The Magnetic and Structural Properties of the Alloys of Iron Produced by Mechanical Alloying

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Abstract

In this study, nanostructured powders, $(Fe_{65}Co_{35})_{100-x} Cr_x$ with (x=0, 10), were synthesized by a high-energy mechanical grinding process, usually used to obtain soft magnetic systems. For this purpose, the metal elements Fe, Co and Cr, of respective purities 99.9, 99.8 and 99.5% and of average size less than one hundred microns, were milled at different times, ranging from 1 hour to 36 hours. In a second step, the nanopowders obtained were characterized by several techniques, namely X-ray diffraction (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM) techniques. The analysis of the results obtained showed the complete formation of the $(Fe_{65}Co_{35})$ and $(Fe_{65}Co_{35})_{90}Cr_{10}$ phases from 12 hours of grinding. For $(Fe_{65}Co_{35})$, the remnant field Br and the saturation magnetization Ms have similar evolutions namely, a decrease between 8h and 24h, followed by an increase until the end of the grinding. In addition, the high values of Br and Hc suggest that this system is magnetically hard. The presence of chrome in the ternary $(Fe_{65}Co_{35})_{90}Cr_{10}$ amplifies the maximum value of Hc, while maintaining a similar behavior.

Keywords: Mechanical Alloying, Ternary Systems, VSM, Hysteresis Cycles

Introduction

Nowadays, nanostructured alloys are recognized as materials with a wide range of applications [1, 2]. Their unique properties, mainly due to the shape and size distribution of nanoparticles, the high ratio between their surface and volume, as well as the specificity of their surface, particularly chemical and electronic, have allowed the emergence of new physical (magnetic, optical, etc.) and chemical (surface reactivity, catalysis, etc.) characteristics, thus opening the way to innovative investigations in many fields of technology [3, 4]. On the other hand, the irrepressible tendency of the continuous miniaturization of multiple devices, in the form of nanostructured thin layers, generates crystallite sizes of these materials of the same order of magnitude as the typical magnetic domains existing within them, namely, 5-10 nm. This situation is likely to create nano-memories. However, when the size of nanoparticles decreases, thermal fluctuations have a negative effect on their behavior. For this reason, the ferromagnetic character of Fe nanoparticles, among other things, is transformed into super-paramagnetism and their overall magnetization becomes unstable. In general, the operation of associating one or more elements with the base matrix of the Iron is carried out in order to optimize a specific magnetic property according to the desired application. From the Slater-Pauling curve, it appears that the bimetallic nano-system (Fe, Co) has the highest magnetization compared to other systems and therefore the highest saturation magnetization is obtained with a concentration of 35% of cobalt [5-7]. Nevertheless, (Fe, Co) is also well known to be a soft ferromagnetic, having a low coercive field, a low hysteresis cycle, as well as a low eddy current loss and low remnant [8]. Based on this information, we have chosen to study the influence of the addition of chromium "Cr" to improve the overall behavior of binary nano-alloys $(Fe_{65}Co_{35})$, in particular its magneto crystalline anisotropy and anti-corrosive properties, in order to be used as magnetic recording materials. However, it is important to note that the quality, nature and values of all these properties depend on the preparation methods [9, 10]. Among them, high-energy grinding is a very powerful mechanosynthesis (MA) technique, easy to handle, inexpensive [11]. This method was therefore chosen to prepare our samples of $(Fe_{65}Co_{35})_{1-x} Cr_x$ (x = 0.10), this process is known to cause a gradual refinement of the internal structure of the powders up to the nanoscale, first generated by a plastic deformation followed by multiple fragmentation and welding of the crystallites, until the final formation of the desired solid solutions. The nano-materials obtained are of great interest for magnetic studies, since the reduction in grain size thus caused reaches that of the magnetic domains contained in these nano-systems, offering the possibility of minimizing the influence of magnetic walls [12, 13]. This work will focus first on the problems of synthesis of nano-alloys by mechanical grinding and in a second step; a structural, morphological and magnetic study and analysis will be carried out. The effect of chromium will be highlighted.

