# Synthesis and magnetic-structural characterization of sub-nanoparticles Cu-Co solid solution ( 10nm) by mechanical alloying

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## Abstract

*The synthesis by high energy mechanical milling of metallic sub-nanoparticles of Cu-Co by means of a mechanochemical process is reported. A reaction is promoted between metallic chlorides (CuCl, CoCl) and Na in a dispersive medium (NaCl). Such an environment hinders agglomeration of the chemically reduced metals beyond a few subnanometers producing a fine dispersion of nanoparticles. The present work describes the synthesis of Cu-Co subnanoparticles (sNps) in 20 at.% Co as a function of milling energy ($E_M$) and particle volume fraction ($F_v$). Characterization is made by means of X-Ray diffraction, semiquantitative chemical analysis using energy dispersive spectrometry (EDS), transmission electron microscopy (TEM) in high resolution mode and electron paramagnetic resonance (EPR). Fine dispersions of nanoparticles are obtained with sizes smaller than 5 nm. Additionally, the results presented, might complement the study in different areas such as giant magnetoresistance and catalysis in this Cu-Co binary system.*



## 1. Introduction

Reactive mechanical alloying has been already applied in recent years to produce nanoparticles [1, 2], several investigations have demonstrated that the use of a mechanochemically induced solid state reduction can be an alternative and efficient method to produce metallic nanoparticles with low cost and in large amounts. Schaffer et al. [3] have used mechanical milling to synthesize pure metal nanoparticles for different applications including magnetic recording media, electrocatalysts and composite materials [4-6], most recently, other study suggests that Co and Cu can each individually contribute to syngas conversion with CuCo catalyst [7]. Ding et al. [8] have shown that by controlling the relative volume fraction of the product phase it is possible to synthesize ultrafine particles of Cu. Thus mechanical milling coupled to a chemical reduction has important applications and useful for a wide variety of metallic systems. In the preset work, the technique is applied to synthesize sub-nanoparticles of CuCo alloyed of these two metals in amounts below the saturation concentration of Co in Cu (i.e. 23% at Co approximately).

Nanoparticles of solid solution CuCo have electrical, catalytic and biomedical potential application [9-11]. The combination of both elements in a single particle increases the versatility of the application. For example, it is well known that giant magnetoresistance (GMR) can be achieved in this system when produced between fine alternate layers [12].

The magnetic characterization by EPR in this particles evinces the electronic state within the particles in this state very reduced structurally and the electrical interaction (ie spin interaction) between Co atoms and Cu atoms applicable in spintronics[13], in the practical realization of such devices it is important identify magnetic materials and electronic transport properties. In the present investigation, a relatively simple technique is used to produce nanoparticles with non-equilibrium solid solutions of Cu-Co. This can derive into different configurations after phase separation in this system with practically null mutual solubility with a controlled heat treatment to separate the phases in the same particle (ie particles with core-shell structure) currently investigated by the authors . The reduction of metals from their chlorides is made in a protective environment (NaCl) which also promotes an appropriate dispersion.

In this report, we concentrate particularly on the synthesis and characterization of CuCo sub-

nanoparticles (called sNps) with a non-equilibrium solid solution by reactive milling.

## 2. Experimental Procedure

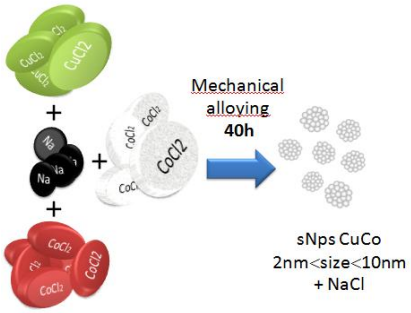
Mechanical milling is used to synthesize all samples. A chemical reaction is induced by adding a metallic chloride or mixture of metallic chlorides ($CuCl_2$ and $CoCl_2$) into the mill together with Na and an excess amount of NaCl. The reaction is as follows (see scheme 1):

$$CuCl2+ CoCl2+4Na \Rightarrow (CuCo)_{sNps}+4NaCl$$

During milling Na reduces the chlorides and nanoparticles are formed by milling and dispersed by the excess NaCl. The chemical reaction also produces NaCl. In all cases, the mill is loaded with a mixture of chlorides and Na of 3 g. The proportions of reagents are calculated stoichiometrically according to the simple chemical reaction to be induced (see Table 1). All powders in use are chemically pure (around 99.99% purity) and less than 100 mesh in size. As for the excess NaCl, two different amounts are added depending on the desired volume fraction (fv) of nanoparticles i.e., 3 and 6 g.

