

# Influence of oxide additions in Cu-Co-Fe composite powders obtained by mechanical alloying

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**Keywords:** Composite powder, mechanical milling, Cu-Fe-Co, ceramic reinforcement, magnetic properties, catalysts, microelectronics.

**Abstract.** Nanocrystalline composite powders were prepared by mechanical alloying of pure Cu, Fe and Co as metallic major part and Al<sub>2</sub>O<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> as ceramic reinforcement in a high-energy ball mill. Alloys of the copper-iron-cobalt system are promising for the development of new materials and applications. Cu-Fe-Co is used in different applications depending on the properties required. These can be related for example to toughness when used as rock cutting tool, to magnetic and electric properties for microelectronics or to chemical behaviour when used as catalysts in bioalcohol production industry. The objective of the present study is to contribute to understanding how and to which amount the ceramic reinforcement affects the properties for which this Cu-Fe-Co system is used as well as to envisage other less frequently uses for the composite powders. Structural and magnetic transformations occurring in the material during milling were studied with the use of X-ray diffraction, scanning quantum induction device (SQUID) and magnetic force microscopy (MFM). In mechanical alloying the transformations depend upon milling time. The results showed that milling the elemental powders of Cu-Fe-Co in the mass proportion of 50:25:25 respectively for times up to 10h leads to the progressive dissolution of Fe and Co atoms into FCC Cu and the final product of the MA process was the nanocrystalline Cu containing Fe and Co with a mean crystallite size (from coherent crystal size determination by diffraction) of 20 nm aprox. When ceramic particles are milled together with the metals (at proportions of the oxides between 1-10%) this mechanism is retarded. On the other hand, the lowest mean crystallite size is reached without ceramic particles in the milling process. However the composite powder produced in all the cases stabilized similar lowest crystallite size between 45-50 nm. Mechanically alloyed metallic-ceramic composite powder showed lower saturation magnetization than the metallic system but enhanced coercive field (significantly for hematite reinforcement). All the studied systems are intermediate ferromagnetics ( $H_c \approx 104$  A/m). Milling time significantly affects the structure, composition and properties for both metallic and composite systems.

## Introduction

Mechanical alloying is a well-known powerful method for the synthesis of nanocrystalline powders [1-3]. It involves repeated fracturing and rewelding of particles, leading to size reduction and particle shape changes. In addition, mechanical alloying techniques (MA) are widely used for the production of soft magnetic alloys.

Copper and copper alloys are one of the major groups of commercial materials used in engineering, due to their excellent properties, although for some applications these materials need to be strengthened by alloying or by introducing different insoluble elements or compounds to achieve particle strengthening and form a metal composite material (MCM). Cu-Fe-Co alloys have useful magnetic properties; this is the reason for their potential to be used in very different fields such as microelectronic parts and circuit systems or applications that make use of their giant magnetoresistance effect (GMR) [4]. The limited solubility of iron and cobalt in copper allows the matrix to retain high conductivity. As a result, this composite may be useful in applications in which high conductivity and high strength are required [5]. Another field in which this metallic

combination is used is for adsorption, activation and conversion of CO<sub>2</sub> to CO. These processes carried out on transition metal (Fe, Co, Ni and Fe) surface catalysts supported by Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and others have been of interest for many years. A strong correlation was discovered between intrinsic activity of heterogeneous and homogeneous CO<sub>2</sub> catalysis as a function of 3d metal [6]. On the other hand, there is wide agreement that mass production of fuel cells for transportation and domestic uses will lead to scarcity and cost-increase of Pt-based catalysts. It is, therefore, reasonable to research focused on Pt replacement by more abundant transition metals such as Fe, Co, Cu, Mn, Mo for multielectron transfer catalysis [7]. In the case of oxygen reduction it is well known that using a Fe-Cu center the catalytic problem is solved in nature [8].

