



Summary

Permanent magnets constitute an essential part of our society, for motors and generators as well as for other electronic devices such as biomedical sensors and scanners. The ever growing technological demand has driven, since their discovery, the difficult task of improving the properties of these materials. Since the 1960s, a large portion of the world production of such magnets is based on rare earths like Sm and Nd. The situation has become even more complex due to the fact that almost all of the world mines of rare earths are located in China, which has dramatically increased the prices and supply risks. In this article, the challenge of the permanent magnets will be revised, and its potential solutions addressed.

1. Introduction

A permanent magnet is a material able to spontaneously create a magnetic field. This property has turned them into ubiquitous elements of our society given that, in an appropriate configuration, they permit converting magnetic into mechanical energy and vice versa. Motors and generators are so present in our everyday life that we almost take them from granted and don't notice them [1]. Besides, they play a key role in the development of biomedical detection techniques. Thus, permanent magnets are nowadays employed in a vast amount of sensors and transducers and their presence is essential in magnetic resonance equipment as well as in other clinical and bioengineering systems [2]. These examples come to show that any list of applications of permanent magnets will almost inevitably be incomplete, although the following piece of information will shed some light on their importance. in our day-to-day life: a refrigerator contains approximately 70 magnets and 400 of them are found inside a standard car. Their production is estimated at 500.000 tons per year worldwide, constituting a market worth 6000 million euros. Moreover, the sustainable development of our technology relies on them to a relatively large extent, as is supported by the fact that they are massively used in wind turbines and hybrid vehicles, which is believed to strongly contribute to the 7% per year increase in their market that is envisioned for the following years [3].

The scientific analysis of the properties of a permanent magnet starts by defining the energy product (BHmax) as the parameter determining the magnetic energy stored in a given magnet [4]. Larger energy products open the door to ever smaller and more efficient devices. Two intrinsic properties contribute to (BHmax): magnetization and coercivity. The first (magnetization) basically constitutes a measure of the intensity of the magnetic field generated by the magnet; and the second (coerci-

by Adrián Quesada



vity) corresponds to the magnetic field that is required to demagnetize the magnet after it has been under an applied magnetic field.

The value of coercivity provides information on how robust the magnet is and is associated with the anisotropy, which closely depends on the crystalline structure.Transition metals (Fe, Ni, Co) offer the highest saturation magnetization values, however their simple crystalline structures (cubic) imply small coercive fields [5]. On the other hand, magnetic materials with structures allowing higher anisotropy constants (for instance transition metal oxides) usually present lower magnetizations. Thus, the first challenge with which permanent magnets confront us is to be able to unify and maximize in a single material these two, a priori antagonistic, properties.



Figure 1. a) Magnetization curve vs applied field ("hysteresis loop") corresponding to a permanent magnet (ferromagnetic material). Saturation magnetization and coercivity values are highlighted. b) Corresponding magnetic induction vs applied field curve. The energy product (BHmax) is defined as the maximum area enclosed below the curve at the second quadrant.

2. Development.

Progress in permanent magnet technology has been fueled by the materials science challenge that began, in the dawn of the 20th century, the search for the highest energy product achievable. Figura 2 shows its values for different types of existing magnets [2]. tance to corrosion and oxidation, as well as their reduced costs, launched their use in society. Ferrites are spinels and perovskites whose structures accommodate large anisotropies. However, their magnetization values are rather modest. It is worth noting that ferrites are ferrimagnetic materials, in which two sublatticescoexist with opposing magnetic moments that partially cancel one another. Moreover, they are not extremely well suited to high tempera-



Figura 2. Evolution of the energy product value for different families of permanent magnets. (Modified from reference [2])

The first magnets mankind exploited were the carbon steels, presenting energy products around 15 kJ.m⁻³. In order to avoid the magnetic domain wall motion (which drastically reduces coercive field), they are commonly alloyed with tungsten and chromium, thus forming carbides. Although they possess high saturation magnetization, their tendency to demagnetize strongly limits their proliferation.



In the early 30s ferrites, Fe-based oxides, made their appearance, offering harder magnetic properties (i.e., larger coercive fields). Their energy products didn't substantially improve the steels, but their resisture applications due to their Curie temperatures (temperature at which the magnetic order is suppressed by thermal fluctuations) being in many cases not so far from room temperature. Nevertheless, they remain nowadays the most employed magnet in large scale applications.

Alnicos constitute the third group of permanent magnets. Born in the 30s, they also share with ferrites the high coercivity compared to steels. Their properties are associated with a biphasic nanostructure: Fe-Co needles embedded in a non-magnetic AlNi matrix. While occupying a relevant place in high temperature applications due to their higher Curie transition, their fragility and higher cost (compared to ferrites) restrict their impact. Another important limitation is triggered by their high electrical conductivity: they present a tendency to form eddy currents in the presence of alternating fields that destabilize the magnetization y yield energy losses.