Experimental Details

Nano-alloys have been obtained by using high-energy mechanical grinding, the basic elements are iron, cobalt and chromium, their respective purities are 99.0%, 99.8% and 99.5%, their average

crystallite sizes do not exceed 100 microns. For our study, we used a Fritish Pulverisette 7 type planetary mill, consisting of two jars that rotate around a vertical axis (its own axis); in the opposite direction of the rotational movement animating the plate (disk), that carries it. The grinding operations are carried out in an argon atmosphere. Choosing a mass of 2.25 G for binary and ternary one, we were brought to prepare alloys whose nominal compositions are of the $(Fe_{65}Co_{35})$ type for the binary one and $(Fe_{65}Co_{35})_{90}Cr_{10}$ for the ternary one. It is resulted from it that the two types of alloys of the mixture differ by the percentage from each component (Fe, Co and Cr) with respect to the total weight of the sample and this, as follows:

$Fe_{65}Co_{35}$	$(Fe_{65}Co_{35})_{90}Cr_{10}$
Fe = 1.4625g Co=0.79g	Fe = 1.31625g Co=0.70875g Cr=0.225g

In addition, the sequence of the experiment is 30 minutes of grinding and then 15 minutes of rest. For a better characterization of our samples, we used several techniques to know; X-ray diffraction measurements are performed in a PANalytical X'PERT PRO MDP type diffract gram (PHILIPS), using the Kα copper line, corresponding to a wavelength equal to λ = 1.45405A, with a scanning at 2θ ranging from 6 to 130°. The morphology of the powders was observed in a scanning electron microscope, type ZEISS EVO MA25, equipped with an energy dispersive X-ray (EDX) analyzer. The magnetic properties of the nano-alloys were measured by a vibrating sample magnetometer (VSM) at room temperature, type Micro sense of the EV9 model.

Results and discussion
Structural study
Figure 1: Shows the diffraction patterns of binary $(Fe_{65}CO_{35})$ and ternary $(Fe_{65}Co_{35})_{90}Cr_{10}$ as a function of grinding time.
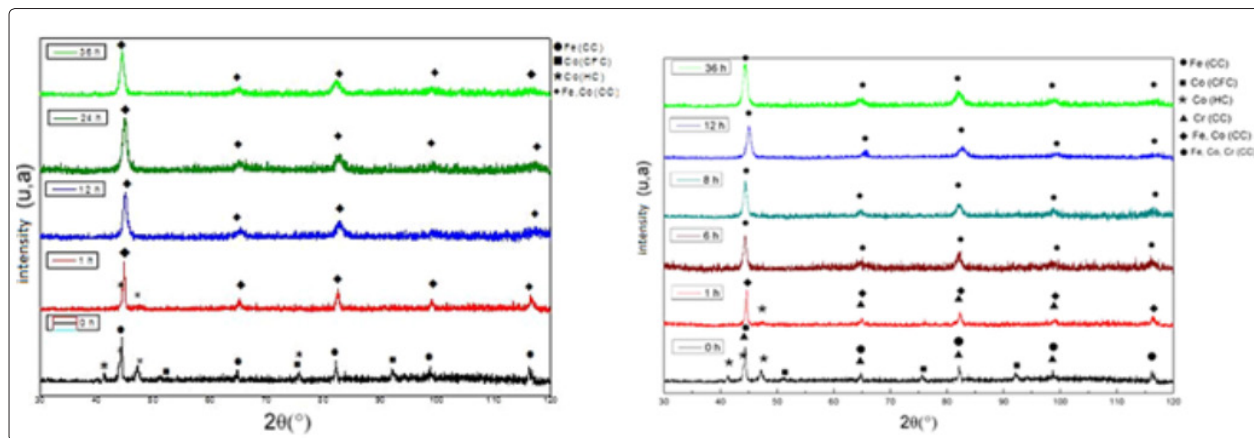

Figure 1.a: Nanopower diffractogram $(Fe_{65}Co_{35})$ **Figure 1.b:** Nanopower diffractogram $(Fe_{65}Co_{35})_{90}Cr_{10}$

