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Heavy rare earth free, free rare earth and rare earth free magnets - Vision and reality

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ABSTRACT

It is commonly understood that among the intermetallic phases used for permanent magnets, practically none can fully realize its potential based on the intrinsic magnetic properties. We discuss different reasons leading to this limitation, known as the Brown paradox, and propose some possible ways of overcoming it. We compare the intrinsic magnetic properties of $(Nd_{1-x}Ce_x)_2(Fe_{1-y}Co_y)_{14}B$ single crystals with the extrinsic characteristics of sintered and hot compacted magnets made from the very same alloys. In addition, looking at RE-free materials, our results obtained on Mn- and Co-based RE-free single crystals are compared with the hard magnetic properties of Mn-based permanent magnets.

The current industrial demands for high-performance permanent magnets is expected to grow quickly as we are witnessing global expansion of wind turbines, hybrid-electric vehicles, robotics and automation, household electrical appliances, and power and consumer electronics. Most importantly, the transition towards renewable energy sources (primarily wind energy) and efforts to reduce the CO_2 emission (mainly by developing e-mobility) accelerates the ever-growing demand for cost- and resource-efficient permanent magnets [1].

A suitable magnetic material should fulfil several criteria. Firstly, the main phase of the magnet must exhibit a high spontaneous magnetization M_s concurrently with both a high uniaxial magnetic anisotropy constant K_1 and a high Curie temperature T_C. Secondly, a specific micro- or nanostructure has to be established in the materials in order to convert their good intrinsic properties into technically acceptable extrinsic characteristics. The most important extrinsic properties are the coercivity H_c (mostly determined by K_1, grain size and a properly engineered intergranular phase) and a high remanent magnetization M_r (determined by M_S, the degree of texture and minimized secondary phases). We have summarized recently the most relevant intrinsic and extrinsic factors influencing the hysteretic properties [2]. Advanced hard magnetic materials should demonstrate both a high remanent magnetization (B_r > 1.35 T) and a large coercivity (H_c > 1.5 T) at room temperature, as well as the ability to operate in a temperature range of −50… + 200 °C [3,4]. Besides these essential magnetic properties, the mechanical stability, corrosion resistance, shapeability, sustainability and recyclability are further required material attributes of a modern magnet.

The most powerful permanent magnets are based on intermetallic compounds containing rare-earths (RE) metals, such as Nd, Sm, Dy, Tb, and *3d* metals, such as Fe and Co. Since the single-electron spin-orbit coupling constant $\zeta \sim Z^2$ where Z is the atomic number, the rare-earth elements are necessary to provide strong spin-orbit coupling for high magnetocrystalline anisotropy and therefore ensure large magnetic hysteresis, while the *3d* metals are responsible for high spontaneous magnetization and a significant Curie temperature. The *3d* metals (mostly Fe, Mn, Ni) are widely available, whereas the RE metals and Co are to some extent resource critical [5]. For example, Nd, Dy and Tb are essential ingredients of modern high-performance $Nd_2Fe_{14}B$-based permanent magnets. Partial substitution Nd by Dy or Tb (2–10 w% of Nd) improves the magnetic anisotropy that accordingly leads to higher coercivity and better thermal stability [6]. Nonetheless, due to recent and ongoing supply chain vulnerability and price volatility of rare-earth metals (the consequence of the 2010/2011 Rare Earth Crisis), there is a continuing risk of a shortage of rare-earth elements, especially valid for Dy and Tb [7,8]. As a consequence, researchers and funding agencies round the world focus on the development of novel hard magnetic materials with a reduced critical rare-earth content, but with their properties comparable (or better) than Nd,Dy-Fe-B permanent magnets [9].