One of the production methods for these alloys starts with the powder of the three metals, as the binary systems Fe-Cu and Co-Cu show immiscibility a metastable solid solution of the ternary Cu-Fe-Co can be produced by mechanical alloying. The metallic combination may need different ceramic support depending on the application for this reason the elementary metals are milled together with the ceramic in order to study the final composite powder behaviour. Magnetic properties depend on crystallite size, lattice strain and element shape. All of these factors determine the hysteresis loop and consequently affect magnetic parameters such as saturation magnetization, M<sub>s</sub>, coercivity, H<sub>c</sub>, and remanence, M<sub>r</sub>. Magnetic force microscopy (MFM) has become one of the most widespread tools for studying the magnetic domains of ferromagnetic samples [9]. Some authors [10-12] report MFM investigations of ribbons of melt-spun nanomaterials and electrodeposited layers and films, but the use of MFM in the study of mechanical alloyed nanopowders has not been widely reported yet [9].

The present study is focused on the effect of alumina, hematite and silica additions to Cu-Fe-Co at different percentages of the ceramic material to evaluate how the microstructure, the coherent diffraction domains size and the magnetic properties are affected. The microstructure, magnetic properties and magnetic domains variation of all samples were investigated by X-ray diffraction (XRD), SQUID Magnetometer and Magnetic Force Microscopy, respectively.

## Material and methods

Element powders of Cu, Fe and Co (mass ratio 50:25:25) were used as the starting materials, with particle size of 15-20 μm, 4-6 μm, and 1-2 μm, respectively. The ceramic material selected to be added in 1, 3 and 10 wt% to the metallic system was α-Al<sub>2</sub>O<sub>3</sub>, α-Fe<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> (α-quartz) with a particle size of around 1 μm. Four sets of samples with the same compositional ratio were processed by high-energy ball milling in a Fritsch planetary monomill Pulverisette P6 with steel balls and vials. This equipment works at the specific impact energy of the balls of 6-7 kJ/s<sup>-1</sup>kg<sup>-1</sup> [9]. The experimental conditions of the mechanical alloying process (MA) were the following: disc rotation speed of 300 rpm (Ω) and vial rotation speed of 546 rpm (ω) and the ball-to-powder weight ratio was 16:1 in all experiments. The process was performed under Ar atmosphere to prevent oxidation.

**Characterization techniques.** The microstructural characterization of samples was carried out by X-Ray powder diffraction (XRD) performed in the classical *Bragg-Brentano PANalytical X'Pert PRO MPD θ/θ* geometry, on a wide angle diffractometer, using Cu Kα radiation (λ=1.5418Å). Scans were collected in small angular steps of 2θ=0.017°. The phases formed during processing were identified by X'Pert HighScore Plus software. FullProf\_Suite standard software was used as a graphic tool to carry out the diffraction profile fitting peak-to-peak to obtain the full width at half-maximum (FWHM) of each sample. The adjustment was performed using the pseudo-Voigt function. The XRD microstructural analysis was based on the fact that the diffraction profiles of a polycrystalline solid have a shape determined by the imperfections of the material, among other factors. Since the mechanical alloying process causes severe plastic deformation which introduces many defects and stresses in the alloyed system, in this type of samples, the main factors that contribute to broadening are the instrumental broadening profile and the intrinsic broadening profile (included crystallite size and microstrain). In this study, the deconvolution hypotheses in all the

samples were analysed to determine which was best for representing the intrinsic broadening. The crystallite size ( $D$ ) and microstrain determination were carried out using the copper diffraction peaks (as iron and cobalt atoms rapidly diffused within the lattice of Cu and disappeared as diffraction peaks during MA).

In all the samples, the variation of magnetic parameters with processing time and ceramic additions, was measured at 5K and 300K for some compositions in a maximum field of 50 kOe using a SQUID MPMS-XL superconducting quantum interference device from Quantum Design. The magnetic domain structure was imaged using magnetic force microscopy (MFM) (AFM Dimension 3100, Veeco).

## Results and Discussion

**Microstructural transformations associated with mechanical alloying.** The structural evolution and phase formation of the as-milled powders was examined by microscopy and also by recording the X-ray diffraction (XRD) patterns as a function of milling time and ceramic additions. As an example, Fig. 1 shows the different morphology of the powder, Cu50Fe25Co25 and Cu50Fe25Co25+3% Al<sub>2</sub>O<sub>3</sub> (in mass), after 10h milling: ductile-ductile mechanism and ductile-brittle mechanism respectively.