| X[at.%] | $CuCl_2$[g] | $CoCl_2$[g] | Na[g] |
|---|---|---|---|
| $Cu_{100}$ | 2.23 | 0.00 | 0.77 |
| $Cu\text{-}Co_5$ | 2.11 | 0.11 | 0.77 |
| $Cu\text{-}Co_{20}$ | 1.68 | 0.55 | 0.77 |
| $Co_{100}$ | 0.00 | 2.23 | 0.77 |

**Table1.-** summarized of proportions of reagents (other compositions are used for the purposes of discussion)




**Scheme 1.-** Synthesis of CuCo sNps by mechanical alloying

This produces two different values of particle fv for the final mixtures i.e., 5 and 2.3%, respectively. Milling is performed in steel vials using two sizes of stainless steel balls, 0.5 cm (0.28 g) and 0.95 cm (0.51 g) with a relation between powder weight and balls of 2:5 and 4:5 for the two fv values, 5% y 2.3% respectively. Vials are sealed in argon atmosphere before milling. Different milling times are investigated from 10 to 40 h in a high energy mill (SPEX-D8000).

As milled samples are characterized by X ray diffraction (XRD) in a $20^o<2\theta<120^o$ range with a step interval of 0.04 $min^{-1}$ using a GBC diffractometer equipped with a monochromator (Co-$k_{\alpha 1}$= 1.7889 Å). Lattice parameters are calculated by using data from each identified peak and performing a linear regression as a function of $\cos 2\theta/\sin\theta$ [14]. Average particle diameters are determined for 20 h, 30 h and 40 h of milling by using the full width at half maximum-FWHM=<β>) of the (111), (200), (220) diffraction peaks that correspond to the fcc Cu rich phase. Scherrer's equation ($D \cong \lambda K_{\alpha 1}/[<\beta>\cos\theta]$) has been also used to determine average sizes.

The particle size and morphology are locally determined by electron microscopy in high resolution images. The electron microscope (FEI ® aberration corrected Titan) has been operated at 300 kV in transmission mode. The images are analyzed with the software package Digital Micrograph. All as milled samples are cleaned in anhydrous methanol to dissolve the excess NaCl and then drops of the suspension are deposited onto 3 mm diameter Cu grids.

The as milled powders have been investigated by measuring their magnetic properties. Results for EPR (electron paramagnetic resonance) are reported here. EPR measurements have been carried out at an X-band frequency of 9.4 GHz with a JEOL JES RES 3X spectrometer operating at a 100 kHz field modulation. The EPR X band spectra are recorded at room temperature. The g values are calculated by measuring the magnetic field with a resolution of ± 0.01 mT. Microwave frequency parameters are used and 2, 2, diphenyl-1-picrylhydrazyl (DPPH) as marker.

## 3. Results and discussion

Figure 1 shows a SEM image of the as milled powders. This secondary electrons image is rather homogeneous as expected for a mixture of metallic nanoparticles and NaCl. The overall chemical composition is derived from EDS measurements. Representative spectra are also shown in Figure 1. As milled powders of Cu, Co

and Cu-20 at.% Co are given in Figure 2 after 40 h of milling (results of Cu and Co are displayed for comparison and discussion). Clear $K_{\alpha 1}$ peaks corresponding to pure Cu (Fig 2a), pure Co (Fig. 2b) and a mixture of Cu and Co (Fig. 2c) can be found together with those corresponding to Na and Cl. These results suggest that the reduction of the metallic chlorides has taken place; additionally there is a very little content of Oxygen or other typical impurities for the processing technique in use. Especially the absence or very slight content of Fe appears to be below the detection limits of the technique. Nevertheless even if such slight contamination would exist, the presence of Fe would modify very little the present results since it has a very similar nature to the Co that is here investigated. Measurements for several as milled mixtures are shown including the pure metals and after 40 h of milling time. In all cases a precision of around 2 at. % is reached. Thus the detected oxygen is considered to be unrelated to the chemical composition of the sNps since it is within the error band of the determination.

