

Preparation methods for bulk materials

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Introduction

The progress in the field of permanent magnets has been dramatic over the last 35 years. This would have been impossible without a fundamental understanding of the physical phenomena responsible for hard magnet properties, which lead to the discovery of new families of permanent magnet materials based on rare earth (R) - transition metal (T) compounds. The search for new materials with superior properties focuses on compounds with high values of Curie temperature ($T_C > 500\text{K}$), high saturation magnetisation M_S ($\mu_0 M_S > 1\text{T}$, with μ_0 the permeability of free space ($4\pi \cdot 10^{-7} \text{Tm/A}$)) and high magnetocrystalline anisotropy, H_A . These intrinsic properties depend on crystal structure and chemical composition and it will be elucidated that a favourable combination of these values does not lead automatically to a good hard magnet material but can only be regarded as a prerequisite. The final suitability can only be assessed when the extrinsic properties such as coercive field H_C , remanent magnetisation B_r and maximum energy product $(BH)_{\text{max}}$, derived from the intrinsic properties by the preparation of appropriate microstructures, fulfil certain criteria.

Recent developments in the preparation of bulk rare earth-transition metal (RPMs) and FePt magnets are reviewed and emphasis is placed on research work at IFW Dresden. The approach of this contribution is twofold: (a) the most relevant processing routes for the synthesis of bulk magnetic nano- and microstructures are described and (b) some basic coercivity mechanisms in the different types of magnets are elucidated and intergrain exchange-coupling processes are analysed.

Principle synthesis methods include the traditional powdermetallurgical sintering route and more recent techniques such as high-energy ball milling, melt spinning and hydrogen-assisted processing methods (e.g. reactive milling, hydrogen decrepitation (HD) and hydrogenation-disproportionation-desorption-recombination (HDDR)). These techniques are applied to NdFeB-, PrFeB-, SmCo-based systems as well as to $L1_0$ -type FePt with the aim to produce high remanence magnets with high coercivity. Advanced structural characterisation techniques such as high-resolution electron microscopy and electron backscatter diffraction (EBSD) are utilised for the optimisation of the respective microstructures. Concepts of maximising the energy density in nanostructured magnets by either inducing a texture via anisotropic HDDR processing or hot deformation, or enhancing the remanence via magnetic exchange coupling are evaluated. A model for the texture memory effect in HDDR processed $\text{Nd}_2\text{Fe}_{14}\text{B}$ materials is introduced. Highly textured Nd-rich $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ obtained by hot deformation show unique magnetic microstructures based on cooperative phenomena. Magnetic force microscopy (MFM) is used to epitomise the so-called 'interaction domains'. For nanostructured isotropic, multi-phase $(\text{Nd,Pr})\text{FeB}$ -based materials, enhanced remanences, larger than those predicted by Stoner-Wohlfarth for systems of isotropically oriented, magnetically uniaxial, non-

interacting single domain particles, are observed. Coupling phenomena have been studied by analysing the evolution of the δJ values obtained from recoil loops measured during the demagnetisation process in dependence on composition, temperature and grain size. Recently significant progress has been made in the development of high temperature 2:17-type $\text{Sm}(\text{Co}_{\text{bal}}\text{Fe}_v\text{Cu}_y\text{Zr}_x)_z$ magnets and operating temperatures of up to 500°C are now feasible. The evolution of nanostructure, microchemistry and magnetic properties during a complex heat treatment regime of melt-spun and sintered $\text{Sm}(\text{Co}_{\text{bal}}\text{Fe}_v\text{Cu}_y\text{Zr}_x)_z$ magnets is described. A characteristic gradient of domain wall energy within the $\text{Sm}(\text{Co,Cu})_5$ cell boundary phase depending on subtle changes in microchemistry, namely the Cu content, is responsible for a specific domain wall pinning mechanism.

