Chapter 4

Conclusions

In this work, a novel route for the improvement of the permanent magnet properties (coercivity, squareness ratio and energy product), at room temperature, has been developed.

Usually, magnetic hardening is accomplished by means of particle size reduction (to achieve a monodomain state), search of materials with a large magnetic anisotropy or exchange coupling soft and hard magnetic phases, producing the so-called *spring magnets*. In the latter case, the resulting composites exhibit a higher saturation magnetization than the hard phase alone but, due to the coupling with the soft phase, the coercivity is unavoidably reduced. In the present work, it has been shown that exchange interactions between FM and AFM phases result actually in the opposite effect: an enhancement of coercivity and a decrease of the saturation magnetization (due to the AFM phase). However, the net effect after optimization of the FM:AFM ratio and milling conditions is, as in the case of *spring-magnets*, an enhancement of the energy product.

To induce FM-AFM coupling ball milling of FM (Co or $SmCo_5$) with AFM (e.g. NiO) powders has been carried out. The milling process generates an optimum microstructure, in which FM and AFM grains are soldered together and some agglomerates, with a large amount of FM-AFM interfaces, are developed. In the case of Co + NiO, the as-milled powders are subsequently heated and field cooled from above T_N (NiO). This is generally a necessary requirement to induce FM-AFM coupling. Unfortunately, when trying to extrapolate the same procedure to $SmCo_5$ + NiO all hard magnetic properties are lost during heat treatments. However, in the as-milled state a significant enhancement of H_C and M_R/M_S is observed in this case with respect to $SmCo_5$ ball milled alone. Moreover, when milling $SmCo_5$ with CoO (which develops in a similar microstructure to $SmCo_5$ + NiO), the maximum H_C and M_R/M_S are not found to be enhanced with respect to $SmCo_5$ alone. This indicates that some FM-AFM exchange interactions can be actually induced by simply ball milling hard-FM with AFM powders. Consequently, the field cooling process can be considered to take place during the milling, since due to the impacts between powders and balls the temperature can be locally raised to above T_N (NiO). Moreover, the large $SmCo_5$ magnetocrystalline anisotropy allows the FM grains to create considerable microscopic magnetic fields to the neighboring NiO particles during the cooling after each impact.

It is also noteworthy that an optimization of the FM:AFM ratio is required in order to observe, not only enhancements in H_C and M_R/M_S, but especially to reach an improvement of the energy product. This is because of the opposing effects of the AFM. On the one hand, the FM-AFM coupling brings about enhancements of H_C and M_R/M_S. However, on the other hand, due to the zero net magnetization of the AFM, the saturation magnetization of the composites is found to reduce proportionally to the AFM content. As a result, the largest coercivities are usually observed for different compositions than the maximum energy products. Therefore, tuning of the FM:AFM ratios is required depending on the desired final properties.

The novel aspects presented in our work can be briefly summarized as follows:

- Up to date, all fine-particle systems displaying FM-AFM exchange interactions effects have consisted of Fe, Co or Ni (or some related alloys) surrounded by AFM or ferrimagnetic phases directly derived from the *same* transition metal, such as Fe-FeO, Fe-FeS, Fe-Fe_2N, Co-CoO, Co-CoN, etc. In the present work it has been shown, for the first time, that combinations of FM and AFM fine particles of *different* transition metals can also exhibit exchange bias effects.

- The method used to induce the coupling has been seldom used in the past for this purpose since, in the majority of previous works, the FM-AFM particles have been prepared by chemical treatments (oxidation, sulphuration, nitrogenation, …) of the surfaces. In comparison to these techniques, ball milling is easier and cheaper to scale to industrial production.

- In the majority of fine-particle systems studied so far, the effects of the coupling (H_C enhancement and loop shift) are only observed at temperatures *below* room temperature, thus obviously limiting technological applications of these phenomena. On the contrary, in the present work, the enhancements of H_C, M_R/M_S and $(BH)_{Max}$ are observed at room temperature or even above (in the case of Co-NiO).

Finally, we consider that this work is likely to motivate future studies on the subject, from both theoretical and technological points of view. It is remarkable that, although the FM-AFM coupling effects were discovered about 50 years ago, the exact mechanisms governing the interactions have not been fully elucidated yet. Therefore, in this sense, new routes for fine particles and nanostructures processing, with better control of the FM-AFM interfaces, are needed in order to deepen on the fundamental aspects of the FM-AFM coupling in fine particles. Furthermore, the technique used in the present work to induce the coupling can be easily extended and applied to other systems, such as ferrites or NdFeB, which, in principle, are not expected to deteriorate when heating. In this sense, AFM not containing oxygen, such as metallic AFM, could also be good candidates to better scale the procedure presented in this work to other hard FM systems.