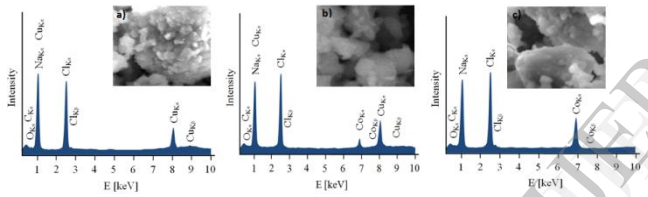



**Figure 1.-** SEM image and EDS spectrum of the as milled powders a) 100 at. % Cu, b) 20 at. % Co, c) 100 at. % Co.

Figure 2 shows representative X-ray diffraction patterns of as milled powders. Samples in this case have been milled for 20h and the chemical compositions include pure Cu and Co as well as Cu-5 at.% Co and Cu-20 at.% Co (the result for Cu-5 at.% Co is shown discussion purposes). Figure 2 also contains information regarding the expected peak positions for different phases including fcc Cu and Co and hcp Co. Peaks corresponding to NaCl are also visible. The reduction of the pure metals is readily demonstrated by the presence of the corresponding peaks. Both hcp and fcc Co phases give rise to diffraction peaks. In the case of pure fcc Co, a lattice parameter of 3.4198 Å can be derived. Co also appears with a hcp structure during the synthesis procedure, the corresponding lattice parameters are $a_0$(hcp)=2.5011nm, $b_0$(hcp)=2.5021nm and $c_0$(hcp)=4.0851. The presence of both phases suggests that the mechanical energy input is affected by the excess NaCl, as desired. It is known that the Co fcc phase is stable at higher temperatures but can be produced by mechanical deformation. The metastable equilibrium can be achieved when deformation provides the required energy. In the present experiment, a rather higher energy input is required to promote the formation of the fcc Co phase since the excess NaCl effectively disperses the reaction products and apparently dissipates a great deal of the mechanical energy input. As a consequence, the milling time to produce fcc Co is increased. As for the CuCo mixtures, the development of a solid solution can already be inferred by the presence of slightly displaced single peaks with respect to the Cu peak positions.

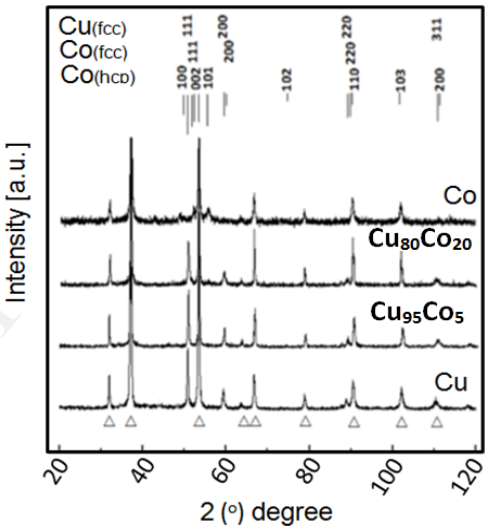



**Figure 2.-**X ray diffraction patterns of as milled mixtures with different compositions and milled for 40 h (representative for two volume fraction $F_V$). The expected peak positions for the different metallic phases are indicated. NaCl peak positions are indicated with △.

There is a characteristic variation of the lattice parameter of the chemically reduced metallic phases as a function of Co content. Figure 3 shows representative results after 40 h of milling. Two different particle volume fractions have been induced by milling but the lattice parameter results are similar. Figure 3 also includes a comparison with measurements found in the literature for massive mixtures of as milled Co-Cu powders. The present results are rather similar to those found in the literature and show a tendency that can be expected for solid solutions. The fcc Co lattice parameter is also included in Figure 2 in order to show this tendency more clearly. The lattice parameter variation can be formally described by the relationship:

$$\mathbf{a_0}\,(C_{Co}) = 3{,}60684 + 0.00806e^{-C_{Co}/11{,}72382}$$

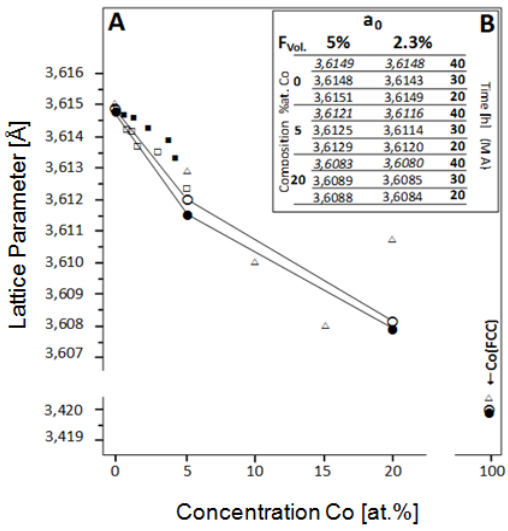



**Figure 3.**-(a) Variation of lattice parameter as a function of Co content after 40 h of milling time for two volume fractions fv = 5 % (○), and fv=2.3 % (●). Comparison to other investigations is given: ■ [15], □ [16] and △ [17], B) Lattice parameters for 20h, 30h and 40h of mechanical alloying.