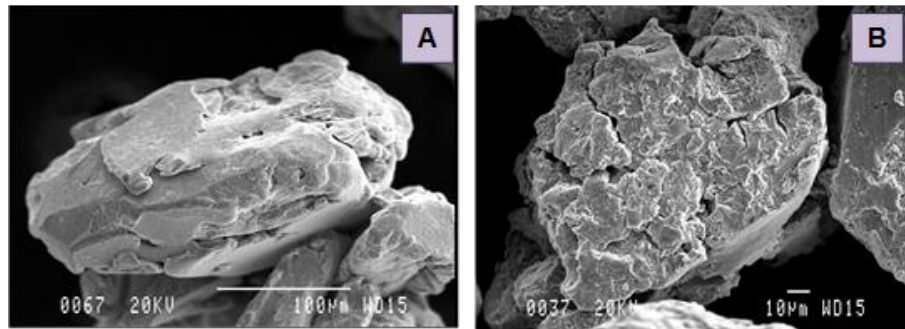


Figure 1. SEM micrographs of powder after 10h milling, (a) metallic system, (b) composite powder (metals + 3% alumina).

Ball milling influences the microstructure of the systems with which it interacts. In the present study it promotes the mechanical alloying of the elementary metals. During milling cobalt first and iron after enter into the copper until they progressively lower their value as elementary metals. Deconvolution of X-ray diffraction peaks is necessary in order to interpret the microstructural changes that can be reached during the milling process. From this, the final formation of some Co-Fe inside the Cu is suggested.

The evaluation of the XRD patterns as a function of milling time let us conclude that the addition of ceramic hindered the metallic alloying. This effect is directly related to the amount of oxides added, for instance lower addition does not influences the process but 3% and 10% significantly controlled the mechanical alloying process. As can be seen in Fig. 2, at the same time of milling composite powders evidence the presence of elementary Fe whereas metallic powder needs deconvolution for a more precise identification.

Fig. 3 shows the deconvolution of the diffraction peaks at  $2\theta = 41.6- 45.2^\circ$  for metallic (milled for 3h and 10h) and composite CuFeCo-10% Al<sub>2</sub>O<sub>3</sub> powders MA for 10h. Four functions with centre angles of 43.17, 43.46, 44.05 and 44.50 respectively, are required to describe the two large peaks of metallic powder milled for 3h while only one peak is needed for longer processing time. Deconvolution suggests that at 3h powder contains Cu, Co, Fe and a new phase in which Cu solubilizes Co and Fe; at 8h milling this latter phase is majoritary and only small amounts of elementary Co and Fe remain; beyond 10h of processing time, deconvolution fits the large peak for Cu(Co,Fe) together with remnant Fe as small broadened peak. The presence of small amounts of Fe

was also found and detected with Mossbauer analyses by Laslouni et al [13] even for longer processing time.

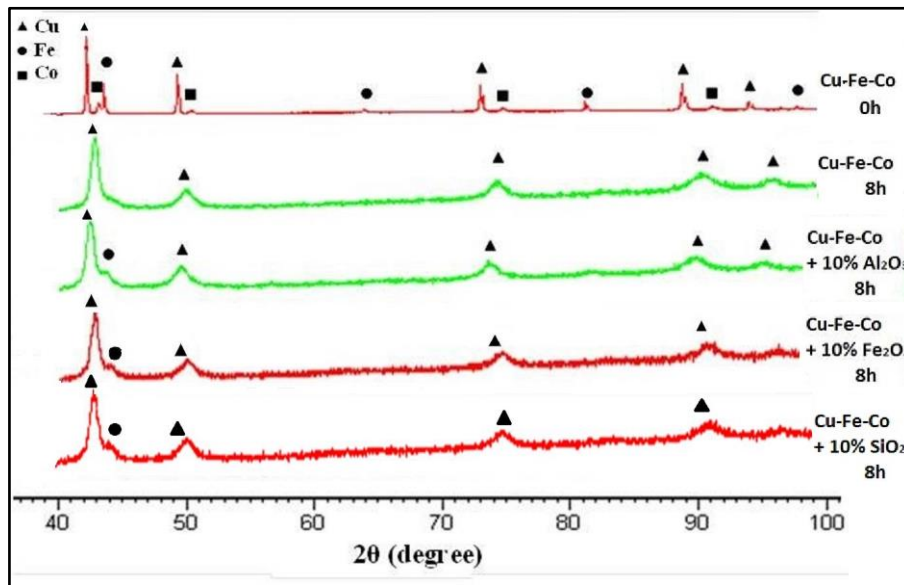


Figure 2. Comparison of X-ray diffraction patterns of mechanically alloyed Cu-Fe-Co composite powders. From top to bottom: Cu-Fe-Co metallic powder (unmilled), Cu-Fe-Co 8h milling, CuFeCo+10% Al<sub>2</sub>O<sub>3</sub> composite powder 8h milling, CuFeCo+10% Fe<sub>2</sub>O<sub>3</sub> composite powder 8h milling and CuFeCo+10% SiO<sub>2</sub> composite powder 8h milling.