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Index

Annex 1

Historical Background and Theoretical Framework

1.1.- Antiferromagnetic and Ferromagnetic Materials (Soft and Hard)

All magnetic materials that exist in nature can be classified into different categories, depending on the type of coupling between their magnetic moments and their response to an applied magnetic field, H. Some of the categories of magnetic behavior are ferromagnetism, ferrimagnetism, antiferromagnetism, paramagnetism or diamagnetism. From a classical microscopic point of view, magnetic moments are associated either with the movement of electrons around the atomic nucleus (orbital angular momentum, which gives rise to the angular moment) or rotation of electrons around their own axis (spin angular momentum, which gives rise to the spin moment) [1-5].

We shall briefly recall some of the well known concepts used in magnetic materials which will be used in this Thesis. In *ferromagnetic* (FM) materials, the magnetic moments tend to align parallel to each other within certain regions (domains). This effect originates a local spontaneous magnetization. If a large enough magnetic field is applied, the magnetization of the different domains align with the magnetic field and the net magnetization reaches a constant value, i.e. the so-called *saturation magnetization*, M_S. Another characteristic of FM materials is that when the magnetic field is removed, some magnetic moments remain aligned in the direction of the previous magnetizing field, originating a *remanent magnetization*, M_R. The negative magnetic field required to reduce M back to zero is denoted as *coercivity*, H_C. A completely analogous behaviour is encountered when the material is saturated in negative magnetic fields. The whole curve obtained when plotting M vs. H is called *hysteresis loop* [1-5].

On the other hand, in the materials known as *antiferromagnetic* (AFM), the magnetic moments tend to align antiparallel to each other. In this case, the net spontaneous magnetization is essentially zero and they do not exhibit any hysteretic behaviour, i.e. when plotting M vs. H a linear graph is obtained. In *paramagnetic* (PM) materials, the magnetic moments do not interact with each other so that, in absence of a magnetic field, they are oriented at random. However, when a field is applied, to a certain extent, the moments tend to align to it. The typical magnetization curves of FM, AFM and PM materials are shown in figure 1.1.

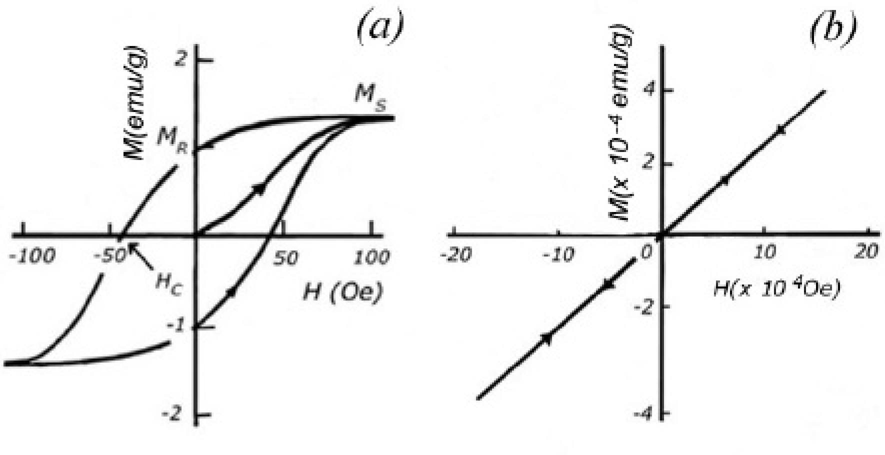

Figure 1.1: Typical magnetization curves for (a) a FM material and (b) a PM or AFM material.

When a FM or AFM material is heated, the thermal energy causes their magnetic moments to fluctuate. If the thermal energy becomes larger than the exchange energy, which keeps the moments parallel (or antiparallel) to each other, the materials tend to lose their magnetic ordering, becoming both of them PM. The temperature at which this transformation occurs is called Curie temperature, T_C (in FM materials) or Néel temperature, T_N (in AFM materials).