where $a_0$ represents the phase lattice parameter and $C_{Co}$ the Co content in atomic percentage. The lattice parameter reaches a value of $a_0$ = 3.6083 Å at approximately $C_{Co}$=20 at.%. This indicates a slight contraction of the Cu lattice that depends on the milling time and it is around 0.001nm for 40h of milling. According to [1,18], several authors have found the development of solid solutions in CuCo after mechanical milling of massive powders. Such a finding has been extensively discussed in the past for the CuCo system that is nearly immiscible under equilibrium conditions. In the present case apparently a similar phenomenon takes place with the formation of sNps. A solid solution is developed when a mixture of Cu and Co chlorides is chemically reduced by milling. This suggests the possibility of synthesizing alloyed nanoparticles with a composition near to the nominally calculated and added to the mill.

Peak analysis is used to derive the particle sizes as a function of milling time and chemical composition. There is a monotonic reduction of particle size, given by the particle diameter $D_p$, as a function of milling time regardless of the chemical composition of the mixture. For example after 40 h of milling, the average particle sizes are smaller than 10 nm. There is a tendency to form smaller particles as the milling time increases for the relative small particle volume fractions under investigation as is shown in figure 4. A simple data fitting routine gives rise to the following relationship involving particle size and milling timet ($t \geq 20$),

$$D_p = 8.1 + 11.6e^{-(t-20)/5.8} \quad [nm]$$

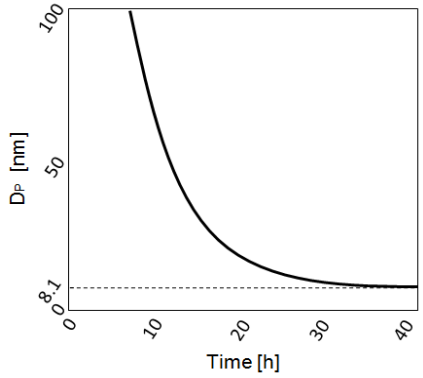



**Figure 4.**-Particle diameter Dp as a function of milling time (representative for FV= 2.3% and FV= 5%)

High resolution electron microscopy has been also used to investigate the as milled powders. Samples have been prepared in methanol to dissolve the surrounding NaCl and image only the synthesized nanoparticles. Two examples are given in Figure 5. The lattice of the nanoparticles is visible but some lines and circles have been drawn to help recognizing the crystalline domains. Particles in the Cu-5 at.% Co mixture (Fig. 5a) show a rather homogeneous contrast as well as those in the Cu – 20 at.% Co sample (Fig. 5b). This suggests a rather homogeneous distribution of Co in the Cu lattice. As for the sizes, nanoparticles can be arranged in two different categories. One of them coincides with the average size derived from X Ray diffraction and in the range between 5 and 10 nm. However there is another set of nanoparticles having sizes close to 1 nm, homogeneous contrast and in a rather large number. Figure 6b gives an example of the observation for the mixture Cu – 5 at- % Co but they can be found in all as milled samples. It is likely that these particles are formed during the milling during the instantaneous contact between the milling balls. Their rather small sizes can be traced back to the dispersion conditions imposed during synthesis which most likely change during the milling period.

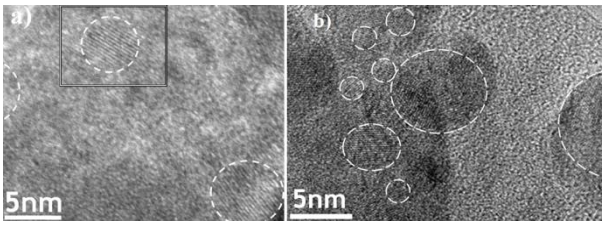



**Figure 5.-** High resolution electron microscopy images (representative) of sNps in the mixtures (a) Cu-5 at. % Co, (b) Cu-20 at. % Cu, after 40h of mechanical milling. Particles are circled to assist visualization.