Fig. 1 shows the three prototypes after processing of RPMs based on $\text{Nd}_2\text{Fe}_{14}\text{B}$ with idealised microstructures. Type (I) is rare earth rich and the individual crystallites are separated by Nd-rich intergranular phase, which basically is a thin paramagnetic layer. This structure leads essentially to a magnetic decoupling and each hard magnetic grain behaves like a small permanent magnet, which results in high coercivities. Type (II) can be obtained using the stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$ composition and the grains are exchange-coupled without an additional phase between them. As a consequence, a parallel alignment of the magnetic moment in the vicinity of the grain boundaries and provided the grains are small enough, a remanence enhancement is observed. A further increase in remanence is found in the type (III) nanocomposite magnet, a two- or multi-phase exchange coupled magnet, where a Nd deficient composition (i.e. Nd concentrations < 11.76 at.%) is used and the coupling occurs between the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains and soft magnetic Fe rich grains.

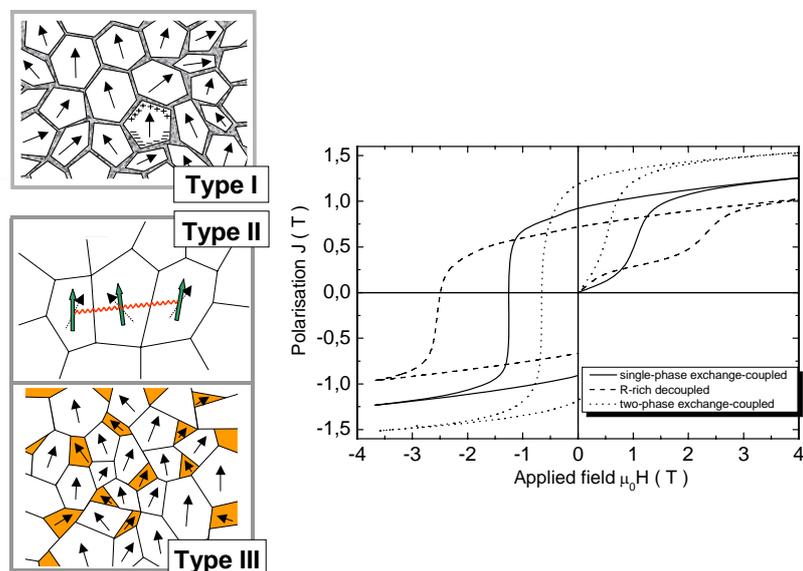


Fig. 1: Three prototypes of RPM's based on $\text{Nd}_2\text{Fe}_{14}\text{B}$ with idealised microstructures. Type (I) is rare earth rich and the individual crystallites are separated by a thin paramagnetic layer (grey). Long-range dipolar interaction is dominant and each hard magnetic grain behaves like a small permanent magnet, which results in high coercivities. The grains in type (II) based on stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$ are exchange-coupled, as no additional phase is present at the grain boundaries, leading to remanence enhancement. Type (III) is a nanocomposite magnet, where a Nd deficient composition is used and the coupling occurs between the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains and soft magnetic Fe rich grains (grey) resulting in a further increase in remanence ("exchange-spring magnet").

An overview of the most relevant manufacturing routes, with special emphasis on nanostructured magnets, is given in the flow chart of figure 2, which illustrates the principal processing routes of RPMs. For the production of high performance RPMs with maximum energy densities a careful control of low level metallic impurities and non-metallic impurities such as oxygen is pivotal during all processing stages, regardless of which processing route is chosen. Each branch ends by machining and magnetising the magnet. The left branch represents classical powder-metallurgical processing resulting in monocrystalline particles of typically $10\ \mu\text{m}$ in diameter, hence large compared to the critical single-domain particle size d_c . The right branch of this figure embodies processing routes, which aim at considerably smaller grain sizes somewhere between δ_w (domain wall width) and d_c .