The use of the ICDD file gradually revealed characteristic peaks first, centered cubic iron (CC), compact hexagonal cobalt (HC), centered cubic face cobalt (CFC), centered cubic chromium (CC) and centered cubic binary (Iron, Cobalt) as well as ternary (Iron, Cobalt, Chromium) centered cubic (CC) on the X-ray diffraction patterns of the processed samples. This behavior is attributed to the respective and inverse evolutions of crystallite size and micro deformation. This can be explained by physical phenomena that occur at the grinding method at different stages. Indeed, during grinding, the emergence of a large number of defects leads to metal diffusion processes. Generally, when the grinding time increases, the iron peaks gradually lose their intensity but gain in width, suggesting that Cobalt atoms (CFC) disappear completely in the binary after one hour of grinding when they do not even exist in the ternary. Only chromium and the binary phase (Iron, Cobalt) remain [14, 15]. On the other hand, for the same time of grinding, the Cobalt atoms in their compact hexagonal phase (HC) remain present [16]. Furthermore, the CFC phase of Cobalt is metastable at room temperature, becomes unstable, and becomes a HCP phase; it disappears after 8 hours of grinding for both alloys [15-17]. These characteristics have already been observed and attributed to allotropic transformation of CFC Cobalt to HCP [18, 19]. These results are comparable to those obtained by other authors [20, 21]. In addition, some analyses of the literature suggest that the peaks of the diffraction pattern evolve mainly due to the existence of a relatively high local temperature during grinding, grain refining processes, and the occurrence of heterogeneous stresses at the atomic scale [22]. In addition, the mean crystallite size and micro deformation of the lattice were determined using the Williamson-Hall method, with the analysis of XRD profiles described by Langford [2, 23].
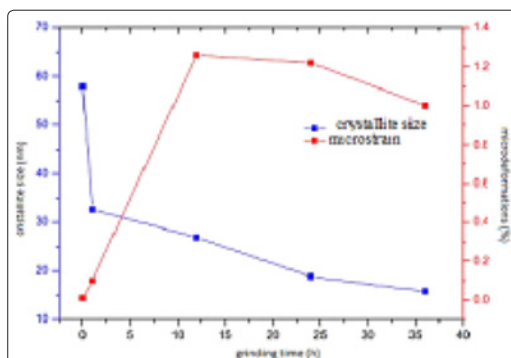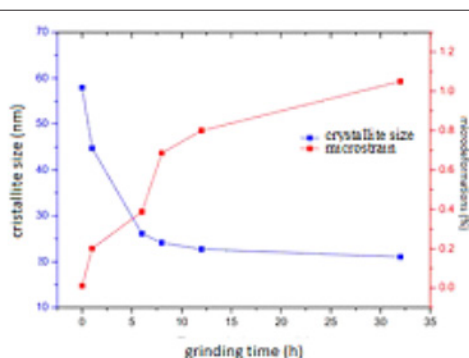
Figure 2: Variations size of crystallises ($Fe_{65}Co_{35}$)

Figure 3: Variations size of crystallises ($Fe_{65}Co_{35})_{90}Cr_{10}$)

The Williams-Hall equation is expressed as follows:

$$Bs = \frac{\cos k\lambda}{d + 2\varepsilon}\sin\theta$$

where Bs is the midheight width of the diffraction peak,
K is the crystallite constant,
d the mean size of crystallites,
λ the wavelength of X-rays,
ε the internal micro constraints
and θ Bragg angle.

$$Bs^2 = Bm^2 - Bc^2$$

With Bc and Bm, the mid-height widths of peak maxima, the first experimental and the second estimated for standard nano-powders used for calibration [24]. The inverse behavior of the evolution of characteristic curves of crystal size and network strain could be explained by Cantor [25]. During the first5 part of the crushing, average stresses at nano-powder levels increase due to the high density of existing dislocations. When a critical value is reached, the crystals reorganize into sub-grains, randomly oriented and forming gaskets of low disorientation [26, 27]. The final crystal size is reached when the movement of the dislocation network is blocked for different reasons, such as the existence of screens and precipitations [28]. The addition of chromium increases the strength and hardness of the material, On the other hand, the size of the crystallites of the ternary is smaller than that of the binary: 21.08 nm for the binary while for the ternary, it is 15.80 nm. The value of the mesh parameter is obtained by extrapolating the value calculated for each brag angle associated with the value obtained by the formula.

