. The effective increase in coercivity in comparison to the Dy free MQU-F reference sample $\mu_0 H_c^{eff}$ amounts 0.29 T/wt%Dy for the hot-compacted sample after annealing for 24 h. This value is higher than that for a homogeneous Dy distribution with 0.2 T/wt% Dy for a sample made from MQU-G powder. For the die-upset sample $\mu_0 H_c^{eff}$ is only 0.16 T/wt%Dy for an optimum annealing time of 3.5 h at 600 °C.

Note that in this investigation non-annealed hot-compacted magnets have been directly die-upset because it turned out, that samples annealed at 600 °C could not be textured to the same extend as their non-annealed counterparts resulting in much lower remanence. This was attributed to some slight grain growth, which makes the following deformation process more ineffective. Furthermore it was found that the remanence of a complete die-upset sample is around 0.08 T smaller than that of a cut sample from the middle because the extreme edges of the sample discs are less textured. This is a general feature for die-upset magnets and has to be considered if the absolute values in this article are compared with other publications.

3.2. Microstructure of hot-compacted magnets

Fig. 3a shows a typical microstructure of a hot-compacted

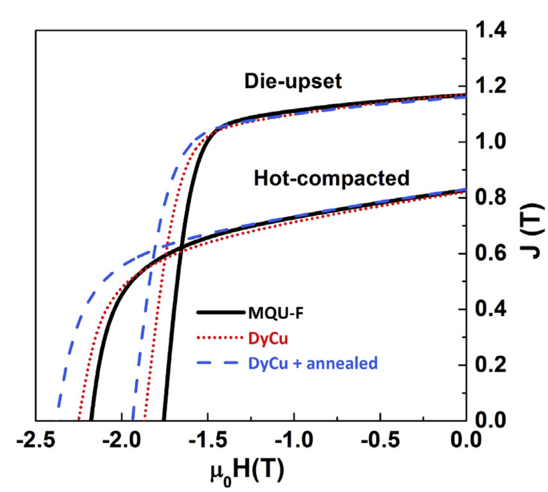

Fig. 2. Demagnetizing branches of hot-compacted and die-upset magnets with 1.1 wt% Dy (1.3 wt%DyCu) before and after annealing at 600 °C in comparison to Dy-free MQU-F samples.