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Multi-phase EBSD mapping and local texture analysis in NdFeB sintered magnets

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Abstract

A combination of electron backscatter diffraction and energy-dispersive X-ray spectroscopy has been used to identify the crystal structure and composition of all the phases present in commercially available NdFeB sintered magnets and to map their spatial distribution. The $Nd_2Fe_{14}B$ and NdO grains were shown to have low defect densities. The fcc Nd-rich and Nd_2O_3 grains had intra-grain misorientation angles of up to 14°, which was shown to be due to defects. Large numbers (~100) of data points for each phase were used to study texture in the NdO, Nd_2O_3 and $Nd_2Fe_{14}B$ phases. The $Nd_2Fe_{14}B$ grains exhibited a ⟨0 0 1⟩ fibre texture. The Nd oxide phases showed no strong texture, which implied that no strongly preferred orientation relationships between those phases and $Nd_2Fe_{14}B$ exist. The result was shown to be valid for optimally annealed samples exhibiting high coercivity and as-sintered samples exhibiting low coercivity.

Keywords: Electron backscattering diffraction; Energy dispersive X-ray spectroscopy; Hard magnets; Rare earth; Sintering

1. Introduction

The large and increasing demand for hybrid electric vehicles and wind turbines for electricity generation has led to renewed interest in the development of NdFeB sintered magnets, particularly concerning their performance at elevated temperatures ($T > 150$ °C). Partial substitution of Dy for Nd is currently used in order to increase the coercivity (H_c) [1,2] to a level sufficient for high temperature applications. The disadvantages of this are a reduction in the energy density, $(BH)_{max}$, caused by the antiparallel coupling between Dy and Fe in the $(Nd,Dy)_2Fe_{14}B$ unit cell [1,2], and the rarity of Dy [3,4]. Currently various approaches are being examined in order to develop Dy-free NdFeB sintered magnets with high H_c for high temperature applications [3–6]. In order to achieve this, it is vital to understand the coercivity mechanism in NdFeB sintered magnets in greater detail.

The microstructure of NdFeB sintered magnets consists mainly of $Nd_2Fe_{14}B$ ($P4_2/mnm$) [1] grains, which have an ⟨0 0 1⟩ fibre texture, surrounded by an Nd-rich phase which forms thin (~1 nm) layers along the grain boundaries and fills the triple points [7]. Other phases, such as $Nd_{1.11}Fe_4B_4$ (*Pccn*) [7,8] and, depending on the composition, α-Fe, may also be observed [7]. The Nd-rich phase may be composed of several phases, depending on the oxygen content [9]. Commonly reported are α-Nd ($P6_3/mmc$, La type) [9–11], NdO (*Fm-3m*, NaCl type) [7,9,11–14], Nd_2O_3 (*P-3m1*, La_2O_3 type) [7,9,15], Nd_2O_3-cubic (*Ia-3*, Mn_2O_3 type) [9,10,12] and NdO_2 (*Fm-3m*, CaF_2 type) [10,11,16]. The phases are usually referred to as Nd oxides for simplicity, but if other rare earth elements are present in the alloy mixed rare earth oxides are formed, e.g. $(Nd,Pr,Dy)_2O_3$. Nd–Cl and Nd–P–S "exotic phases" have also been observed [7].

Although the remanent magnetisation of NdFeB sintered magnets at room temperature is close to the optimum value, there appears to be great potential for improvements in the coercivity. The Nd-rich phases and their distribution in the microstructure are critical for the H_c of the magnet, but currently H_c reaches only 20–30% of the theoretical maximum (Brown's paradox), which is the anisotropy field, H_A [17,18]. Defects in the Nd_2Fe_4B grains are accepted as having

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an important role in limiting the H_c of NdFeB sintered magnets [19,20]. The defects are considered to be regions of the $Nd_2Fe_{14}B$ phase which are not structurally perfect and, therefore, have a lower magnetocrystalline anisotropy [19]. Some features of the coercivity mechanism in NdFeB sintered magnets are still not understood, for example the large (~30%) increase in H_c observed after annealing an as-sintered magnet at low temperature (typically $T \approx 500$ °C) [21,22]. Studies have proposed that the effect of annealing is due to improved distribution of the Nd-rich phases [11,12], which may be enhanced by small alloying additions [23,24], or to dissolution of a metastable ferromagnetic intergranular phase [25], or to relief of strain (defects) at the grain boundaries [15,26]. A further possibility is the formation during annealing of preferred orientation relationships between the Nd-rich and $Nd_2Fe_{14}B$ phases, which could lead to a reduction in the interfacial energy [16]. Makita and Yamashita [16] proposed two approximate preferred orientation relationships with Nd-rich grains identified as NdO_2, although considerable scatter in the data was present. Shinba et al. [12] reported at least seven further approximate orientation relationships with the Nd-rich grains indexed using an fcc structure or Nd_2O_3-cubic. These results indicate that no strongly preferred orientation relationships between the two phases exist. This, in turn, implies that the Nd-rich grains are not strongly textured. The scope of the previous studies was restricted by the typically small volumes available for analysis by transmission electron microscopy (TEM) and, therefore, a study with larger numbers of data points is desirable.