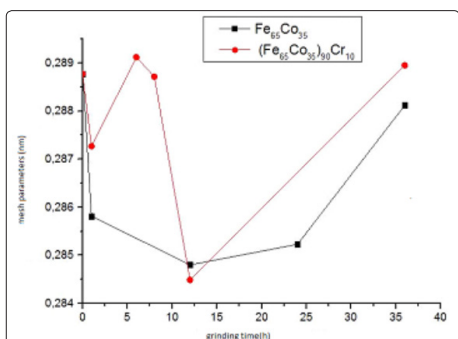Figure 4 shows the variations in the mesh parameter as a function of the grinding time of the two alloys.

Figure 4: Varitation of the mesh parameter

Morphology
Figures 5a and 5b characterize two SEM images, relating to two grinding times, 24 and 36 h, characteristic of the morphology of the nano-powders ($Fe_{65}Co_{35})_{100-x}Cr_x$ (x = 0.10).
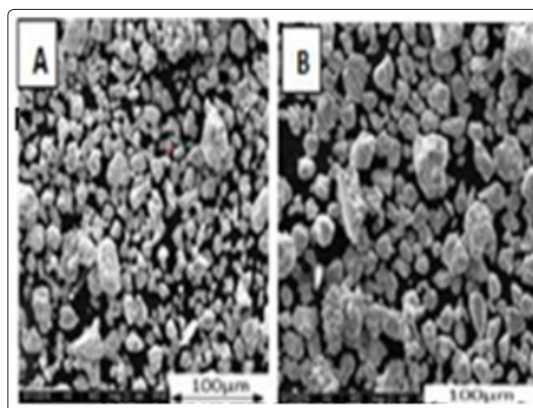

Figure 5.a: Morphology of nanopowder $Fe_{65}Co_{35}$

A) after 24h and B) 36h grinding
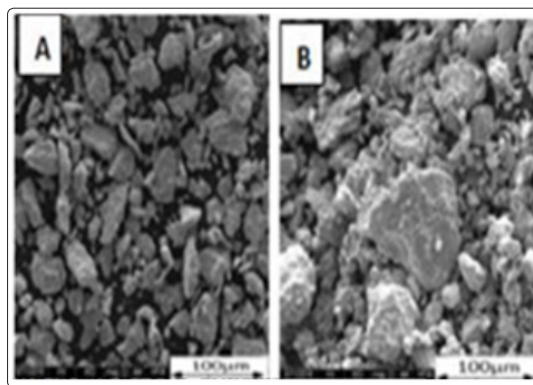

Figure 5.b: Morphology of nanopowder $Fe_{65}Co_{35})_{90}Cr_{10}$

A) after 24h and B) 36h grinding

Qualitative observations of these photos show the existence of crystallites of different sizes and shapes, the classic and expected consequences of the multiple stages undergone by our nanopowders, as reported in the literature, that is, flattening, welding and fracture. These images are also closer to the X-ray diffraction results obtained, as well as their analysis. For the binary, it seems that the crystallites

change shape, passing from an obloid to a sphere; similarly, the average size of these same crystallites seems to decrease, unlike the case of the ternary, which does not evolve in the same direction. The available images tend to suggest that the average size of crystallites is decreasing, but with a possible greater precipitation of elements, separated or not, of which Cr could be the driving force of the process. Furthermore, mapping the distribution of Fe, Co and Cr obtained in ($Fe_{65}Co_{35}$) and ($Fe_{65}Co_{35}$)$_{90}Cr_{10}$ is shown in (Figure 6).
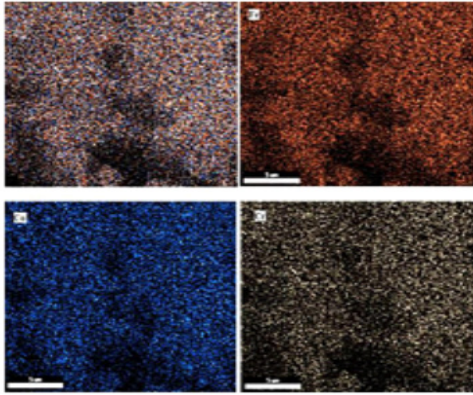