In 1960, the world of permanent

magnets underwent a revolution with the burst in of rare- earth based magnets. Their structure merges, in a single material, transition metals that contribute to enlarge the magnetization, and rare-earths which, through strong spin-orbit coupling (interaction between the atomic magnetic moment with the crystal lattice), amplify their magnetic hardness. The energy products of such magnets reaches record values close to 400 kJ.m-3 for NdFeB, which is five times larger than for any other kind of magnet.



3. The current situation.

As a consequence of their impressive properties and the abundance of raw materials, the market was flooded with rare-earth based permanent magnets, which have come to represent over 50% of total magnet sales, limiting Alnicos and ferrite applications to low cost ones [3]. The situation, however, has dramatically changed in the last few years. On one hand, industrial needs of developing countries has increase the demand, but more importantly, the cost and supply risk of rare earths has skyrocketed due to the fact that China controls an estimated 97% of world rare-earth oxides production [3,6]. Figure 3 exposes the current situation.

Permanent magnets being rare-earths primary application [6], both the European Union and the United States have identified them as materials of great strategic importance (http:// www.ncpa.org/pub/ib112) and have thus initiated, through an increase in the number of research and development projects, the pursue of the new permanent magnets challenge: to be able to fabricate materials with competitive energy products avoiding to a maximum extent the use of rare-earths.

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Figure 3. a) Sales evolution in dollars since 1985 for the four main types of permanent magnets.*b)* Price evolution of Neodymium in the last two years. (Extracted from reference [6]).

4. Solutions.

The scientific community has undertaken such endeavor through different approaches, including reducing the amount of rare-earths in a magnet to even completely eliminate them from the materials. In general, one could say that in the last few years the complex task of increasing energy product values has been focused on trying to improve the intrinsic anisotropy, usually by including other anisotropy sources. Domain wall motion prevention, shape anisotropy or intergrain exchange-coupling are among the examples [7-9]. Efforts have rarely been productive in many cases. Nevertheless, based on an idea published more than twenty years ago, a promising approach stands out as a potential solution to the challenge: to exchange-couple, in a single biphasic material, a hard magnetic compound with soft high magnetization inclusions [10]. Under appropriate microstructural conditions, the resulting permanent magnet will possess improved magnetic properties in comparison to its individual building blocks. The idea relies on increasing the remnant magnetization while avoiding a dramatic decay in coercivity, thanks to the additional anisotropy induced by the exchange-coupling between the soft and hard grains. In order for the coupling to take place, the soft phase

dimensions must be limited to below a certain critical size [10]. These nanostructured exchange-coupled composite magnets are known as "exchange-spring magnets", and several works already report on considerable energy product improvements in such systems [11-13]. It is worth noting that the interfaces in biphasic systems are known to exhibit, in many different cases, different and novel properties with respect to the individual phases alone, especially in nanostructured materials [14-17].

However, a long and winding road lies ahead of materials scientists, the main challenges being associated with phase purity and homogeneity, microstructural control at the nanoscale, particle size control and crystalline alignment [6]. The constant advances in materials synthesis and processing have proved to be powerful allies in this regard [18]. In particular, a recent patent on dispersion processes in oxides presents an interesting opportunity in order to obtain high homogenization in biphasic compounds [19].

Recently, under the umbrella of the European Union's 7th Framework programme, a project entitled NANOPYME [20] has started, in which the Spanish Council for Scientific Research (CSIC) participates through the Institute of Ceramics and Glass Materials (ICV) and the Institute of Materials Sciences of Madrid (ICMM). The project focuses on improving the properties of ferrites by synthesizing and processing hybrid ferrite-metal composites in which the hard (ferrite) and soft phase (metal) will be exchange-coupled.

5. Conclusions

Due to an ever-increasing demand on more efficient, small and cost competitive devices, permanent magnets have constituted, since their discovery, a challenge to materials science. The constant search of increased energy products has encountered a new obstacle in its way with the emergence of the rare-earth crisis. Considerable efforts are being dedicated to obtain magnets with a reduced amount of these critical raw materials, in what could become a beautiful example of how basic research can have an extremely relevant, positive and immediate impact on our society.

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The author:

Adrián Quesada obtained his PhD in Physics at the Universidad Complutense de Madrid in 2009, during which he studied magnetic semiconductor materials. Immediately after, he initiated a postdoctoral scholarship at the Lawrence Berkeley National Laboratory in California, where he was trained in electron microscopies for imaging magnetic domains. Since late 2011, funded by a Juan de la Cierva postdoctoral contract, he develops his research activity within the Ce-

ramic for Smart System group, led by Professor José Francisco Fernández Lozano. Surface and i n t e r f a c e magnetic in-



teractions in ceramic oxides are the focus of his research efforts nowadays.



Institute of Ceramics and Glass





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Design: Carmen Díaz Dorado