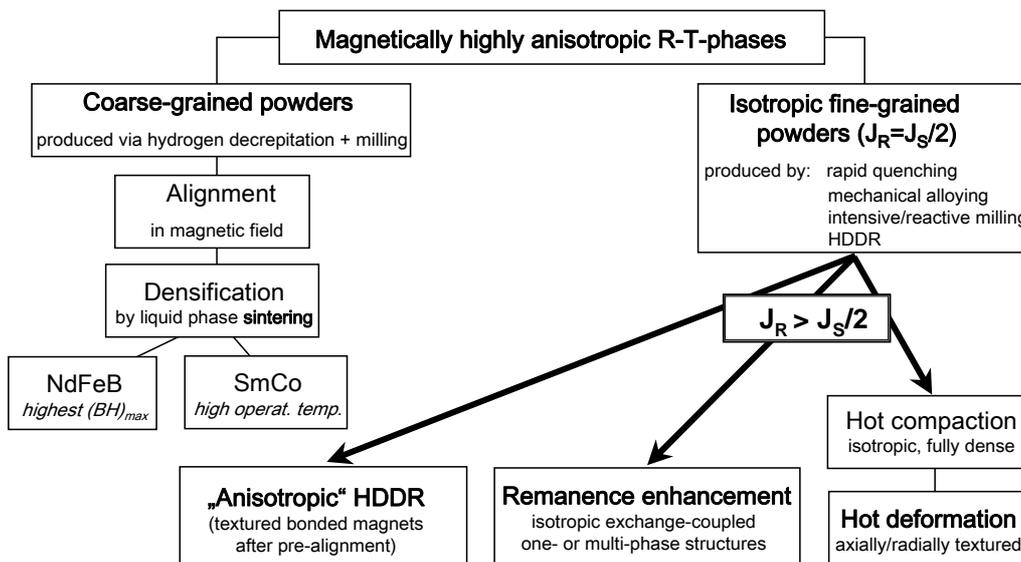


Fig. 2: Flow chart illustrating the principal processing routes of high energy density RPMs based on coarse- and fine-grained powders.

Sintering

Conventional powder metallurgy is used, and generally the following requirements need to be fulfilled: a minimised oxygen content, a maximum volume fraction of the hard magnetic Φ phase with a commensurate reduction in the non-ferromagnetic grain boundary material, a small crystallite size with a narrow size distribution of typically $2\text{-}6\ \mu\text{m}$ and a maximum alignment of the easy axis of magnetisation of the crystallites. Because the compositions of recent high energy density magnets are close to stoichiometry, conventionally cast materials would contain a high proportion of Fe-dendrites due to the peritectic nature of the formation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. Fe is not only detrimental to the crushability during jet milling but also to the magnetic properties of the magnet. The 'strip casting' method suppresses both the formation of free Fe and large pools of Nd-rich phase and leads to a fine grained microstructure, which is very suitable for subsequent hydrogen decrepitation (HD) and jet milling. The strip casting method consists of casting molten alloys onto a rotating water-cooled wheel, leading to the continuous formation of $0.3\ \text{mm}$ thick flake-

shaped ingots with grain sizes ranging from 5-60 μm , the larger ones close to the free surface side.

Pulverisation is usually achieved by jet milling where an ultrasonic flow of inert gas induces mechanical collisions of the particles. During this process oxidation and particle welding have to be avoided, the former being detrimental to densification, the latter leading to misalignment. Milling in liquid media with low moisture and oxygen levels can be beneficial. A large magnetic torque, i.e. large magnetic fields well exceeding 1 MA/m, is necessary in order to achieve a maximum degree of alignment. Mechanical friction is essential to hold the powder particles together when producing the green compact (porous body after predensification) and packing density needs to be maximised in order to avoid particle relocation leading to decreased alignment. The rubber isostatic pressing (RIP) technique was innovated in order to overcome these problems. Near net-shape green compacts are produced using a thick rubber mould confined by a metallic die, the former creating a pseudo-hydraulic pressure. An alternative compaction method is TDP (transverse die pressing). Anisotropic, sintered $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type magnets (type (I) in figure 1) with energy products $(\text{BH})_{\text{max}}$ exceeding 400 kJ/m^3 (50 MGOe) are now produced routinely in industry using these techniques.