Figure 6.a: Mapping of Fe and Co distribution $Fe_{65}Co_{35}$ milled for 36h

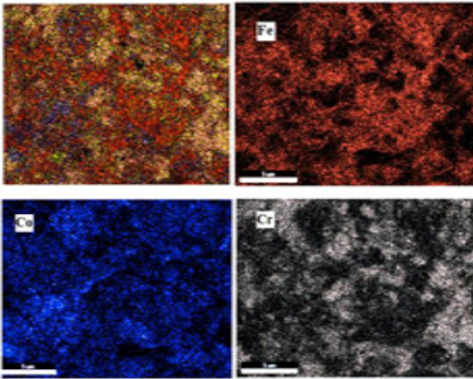**Figure 6.b:** Mapping of Fe and Co distribution ($Fe_{65}Co_{35}$)$_{90}Cr_{10}$ milled for 36h

Magnetic properties

In general, some magnetic properties can be improved when the crystallite size is reduced to the nanoscale while the presence of stresses and defects introduced by mechanical alloying impairs the magnetic property; the overall magnetic property is affected by a competition between decrease in crystallite size and increase in strain [29, 30]. The coercivity is often seen as an important parameter if low losses are to be achieved and affected by most types of defects. These included dislocations, grain boundaries, precipitates and non-magnetic particle distribution. This magnetic property is an important factor for identification of soft magnetic behavior. The high amount of the coercivity is due to internal micro-strain, impurities, pores and defects, which are introduced during milling. To reduce the coercivity, the values of all these factors should be low [31]. (Figure 7 and 8) show the classical hysteresis curves obtained for two nano-structured $Fe_{65}Co_{35}$ and ($Fe_{65}Co_{35}$)$_{90}Cr_{10}$, for different milling times.
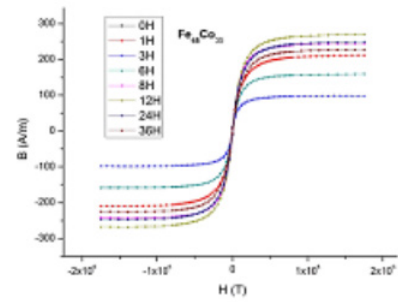

Figure 7: Hysteresis ($Fe_{65}Co_{35}$)

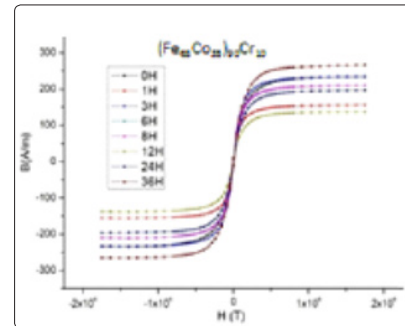**Figure 8:** Hysteresis ($Fe_{65}Co_{35}$)$_{90}Cr_{35}$

Three parameters can be deduced from theses curves, the saturation magnetization, Ms the coercively field, Hc, and the remanent field, Br, in occurrence, as it happens. Their variations with milling time, for the two nano-strucured systems, are represented in (Figure 9, 10 and 11).
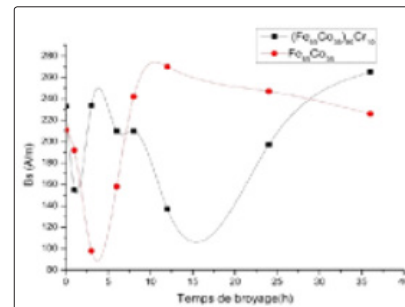

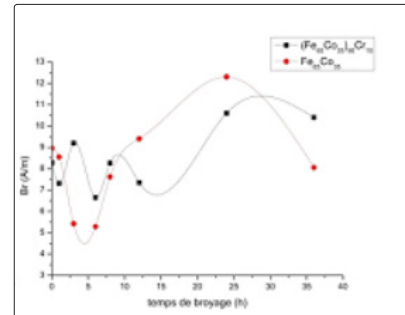**Figure 9:** Varitation of saturation magnetization

