Nanostructured hard magnets

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Permanent magnets find application in a wide variety of devices, from everyday appliances like loudspeakers to motors, data storage and medical (e.g. magnetic resonance imaging) devices. There is a constant search for new materials with superior properties, either in the form of new magnetic compounds or in the form of known materials with improved magnetic properties. Modern high-performance magnets are based on intermetallic compounds of rare-earths (R = Nd, Pr, Sm) and 3*d* transition metals (T = Fe, Co) with very high magnetocrystalline anisotropy, such as $Nd_2Fe_{14}B$ and $SmCo_5$ [1-3]. FePt magnets with the $L1_0$ structure have recently attracted much attention because of their potential usage in ultra high-density data storage and permanent magnets for special applications. The material design on a nanoscale is one of the possibilities to improve the magnet performance. In this presentation, the complex relation between the structure, microstructure and magnetic properties of modern high-performance magnets will be reviewed.

1. Magnetic properties of hard magnetic materials

The interactions on the atomic scale determine the intrinsic magnetic properties of a material, such as the spontaneous magnetisation M_s, the Curie temperature T_c and the magnetocrystalline anisotropy constant K_1. The extrinsic magnetic properties of hard magnetic materials, remanent magnetisation (remanence) M_r and coercive force (coercivity) H_c, are related to magnetic hysteresis and are determined to a great extent by the microstructure. Another key characteristic of a permanent magnet is the energy product $(BH)_{max}$, which is twice the maximum magnetostatic energy available from a magnet of optimal shape. The energy product increases both with increasing coercivity and remanence. However, for materials with sufficiently high H_c, the energy product can never exceed the value $\mu_0 M_r^2 / 4$.

The remanent magnetisation of real magnets is usually below its saturation value (mostly due to lack of grain alignment). In particular, the remanence-to-saturation ratio M_r/M_s is limited to 0.5 for magnets composed of non-interacting uniaxial randomly oriented particles. The processing route for obtaining an anisotropic magnet (e.g. sintering) is in

general more sophisticated than that for a non-textured magnet, thus justifying the efforts to obtain a better M_r/M_s ratio in the latter. A possibility to increase M_r in non-textured magnets is remanence enhancement in the so-called *exchange-spring* or *exchange-coupled* magnets [4-6]. In general, remanence enhancement in this type of magnets is attributed to intergrain coupling via exchange interaction. This coupling causes the magnetisation of neighbouring grains to deviate from their particular easy axis resulting in a magnetisation increase parallel to the direction of the applied field. The exchange-coupling concept has its origin in the random-anisotropy theory [7, 8].

Assemblies of high anisotropy (hard magnetic) grains are termed single-phase exchange-coupled magnets and a combination of a high anisotropy phase with a less anisotropic (soft magnetic) phase is called nanocomposite exchange-coupled magnets. Various combinations of hard magnetic phases with soft magnetic phases have been synthesised including $R_2Fe_{14}B/\alpha$-Fe (R = Nd, Pr), $Sm_2Fe_{17}N(C)_x/\alpha$-Fe, Sm-Co/α-Fe(Co) and FePt/Fe_3Pt exchange-coupled nanocrystalline bulk magnets [4, 9-14], as well as thin films and multilayers [15-17].

2. R-Fe-B (R = Nd, Pr)

An overview of the most relevant manufacturing routes, with special emphasis on nanostructured magnets, is given in the flow chart of figure 1, which illustrates the principal processing routes of rare-earth permanent magnets (RPMs) [18]. For the production of high performance RPMs with maximum energy densities a careful control of low level metallic