The large variety of ferromagnetic materials that exist in nature can be roughly classified into two categories: soft and hard ferromagnetic materials. Soft ferromagnetic materials are characterized by low values of H_C, typically lower than 10 Oe, and large values of M_S, usually higher than 100 emu/g. This results in a narrow hysteresis loop (see fig. 1.2 (a)). Some examples of soft FM materials are Fe, Ni, peramalloy or FeSi alloys. They are used in, for example, electromagnets or transformers cores. On the contrary, hard FM materials, which are also known as *permanent magnets*, are characterized by high values of H_C, typically larger than 350 Oe, and usually smaller values of M_S than soft magnetic materials, i.e. wide hysteresis loops (see fig. 1.2 (b)). Some examples of hard FM are $SmCo_5$, Al-Ni-Co alloys or $Nd_2Fe_{14}B$. Permanent magnets have lots of applications in industry: for example in the fabrication of motors and generators, in telecommunications (headphones, magnetic sensors or high-density magnetic recording media) or in synchrotrons (as systems for elemental particles guidance) [6].

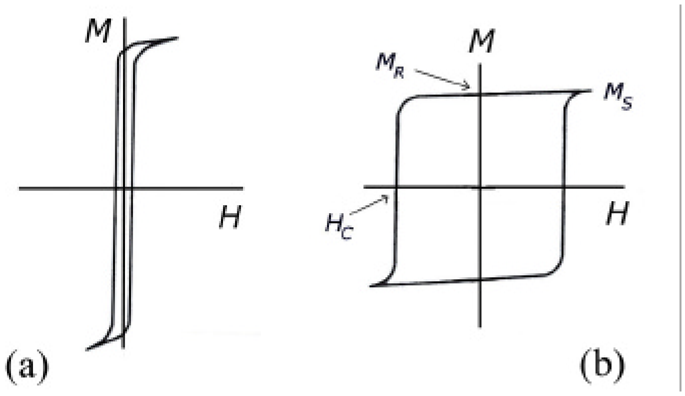

Figure 1.2: Hysteresis loops of (a) a soft magnetic material and (b) a hard magnetic material.

The figure of merit of a hard magnetic material is its *energy product,* which is denoted by $(BH)_{Max}$, and is roughly proportional to the total area enclosed by the hysteresis loop, when plotting the magnetic induction, B, i.e. $B = H + 4pM$, as a function of H. $(BH)_{Max}$ gives a good estimation of the quality of the hard magnetic material, since it is closely related to the overall energy that can be stored in the magnet. Obviously, magnets with higher $(BH)_{Max}$, would require smaller sizes to have the same efficiency.

In order to maximize $(BH)_{Max}$ it is necessary to have a large H_C, high values of M_S and a squareness ratio, M_R/M_S, as close to 1 as possible. The result of increasing H_C is a widening of the hysteresis loop, while increasing M_S results in a lengthening of the loop along the magnetization axis. Finally, an increase of M_R/M_S makes the loop more square. The net effect in all three cases is an enhancement of the energy product.

Figure 1.3 shows a historical evolution of the maximum energy product, $(BH)_{Max}$ that has been accomplished during the last century in different types of hard FM materials.

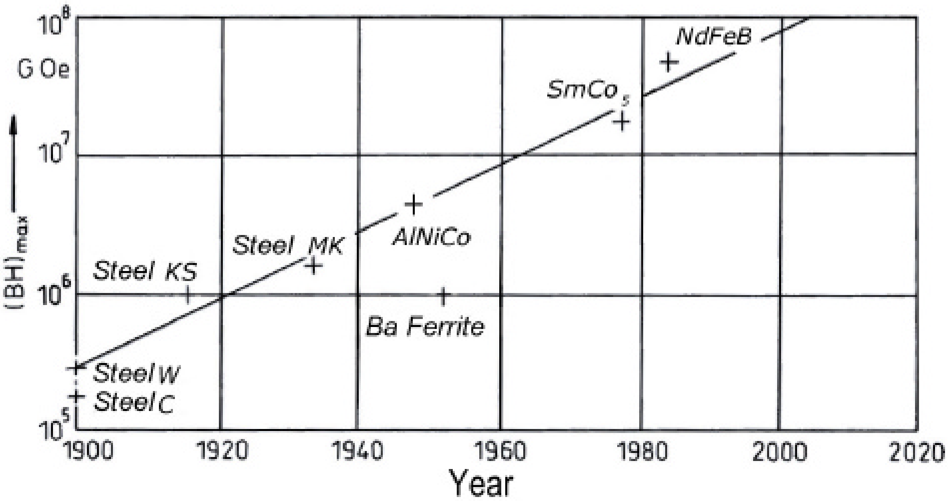

Figure 1.3: Chronological evolution of the energy product values, at room temperature, in permanent magnetic materials during the last century.