Rapid quenching

In the melt spinning method, the most relevant of the rapid quenching techniques, a jet of molten alloy is fired at a water-cooled copper wheel, which is rotating at a high speed. The liquid solidifies at a cooling rate of up to 10^6 K/s and fine, brittle ribbons are thrown off the wheel. The melt undergoes rapid quenching and iron free material can be produced. Depending on wheel speed, ejection conditions and melting temperature substantial undercooling below the equilibrium freezing temperature and, consequently, a very high frequency of crystal nucleation are achieved. The analysis of the devitrification kinetics for the amorphous phase revealed a relatively low growth rate of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. This leads to the ultrafine grain size of typically 20-50 nm on annealing during which coercivity is developed.

The randomly oriented grain structure results in magnetically isotropic magnets, with the remanent magnetisation, B_r , and $(\text{BH})_{\text{max}}$ limited to 0.5 and 0.25, respectively, of the values obtainable for ideal microstructures consisting of single domain grains and with full crystallographic alignment. The ribbons are usually mixed with some kind of polymer resin and are then injection or compression moulded (Magnequench, MQ1). Larger remanences can be obtained when hot pressing the crushed ribbons to full density (MQ2) followed by hot deforming the compact (MQ3) and finally crushing the forgings. This rather complicated route leads to anisotropic powder which can be exposed to a magnetic field in order to obtain aligned NdFeB bonded magnets with energy products of $(\text{BH})_{\text{max}} > 140 \text{ kJ/m}^3$.

A number of reports have been published on $\text{Nd}_2\text{Fe}_{14}\text{B}$, $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$, $\text{Nd}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B}$, $\text{Sm}_2\text{Fe}_{17}\text{N}(\text{C})_x/\text{Fe}$ and $\text{Pr}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ exchange coupled systems. The crystallisation of melt spun $\text{Nd}_4\text{Fe}_{78}\text{B}_{18}$ (“*Coehoorn composition*”) amorphous alloy results in a nanocomposite magnet consisting of only 15 vol.% hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, but of 73 vol.% Fe_3B and 12 vol.% Fe soft magnetic phases with $M_r/M_s \gg 0.5$. An optimum microstructure would consist of a homogeneous dispersion of a hard phase in a soft phase,

both on a 5-10 nm scale. This microstructure can be synthesised by annealing a supersaturated metastable alloy, i.e. nucleation and crystallisation from the glassy state. Many studies have been carried out in order to optimise the magnetic properties by microalloying.

Mechanical alloying

Mechanical alloying, originally established for superalloys, circumvents many limitations of conventional alloying as it is, like rapid quenching, a non-equilibrium processing technique and thus can be used for the preparation of metastable alloys. An interdiffusional reaction, enabled by the formation of ultrafine, layered composite particles during high-energy ball milling, leads to the mixing of the elements. Depending on the thermodynamics of the alloy system, energy input during milling and the mechanical workability of the starting powders, the alloying could take place during milling or during a subsequent heat treatment. Mechanical alloying is a complex process and involves the optimisation of a number of variables. The most important parameters that affect the final microstructure and properties of the powder are: type of mill; milling container; milling speed; milling time; type, size, and size distribution of the grinding medium; ball-to-powder weight ratio; extent of filling the vial, milling atmosphere, process control agent; and temperature of milling. Some of the process variables are interrelated.

In the case of Nd-Fe-B magnets, a layered microstructure of Fe and Nd is formed with B particles remaining undeformed and embedded in the interfaces. The hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is then formed at relatively low annealing temperatures of 600-700 °C and short reaction times of 5-30 min, which is due to the extremely fine distribution of the reactants. A modification of mechanical alloying is the intensive milling technique, where an alloy rather than the elemental powders is exposed to high-energy ball milling. Again, grain growth inhibiting effects of additives such as Al, Ga and Co can be utilised.

Hot deformation

Besides the powder metallurgical sintering route, where an external magnetic field is used to align microcrystalline single crystal particles, and the anisotropic HDDR route, where a field is used to align particles consisting of many 300 nm sized grains with a preferred orientation, the hot deformation-induced texturing of cast alloys or fine-grained powder precursor materials provides a third option for producing textured RPMs with maximised energy densities. A grain alignment along the *c*-axis of the tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase based on either Nd-Fe-B or Pr-Fe-B alloys perpendicular to the plastic flow is achieved after high temperature compressive deformation. The key for the hot workability is the presence of a rare earth rich grain boundary phase, which is liquid at the deformation temperature.