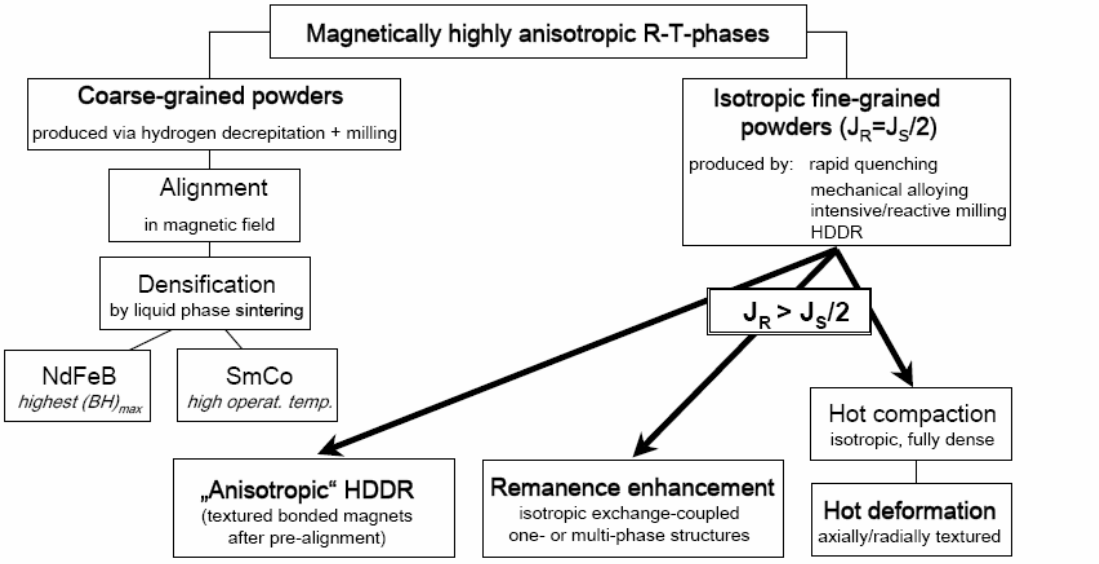

Fig. 1. *Flow chart illustrating the principal processing routes of high energy density RPMs based on coarse- and fine-grained powders.*

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 μm in diameter, hence large compared to the critical single-domain particle size d_c, which is in the range of 200–300 nm for $Nd_2Fe_{14}B$ and $Pr_2Fe_{14}B$. The right branch of this figure embodies processing routes, which aim at grain sizes considerably smaller than d_c.

In general, there exist three prototypes of RPMs based on $R_2Fe_{14}B$. Type (I) is rare earth rich and the individual crystallites are separated by Nd-rich (oxide) 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 coercivity. Type (II) can be obtained using the stoichiometric $R_2Fe_{14}B$ composition and the grains are exchange-coupled without an additional phase between them. 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 rare-earth deficient composition is used and the coupling occurs between the $R_2Fe_{14}B$ grains and soft magnetic crystallites (α-Fe or/and Fe_3B).

In this presentation, 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 $Nd_2Fe_{14}B$ materials is introduced [19]. Highly textured Nd-rich $(Nd,Pr)_2Fe_{14}B$ obtained by hot deformation show unique magnetic microstructures based on cooperative phenomena. Magnetic force microscopy (MFM) is used to image the so-called “interaction domains” [20]. For nanostructured isotropic, multi-phase (Nd,Pr)FeB-based materials, enhanced remanence is observed.

3. $Sm_2(Co,Cu,Fe,Zr)_{17}$-type magnets

$Sm_2(Co,Cu,Fe,Zr)_{17}$–type magnets are typical pinning hardened magnets, i.e. reverse domains are prevented from growing by various pinning centres. Recently significant progress has been made in the development of high temperature $Sm(Co_{bal}Fe_vCu_yZr_x)_z$ magnets and operating temperatures of up to 500°C are now feasible [21, 22]. This extraordinary behaviour has to be attributed to the special composed of a three-phase system: Fe-rich rhombohedral 2:17 pyramidal cells, Cu-rich hexagonal cell walls of 1:5 structure and Zr-rich lamellae of 2:17 phase intersecting the cells perpendicular to the *c*-axis. The evolution of

nanostructure, microchemistry and magnetic properties during a complex heat treatment regime of melt-spun and sintered $Sm(Co_{bal}Fe_vCu_yZr_x)_z$ magnets is described. A characteristic gradient of domain wall energy within the $Sm(Co,Cu)_5$ cell boundary phase depending on subtle changes in microchemistry, namely the Cu content, is responsible for a specific domain wall pinning mechanism.

4. $L1_0$-type Fe-Pt magnets

Since the mid-1930s Fe-Pt alloys are known to exhibit high coersivities due to high magnetocrystalline anisotropy of the $L1_0$ FePt phase [23], but the high price prevented widespread applications of these alloys. Distinct advantages of Fe-Pt alloys are, as opposed to the rare-earth-transition-metal-based compounds, that they are very ductile and chemically inert. These magnets present interest for specialised applications such as in magnetic micro-electromechanical systems (magnetic MEMS) or in aggressive environments, for instance, in dentistry, where they are used as magnetic attachments to retain dental prostheses in the oral cavity.

Through the use of mechanical alloying and subsequent heat treatment the formation of chemically highly ordered $L1_0$ FePt and, in the case of the Fe-rich and Pt-rich compositions, $L1_2$ Fe_3Pt and $FePt_3$ phases, respectively, is achieved. Whereas in Pt-rich alloys the decoupling effect of the $FePt_3$ phase leads to coercivity improvement, in Fe-rich nanocomposites a peculiar nanometer scale multilayer structure gives rise to remanence enhancement due to large effects of exchange interactions between the crystallites of the phases [14, 24]. The structure, magnetic properties [25] and magnetisation reversal processes of these alloys are described.

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