1.2.- Hard Magnetic Materials

1.2.1.- Ferromagnetic materials consisting of a single ferromagnetic phase

Traditionally, the most commonly used permanent magnetic materials have been hardened steels, Al-Ni-Co alloys and Ba or Sr ferrites. However, during the last 30 years, new materials have emerged, such as $SmCo_5$ or $Nd_2Fe_{14}B$, in which $(BH)_{Max}$ has been enhanced by one or two orders of magnitude. Hard magnetic materials might also be classified according to the phases present as single and multiphase materials. Except for AlNiCo (which actually consists of two phases, one ferromagnetic and another non-magnetic), all the above mentioned materials are essentially monophasic. Single-phase magnets, based on rare-earth intermetallics, were first developed more than 20 years ago, usually by crystallization from an amorphous precursor, either by ball milling or by melt spinning and subsequent heat treatments [7-11]. They can be also produced using chemical routes [12]. Typical values of H_C of around 15 kOe were obtained in $Nd_2Fe_{14}B$, for grain sizes around 80 nm.

There are several important factors, either intrinsic or extrinsic, that affect the macroscopic properties of single-phase ferromagnetic materials, such as magnetocrystalline anisotropy, crystallite size, particle alignment, shape anisotropy (or other types of induced anisotropies, e.g. stress anisotropy) or exchange interactions [3,6]. *Magnetic anisotropy* is the preference for the magnetization to lie in a particular direction in a material. Magnetic anisotropy can be either an intrinsic property of the material (e.g. magnetocrystalline anisotropy) or can be externally induced (e.g. shape anisotropy or stress anisotropy) [1-4]. The main factors that control the properties of single-phase permanent magnetic materials are briefly discussed in the following paragraphs.

(i) *Magnetocrystalline anisotropy* is closely related to the crystalline structure of the ferromagnetic material and is originated from the interaction between the spin part of the magnetic moment and the electronic orbital shape and orientation (spin-orbit coupling) as well as from the chemical bonding of the orbitals of a given atom with their local environment (crystalline electric field). If a magnetic field is applied to a single crystal ferromagnetic material, the field strength needed to saturate it is found to be smaller when applied along certain directions, which are called *easy-axis* directions. On the contrary, larger fields are required to saturate the material in other directions. These are called *hard-axis* directions. Similarly, after saturation, reduction of the field to zero leaves a larger remanent magnetization when the field has been applied along the easy axis, while for fields applied along the hard axis leaves a much smaller M_R. In addition, in absence of an external field, the magnetization prefers to lie along the easy directions. Materials with only one easy axis direction are designated as *uniaxial anisotropy* materials. Such is the case, for example, of hexagonal cobalt. However, cubic materials, as for example Fe or Ni, have more than one easy axis [2-4].

When a magnetic field is applied to a ferromagnetic material, a certain work is required in order to move the spins out of the easy axis direction. Therefore a certain energy, called anisotropy energy, is stored in the magnet when the magnetic field is applied in a direction different from the easy axis. The magnitude of the anisotropy energy depends on a certain number of anisotropy constants, which vary both with the crystalline structure of the material and temperature.

The role of the magnetic anisotropy on the macroscopic properties of hard magnetic materials can be estimated in a first approximation by the Stoner-Wohlfarth model [13], which assumes coherent rotation of the spins in monodomain, non-interacting particles, with uniaxial anisotropy. According to this model:

$$H_C = \frac{2K_u}{M_S} \tag{1.1}$$

where K_u is the uniaxial anisotropy constant and M_S is the saturation magnetization of the material. From equation (1.1) it is clear that a possible way to enhance $(BH)_{Max}$ is to look for materials with high values of K, so that their H_C becomes also large.