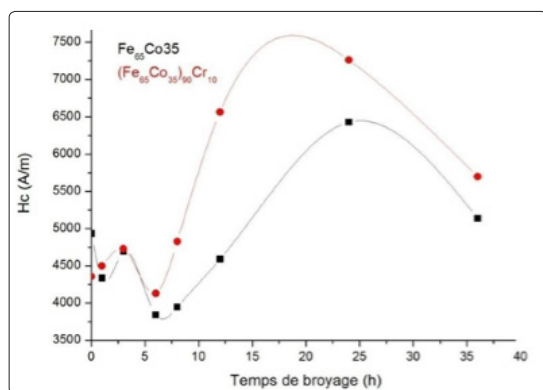**Figure 10:** Evolution of coercively field Br

Figure 11: Hc Coercively Variations

Hc values vary from 3900 to 6300 A/m for $Fe_{65}Co_{35}$ and from 4000 to 7200 A/m for $(Fe_{65}Co_{35})_{90}Cr_{10}$, indicating that these latter are globally superiors to the former. The addition of Cr seems to strengthen Hc. Here again, For t ≥ 12h milling, the binary and ternary nanosystem behaviors are similar, with a maximum around 24h.More precisely, the magnetic properties of a nanostructured system are the result of a compromise between two phenomena, during mechanical alloying process; the diminution of crystallites sizes to the nano-scale enhanced them, while the plastic deformation that appears, creates stresses, induces defects and finally, causes their partial deterioration Br and Bs generally admit the same global shape. Moreover, they have high values, suggesting that the two nano-structured alloys are associated to high magnetic energies, thereby conclude that they are magnetically hard. Nowadays, it is largely admitted that Hc, which is sensitive to nanostructure, is proportional to d6, if the crystallite sizes, d, are of the same order than the magnetic domain, typically d ≤ 20mn, and inversely proportional to micrometric d [32].

Conclusion

Durant le broyage, les pics caractéristiques des DRX ont progressivement diminué en intensité mais se sont élargis en même temps; ceci est le résultat d'une compétition entre un processus d'affinement des cristallites et l'existence de microdéformations internes, conséquemment à des phénomènes de diffusion atomique. In this study, nanostructured powders, during grinding, the characteristic peaks of DRX gradually decreased in intensity but widened at the same time; this is the result of a competition between a refinement process of crystallites and the existence of internal microstrain, as a consequence of atomic diffusion phenomena. Simultaneous and respective variations in the size of crystallites, "d" and "ε" micro deformations and the mesh parameter "a" are derived from these mechanisms. It should be noted that chromium slightly slows down the evolution of "a" and "d" respectively, unlike "ε". The use of the ICDD file gradually revealed characteristic peaks first, centered cubic iron (CC), compact hexagonal cobalt (HC), centered cubic face cobalt (CFC), centered cubic chromium (CC) and centered cubic binary (Iron, Cobalt) as well as ternary (Iron, Cobalt, Chromium) centered cubic (CC) on the X-ray diffraction patterns of the processed samples. Cobalt atoms evolve from a compact hexagonal-centered cubic structure and disappear after 1 h of grinding. After 8 hours of grinding, cobalt under its new form disappears in both nano-systems, while the atoms of the center-facing cubic chromium disappear in the ternary composition after 6 hours of grinding. Processes of diffusion and precipitation of various atomic entities within the iron subnet, as well as the formation of binary and

ternary solutions, centered cubic, could explain these phenomena. The binary alloy ($Fe_{65}Co_{35}$) is formed from 12 hours of grinding and then stabilized, probably due to the disappearance of cobalt. In addition, Br and Ms have similar behaviors, with high Br values and Ms. as Hc are also very high, it appears that ($Fe_{65}Co_{35}$) admits significant magnetic energy and is therefore magnetically hard. For ternary ($Fe_{65}Co_{35})_{90}Cr_{10}$, a form of instability was observed up to 12h of grinding, particularly in the Br curves, thus delaying the start of formation of these nano-alloys. Finally, Hc variations are generally comparable for binary and ternary, although higher for ternary.

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