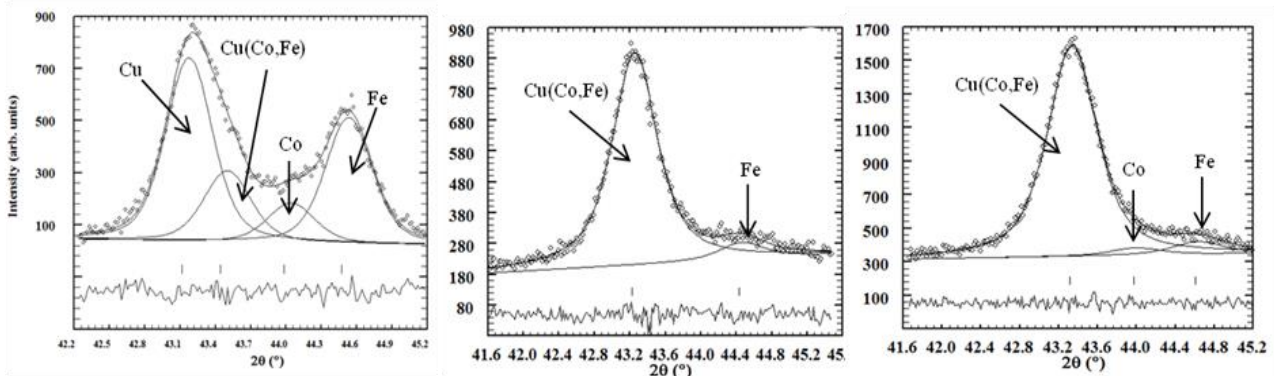


Figure 3. Observed (points) and deconvoluted (solid line) X-ray diffraction pattern of (111) peak for 3 h (left) and 10 h (center) of metallic powder and 10 h of 10% Al<sub>2</sub>O<sub>3</sub> composite powder (right). Positions of the Bragg reflections are represented by vertical bars. The observed-calculated difference pattern is depicted at the bottom of each figure. (For metallic powder milled 3h sample:  $R_p=4.6\%$ ;  $R_{wp}=7.7\%$ ;  $R_{exp}=5.3\%$ ; for metallic powder milled 10h sample:  $R_p=3.6\%$ ;  $R_{wp}=4.5\%$ ;  $R_{exp}=5.1\%$ ; for composite powder milled 10h sample:  $R_p=2.7\%$ ;  $R_{wp}=3.6\%$ ;  $R_{exp}=3.9\%$ ).

At 10h of processing time, deconvolution fits the large peak for Cu(Co,Fe) together with remnant Co and Fe as small broadened peaks. Peak function centre angle of  $2\theta = 43.32^\circ$  and  $43.31^\circ$  is considered to belong to Cu(Co,Fe) phase. As can be seen when Al<sub>2</sub>O<sub>3</sub> is present the diffusion of Fe and Co is detected at longer milling time, between 8h and 10h. This can be explained by the fact that alumina acts as to block the diffusion of iron atoms. Hence if ceramic particles are introduced in the MA process mass transfer is hindered and the kinetics to produce any kind of solid solution wane as it is found experimentally in the present study.