Electron backscatter diffraction (EBSD) has been used to characterise the local crystallographic orientation in several different NdFeB materials [27–29]. The sample areas available in EBSD are typically much larger than is available in TEM, but previous EBSD investigations have been limited to the $Nd_2Fe_{14}B$ phase. The aims of the current work were therefore to extend the study of NdFeB magnets by EBSD to cover all the phases present and to compare the crystallographic orientation of the Nd-rich oxide phases, using large data sets, in as-sintered and optimally annealed samples.

2. Experimental

Commercially available, Dy-free, NdFeB sintered magnets in the optimally annealed and as-sintered states were prepared using standard metallographic procedures, i.e. grinding with SiC paper and polishing using a colloidal suspension of SiO_2. The analysis was carried out in a Zeiss Leo Gemini 1530 scanning electron microscope, equipped with a field emission gun. An EBSD system from HKL and an energy-dispersive X-ray spectroscopy (EDX) system from Bruker were used.

For EBSD the electron beam was placed on a grain of interest and the resulting EBSD pattern was recorded for indexing offline using a semi-automatic process. Firstly, either the band detection algorithm or, in the case of poor pattern quality, manual selection was used to locate eight bands in each pattern. This large number of bands is commonly regarded as appropriate when needing to distinguish different phases. A phase database was then constructed which contained diffraction information about the appropriate phases. The automatic indexing algorithm was then used to search these phases for possible solutions matching the eight bands detected in the diffraction pattern. The solutions were manually inspected in all cases to ensure an excellent fit with the diffraction pattern and, therefore, correct indexing. The mean angular deviation (MAD) is a parameter generated by the software to describe the quality of fit of the solution to the diffraction pattern. The MAD was <1° for all the patterns indexed in this work.

EBSD mapping was carried out in several areas using a step size of 0.4 μm. The rhombohedral (3-fold) symmetry of the Nd_2O_3 *P*-3*ml* structure led to pseudo-symmetry problems; rotations of 60° about ⟨0 0 0 1⟩ between neighbouring points were recorded, which were in fact indexing artefacts. In order to remove these artefacts a model structure with hexagonal symmetry and the same *c*/*a* ratio as the Nd_2O_3 *P*-3*ml* structure was used. The EBSD patterns from all phases in the maps were indexed offline and the indexing parameters were optimised, giving a maximum automatic indexing rate of 81%. Zero solutions (i.e. non-indexed points) within $Nd_2Fe_{14}B$ grains were removed by filtering in order to improve the appearance of the maps. Filtering was not carried out for the Nd-rich phases and only unfiltered data was used for further analysis. Automatic indexing was not possible for some of the Nd-rich grains in the scan areas. The diffraction patterns corresponding to those grains were analysed using the semi-automatic procedure described above. In order to complete the map, the position, phase, orientation and band contrast data for those patterns were inserted into a database containing similar data for the automatically indexed points. Phase, band contrast and orientation maps were produced using a program written by the author.

The oxygen content of the alloys was measured by carrier gas hot extraction. Samples were cleaned under an Ar atmosphere, using SiC paper and ethanol, to remove any surface oxide. The samples were then transferred under an Ar atmosphere and measured without any contact with air. Eight samples were measured to obtain an average value.

3. Results and discussion

3.1. EBSD pattern indexing

The EBSD patterns from the Nd-rich phase grains clearly divided into two groups: one with hexagonal/rhombohedral (hex/rhom) symmetry (Fig. 1a) and the other with cubic symmetry (Fig. 1b). There are two phases with hex/rhom symmetry that are commonly reported in the literature concerning Nd-rich grains: α-Nd (hexagonal) [9–11] and Nd_2O_3 (rhombohedral) [7,9,15]. In order to determine