Various approaches can be used in order to reach this ambitious goal, and the most promising of them are listed below: (1) Enhancing the coercivity of Dy-free magnets by reducing the grain size [10,11]. (2) Implementing the Grain Boundary Diffusion Process (GBDP) which allows to drastically reduce the Dy content in NdFeB magnet by concentrating the precious Dy or Tb only at the grain boundaries, effectively improving the coercivity of the entire magnet [12–15]. (3) Substituting Nd by more abundant Ce (we term this “free RE” [16]), which leads to a decrease in the price [17]. (4) Developing of new classes of RE-lean permanent magnets, based on phases with a RE content lower than in the $Nd_2Fe_{14}B$ phase ($SmFe_{11}Ti$, $Sm_2Fe_{17}N_x$, $NdFe_{11}TiN_x$ are promising

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candidates) [18]. (5) Developing the additive manufacturing technique, which potentially offers an effective way for fabricating permanent magnets and can be adopted for production of complex magnetic systems with minimum material (RE) waste [19].

Concurrently, we can observe steadily growing interest in new magnets containing no rare-earth elements at all. The most important problem needed to be solved here consists in achieving hard magnetic properties, which are comparable with the B_r and H_c of RE-based magnets, or, at least, these parameters must be better than commercially available hard ferrites [20]. Several approaches can be pursued: (1) Experimental combinatorial material science [21,22]; (2) Computational material science [23]; (3) Re-examination of the less studied *3d* compounds, somewhat neglected since the discovery of the Nd–Fe–B magnets 35 years ago [24] (4) Exploitation of additional degrees of freedom, for example field-assisted processing or, high pressure synthesis to form otherwise metastable or unstable phases [25].

All these approaches used for both RE-lean and RE-free magnets have one ultimate goal: bring about the extrinsic magnetic parameters of the magnet B_r and H_c as close as possible to their upper limit determined by the intrinsic magnetic properties of the material K_1 and M_s. It is commonly understood that among the intermetallic phases used for permanent magnets production, practically no one can fully realizes its potential defined by K_1 and M_s. [26]. Goals of this paper are the discussion of possible reasons for this underperformance and the consideration of possible ways to realize the ultimate ambition: exceptional high energy products at elevated temperatures.

Macroscopically the magnetic anisotropy of uniaxial magnets can be easily evaluated using the anisotropy field H_a corresponding to the minimal external magnetic field needed for complete rotation of the M_s vector from the easy to the hard direction of magnetization. Generally, the coercivity cannot be higher than the anisotropy field H_a: $H_c < H_a = 2K_1/\mu_0 M_s$. In the idealized case of uniform rotation of magnetic moments in single domain particles, the Stoner and Wohlfarth model [27] gives the upper limit of coercivity value as $H_c = H_a$ if the magnetic field is applied along the easy direction. It means that in order to achieve maximum coercivity, the size of grains or particles should be very close to the critical single domain or coherent rotation critical diameter d_c. For the grain sizes considerably less than d_c, the magnetization can randomly flip from one direction to the opposite one due to thermal energy excitation; hence the coercivity is negligible (superparamagnetic state). On the hand, for grain sizes significantly larger than d_c, the magnetic structure of particles will be split into magnetic domains, and magnetization processes will occur by domain wall movement, causing the drastic reduction of coercivity (for $Nd_2Fe_{14}B$ $d_c = 300$ nm, for hard ferrites $d_c =$ 1000 nm and for $SmCo_5$ $d_c = 2000$ nm [28]).

There are different technological ways to obtain particles of that size or aggregates consisting of crystallites with sizes ≤ d_c: surfactant-assisted high energy ball milling, gas atomization, chemical reduction from oxides, rapidly quenching, recrystallization from amorphous state, hydrogenation-disproportionation-desorption-recombination (HDDR) process, etc. [29]. If isolated single domain particles are used, they should be bonded or consolidated and textured. The major difficulty consists in the practical impossibility of aligning these particles in a magnetic field of reasonable magnitude (in industry a field of 1–2 T is commonly used). This makes it impossible to achieve a reasonable texture and M_r in, for example, polymer bounded magnets made from single domain particles. Moreover, even after isotropic cold compaction of the loose powder with polymer, the residual porosity of the pellet cannot be smaller than 35 vol% [30], which significantly reduces the spontaneous magnetization per volume unit.