Interstitial modification

Ternary carbides $\text{R}_2\text{Fe}_{17}\text{C}_x$ ($x \leq 1.5$) can be prepared by standard casting techniques, higher C concentrations can be achieved by either substituting Ga for part of the Fe in cast materials or by exposing fine particles of the binary compound to hydrocarbon gases at

elevated temperatures. Similarly, a simple gas phase nitrogenation according to: $2R_2Fe_{17} + 3N_2 \Rightarrow 2R_2Fe_{17}N_3$ can be carried out at 1 bar nitrogen gas and temperatures of about 400-500 °C.

The absorption of nitrogen atoms takes place once the temperature is high enough to overcome the activation energy for the absorption process. This gas-solid reaction consists of adsorption of the gas molecules, their dissociation and subsequent chemisorption of e.g. N atoms and finally long-range diffusion into the metal matrix. A detailed understanding of this irreversible nitrogenation process is necessary in order to optimise the final magnetic properties and it is still a matter of discussion whether, in a thermodynamic equilibrium, a solid solution or ternary nitrides with fully nitrated and non-nitrated layers are obtained. The relatively slow diffusion of the N atoms into the matrix makes it necessary to use fine ground particles obtained after intensive milling or HDDR; microcracks and microcrystalline provide fast diffusion paths so that shorter annealing times and lower temperatures can be used. However, the latter remain critical processing parameters as the decomposition in RN and Fe according to $R_2Fe_{17} + N_2 \Rightarrow 2RN + 17Fe$ is the preferred reaction from a thermodynamical point of view. Long range diffusion of metal atoms is required for this reaction and insufficient kinetics make the preparation of ternary nitrides possible despite the metastability of the latter compared to the binary nitride and Fe metal. The limited thermal stability of the ternary nitrides restricts the applicability of this class of compounds to metal or polymer bonded magnets. The decomposition temperature can be increased by additions such as Al, Si or Ga and generally it can be stated that the carbides are superior to the nitrides in terms of their thermal stability.

Hydrogen Decrepitation

Decrepitation means the self-pulverisation of large metal particles into powder, a common phenomenon that results from a combination of hydriding volume change and the brittle nature of hydriding alloys (especially when they contain some H in solution). The morphology of the decrepitated powder affects the heat transfer, this however, being more relevant for hydrogen storage compounds and of less importance for permanent magnetic materials.

HDDR

The Hydrogenation Disproportionation Desorption Recombination (HDDR) process relies on a different type of reaction and is in principle a strikingly simple method for producing magnetically highly coercive rare-earth transition metal powders (e.g. of $Nd_2Fe_{14}B$ -type) by utilising a fully reversible hydrogen gas-induced chemical reaction. The first stage of the HDDR-process is the absorption of hydrogen by the Nd-rich material at the grain boundaries essentially to form $NdH_{2.7}$. The next stage is the formation of the $Nd_2Fe_{14}B$ -H interstitial solution. This is followed by a complete hydrogen desorption with further increasing temperature before the disproportionation reaction is triggered. In the case of $Nd_2Fe_{14}B$, the HDDR reaction can be described as: $Nd_2Fe_{14}B + (2\pm x)H_2 \Leftrightarrow 2NdH_{2\pm x} + 12Fe + Fe_2B \pm \Delta H$. As in mechanically alloyed or melt spun materials, the coercivity in HDDR processed materials arises from the fact that final grain sizes are significantly smaller than or comparable to the critical single-domain grain size (200-300 nm for

Nd₂Fe₁₄B). The crucial difference, however, to the former two methods is that with the HDDR process it is possible to produce directly highly anisotropic magnet powders without the mechanical deformation necessary for example for melt-spun materials. Here "anisotropic powder" means that the magnetically easy axes (c-axes) of the Nd₂Fe₁₄B grains are aligned in the multigrain powder particles. Consequently, compact textured magnets can be produced by aligning these anisotropic powder particles in a magnetic field.

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