(ii) The control of the crystallite size, in the nanometric range, plays a very important role when trying to achieve large values of $(BH)_{Max}$ [6]. As can be seen in figure 1.4, for non-interacting FM particles, a maximum is obtained when the coercivity, H_C, is plotted as a function of the crystallite size, $<d>$. For large values of $<d>$, when the direction of H is reversed, the magnetization reverses, due to the formation and motion of domain walls. However, if the crystallite size is reduced to $<d>_{Cr}$, the formation of domain walls becomes energetically unfavourable, so that the particles are in a single-domain state. Consequently, the magnetization reverses by means of coherent rotation of spins, resulting in a higher value of H_C. If $<d>$ is further reduced to below $<d>_{Cr}$, thermal fluctuations cause some magnetic disorder in the FM and H_C is progressively reduced. Finally, if $<d>$ is low enough the system becomes superparamagnetic and no hysteresis is observed. This happens when the thermal energy, k_BT (k_B being the Boltzman constant) at a given temperature becomes of the order of the effective magnetic energy, KV, where K is the magnetic anisotropy of the FM and V is the volume of the FM particle. The properties of superparamagnetic particles have been studied by many authors [14,15].

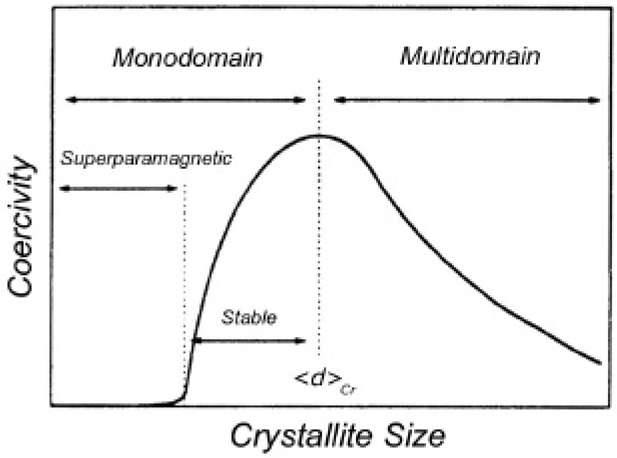

Figure 1.4: Dependence of the coercivity on the crystallite size, $<d>$, for a FM material [6].

(iii) The effect of particle alignment can be also examined in terms of the Stoner-Wohlfarth model [13]. This model predicts that for isolated non-interacting single-domain particles oriented at random the remanent magnetization takes the value M_R =

M_S / 2. This result is the consequence of the fact that, when the applied magnetic field is removed, the spins of each particle tend to align along the easy axis direction of the particle, leading to a value of M_R lower than M_S, given by:

$$M_R = M_S \langle \cos(\boldsymbol{q}) \rangle \tag{1.2}$$

where $\boldsymbol{q}$ is the angle between the easy axis and the applied magnetic field. In the particular case of random orientation one obtains, after averaging $<\cos(\boldsymbol{q})>$, that $M_R = M_S$ / 2. Therefore, in order to maximize M_R/M_S, a magnetic field is often used during the processing route to align the particles and thus make the magnet anisotropic, obtaining M_R very close to M_S.

(iv) As mentioned, apart from the magnetocrystalline anisotropy, other types of magnetic anisotropies (e.g. shape anisotropy or anisotropies due to mechanical tensions, plastic deformation or irradiation by electrons, X-rays, ions, etc.) can also play some role in tuning the macroscopic properties of hard magnets. Among them, shape anisotropy is one of the most important. This anisotropy has its origin in the different magnetostatic energies encountered when the particles are magnetized in different directions, due to their shape. For example, in Alnico-type permanent magnets, annealing and field cooling from above 900 K results in the formation of a microstructure consisting of elongated FM FeCo particles embedded in a non-magnetic NiAl matrix. In AlNiCo an optimum magnetic behaviour (e.g. highest H_C and M_R) is obtained when the acicular FeCo regions are of about 15 nm in diameter and 150 nm in length. Shape anisotropy is also the source of large coercivities in small particles of nanocrystalline Fe or CrO_2 [2-4].

(v) Furthermore, in actual magnets, adjacent particles usually interact with each other. The exchange interactions between different FM grains bring about a decrease of the coercivity, since cooperative reversal of M of several grains can be encountered. Therefore, a good method to increase H_C is to produce a microstructure consisting of isolated, non-interacting, FM embedded in a non-magnetic matrix. As already mentioned, this is the case of Alnico-type magnets. Moreover, in some rare-earth magnets an annealing process is used to segregate non-magnetic phases at the FM grain boundaries and thus reduce exchange interactions between them [6]. However, exchange interactions can also be beneficial in some cases, for example when hard and soft magnetic materials are coupled together, forming the so called *spring-magnets*.