Hence, an ensemble of single domain particles can be a good model object, but it cannot serve as a high-performance permanent magnet. On the other hand, in case of multigrains aggregates, the intergranular interactions (e.g. exchange, magnetostatic) reduce the coercivity of the entire assembly; moreover, the absence of texture in such multigrain fragments in the most cases does not allow aligning the aggregates. An exception is the HDDR process. If optimum parameters are chosen for the HDDR process, the recombined $Nd_2Fe_{14}B$ grains show strong crystallographic texture, inheriting the orientation of the initial $Nd_2Fe_{14}B$ grain, resulting in the formation of textured Nd–Fe–B fine-grained powders [31]. Although for the compaction of such textured aggregates the dilution of the powder is inevitable. Only if the single domain particles or crystallites possess very pronounced shape anisotropy, by using the hot compaction it is possible to provide a high degree of texture in full-dense sample (e.g. die-upset NdFeB-based magnets). At the same time the single domain size of the crystallites in hot-deformed aggregates provides practically no significant benefit anymore and coercivity of such magnets become much smaller than H_a. At the same time, due to reduction of the grain sizes, the temperature coefficient of nanocrystalline die-upset magnets is much better than the one of the sintered samples.

Thus, there are three widely used techniques applied for industrial production of full-dense magnets with aligned micro- and nanograins (textured materials): liquid phase sintering (powder metallurgy) [29,32], spinodal decomposition [33,34] and hot-deformation of nanocrystalline and compacted melt spun ribbons [35]. Only a magnet obtained by one of these three techniques can fully utilize its intrinsic magnetization M_s and can is assessed in this definition as a high-performance permanent magnet.

In reality, even if the grain size of the full-dense magnet is close to the single domain size, the H_c is usually one order of magnitude smaller than the H_a - this situation is known as Brown's paradox [36] and is attributed to the presence of crystallographic defects of various kinds, secondary phases, surface imperfections as well as magnetic inhomogeneities. These inclusions and defects lead to local magnetic softening and reduce the anisotropy field H_a by a factor α, where α is the so-called "Kronmüller factor" associated with nanostructural imperfections and spatial variation of M_s, K_1 and exchange stiffness parameter A [37].

As-cast materials often exhibit $\alpha = 0.01$, and sophisticated processing methods are necessary to reach $\alpha = 0.3$. This maximal achievable coercivity limits the best laboratory-made Nd-Fe-B and Sm-Co-based magnets to roughly 25% of their theoretical H_a and industrial magnets demonstrate even lower values. Thus, it can be concluded that at the current technological level it is impossible to reach the H_c close to H_a in mass production of Nd-Fe-B and Sm-Co-based magnets. Moreover, there are many other intermetallic phases with hexagonal, rhombohedral or tetragonal crystal structures and outstanding intrinsic properties (M_s, K_1), but with $\alpha < 0.1$ (e.g. $SmFe_{11}Ti$, YCo_5, $Sm_2Fe_{17}N_x$, $NdFe_{11}TiN_x$ etc.). Despite of their excellent M_s and K_1, an optimum micro- or nanostructure has not yet been developed for these types of alloys.

At the same time, there are exceptions to every rule and coercivities of about 90% of the theoretical values for $BaFe_{12}O_{19}$ particles were observed by Mee and Jeschke ($\alpha = 0.886$) [38], Haneda et al. ($\alpha =$ 0.895) [39] and other researchers, who applied a co-precipitation technique to obtain small stress-free particles. Recently, it has also been demonstrated [40] that in FePt thin films it is possible to reach $\alpha =$ 0.75 with $\mu_0 H_c = 6$ T (though in this particular case the anisotropy field $\mu_0 H_a \sim 8$ T is lower that $\mu_0 H_a = 11.5$ T reported in the literature for $L1_0$ FePt). However, there is as yet no satisfying way forward for how to apply this to volume magnets and what technological recommendations can be followed for the α improvement. Thus, the challenge is to understand what processing is required for any advanced material to obtain a hard magnet with $\alpha > 0.3$.

Some special technological measures can be used to (partially) overcome the Brown's paradox in small particles. One possible way is to omit the milling or rapidly quenching processes that are commonly used for decreasing the grain size. Instead, one can use a bottom-up approach to obtain particles or grains with their dimensions close to the single domain size but free from nanostructural imperfections and spatial variation of intrinsic parameters. Such obtained particles must be of very high concentrational homogeneity and be free from stresses,

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