The crystal size (D) of all samples was obtained and was dependent on the milling time: two distinct behaviours can be determined: one followed by the metallic powders and another shown by all the composite powders. The evolution of the crystallite size of the metallic series monotonically decreases with increasing milling time, in contrast to all the composite series. At 3 hours milling the

crystallite size for metallic and composite powders was around 80 nm and 50 nm, respectively. This disagreement may be due to the addition of the hard and brittle ceramic materials to the metallic system, which causes a fracture mechanism to become dominant and induces a rapid decrease of  $D$ . In contrast, in the metallic system there was a more equitable balance between welding and fracture, which produced a more gradual decrease in crystal size. At ten hours of processing, all the samples had a very similar crystal size of approximately 40 nm. Therefore, this was a critical point and coincided with the time required to produce the possible solid solutions of Cu(Fe,Co). After 10h milling, the metallic system acquired a stationary value of crystal size. In contrast, the rest of the compositional series had an increase in  $D$ . There was no significant difference in crystal size variation between the three composite series, showing that a rise in the percentage of ceramic in the metallic system promotes a slight decrease in  $D$  as the brittleness of the system is increased.

Magnetic measurements and MFM images showed that the plastic deformation introduced by mechanical alloying leads to a microstrained structure affecting the total energy of the magnetized samples. All samples showed ferromagnetic behaviour as all of them produced hysteresis loops and saturated when a magnetic field of 50 KOe was applied (Fig. 4). Coercivity was dependent on the crystallite size for all the compositional series under study ( $H_c \approx 104$  A/m). The complex magnetic patterns of the composite powders made difficult the magnetic force microscopy particularly alumina and silica additions for which the system does not show clear specific morphology of the magnetic domains and poor magnetic contrast compared to the metallic system.

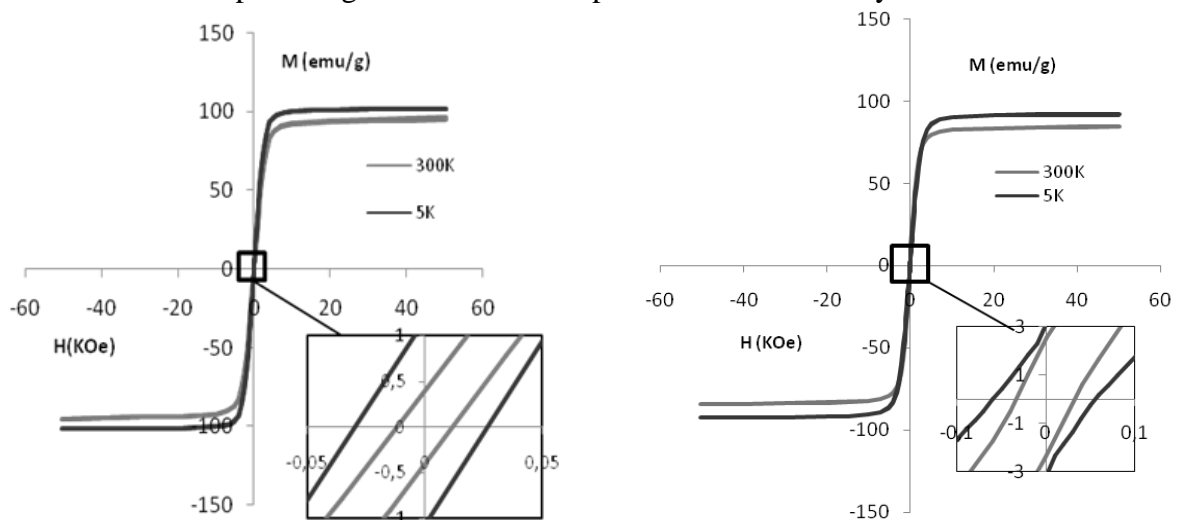


Figure 4. Hysteresis loop at 5K and 300K for the metallic powder (left) and composite sample with 10% of alumina (right) milled for 16 hours.

Finally, the sintering ability of each system was also studied. The present results showed that the alumina and silica particles were rather difficult for sintering the composite whereas hematite was suitable for sintering at temperatures below 550°C.

## Summary

The addition of ceramic particles ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>) in the Cu-Fe-Co metallic powder tends to decrease the crystal size measured by XRD down to 45-50 nm for the same milling time whereas in the absence of oxides, the crystal size reached 20-25 nm at the same milling time.

When the milling time was increased, the saturation magnetization became higher but the coercivity decreased. Consequently, as the processing time increased the material became more soft ferromagnetic. When ceramic particles are added to the Cu-Fe-Co system, the magnetic domains did not show specific morphology as the particles seemed to act as the anchor of magnetic domains and possibly also distorted and prevented them from being uniformly distributed.

Composite hematite powder sintering produces almost fully densified samples.

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