The as milled powders have been investigated by measuring their magnetic properties. EPR is one of the techniques in use and the corresponding results are described in this report. Figure 6 shows results for several Cu-Co mixtures including the pure metals. EPR results can be interpreted to deduce the specific interactions between neighboring atoms in a given material. It is thus to be expected that in the case of nanoparticles of pure paramagnetic Cu, the magnetic moment interaction leads to an spectrum having a flat response with a line of resonance centered at a value of 333 mT and with a g≅2.33 value characteristic of $Cu^{2+}$[19], as shown in Figure 6. In the case of ferromagnetic pure Co nanoparticles the EPR spectrum shows also a shape shows the typical absorption of the Co magnetic component, the height at 0 [mT] from baseline, is associated to the spontaneous magnetization of the nanoparticles obtained at the end of the synthesis process.

As for the alloyed nanoparticles, the EPR spectra show characteristics that vary as a function of Co content and clearly reflect the magnetic moment interaction of Co with the $Cu^{+2}$ nuclei [20]. As the Co content increases from 5 to 20 at.% the general shape of the spectra varies towards that of CuCo and they occur six lines of resonance (see Fig. 6)

The EPR spectra in the case of the CuCo sNps can be explained on the basis of an itinerant electron (S=1/2) that belongs to neighboring atoms. If it is assumed that these atoms are Cu and Co and that this is the average condition in the material, then the formation of a solid solution can be demonstrated. Typically such a condition can also be interpreted as the "formation of a metallic molecule" since the electron is shared simultaneously by the Co and the Cu atoms. Figure 7 shows an schematic illustration of the concept.

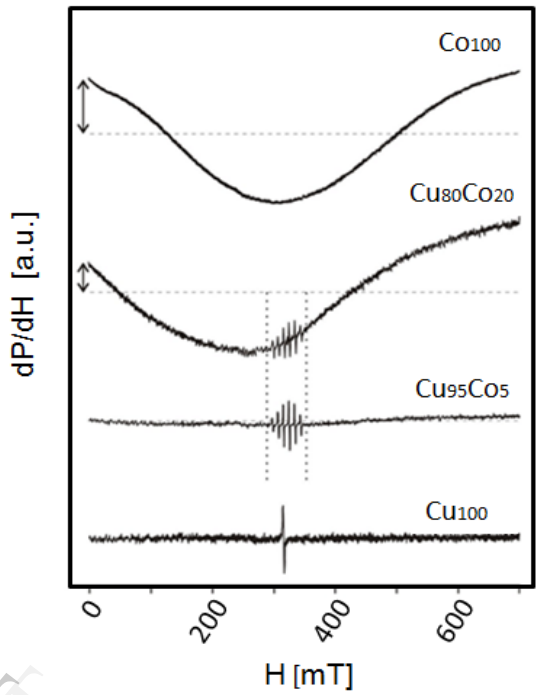



**Figure 6.-**EPR spectra for the different as milled mixtures under investigation see text for discussion.

The itinerant electron has a specific Lande factor g and width Γ with similar characteristics to a free radical. On the other hand, the six lines of resonance (hyperfine unfolding) results from the interaction between the itinerant electron and the total nuclear spin of the Cu and Cu atoms ($I_{Cu-Co}$). The values of ($I_{Cu-Co}$) can be calculated on the basis a of the following rule in quantum mechanics: $I_{Co} + I_{Cu} \geq I_{Cu-Co}$. The value for $I_{Co}$ is 7/2 and for $I_{Cu}$ is 3/2 which in turn leads to $I_{Cu-Co} = 2$, 3, 4 and 5. Additionally the most stable $I_{Cu-Co}$ is located at 2 due minimum energy considerations in comparison with other theoretically likely spins [21].

The hyperfine interaction between the spin S = ½ and $I_{Cu-Co} = 2$ gives rise to an EPR signal with five lines of resonance as shown in Fig. 8. Nevertheless he experimental spectra for CuCo mixtures show six lines of resonance (see Fig. 6). Such a spectra can be reproduced by simply overlapping two quintuplets provided that they are displaced a distance equal to 2g as shown in Fig. 8. The displacement is necessary due to the specific level of covalent bonding between Cu and Co. The superposition of spectral lines also explains the different experimental intensities (see Figs 8 and 6).

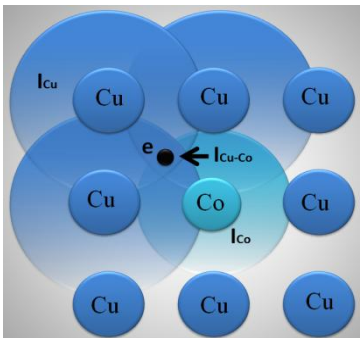



**Figure 7.-** Schematic magnetic moment interaction ($I_{Cu-Co}$, $I_{Co}$) between an atom of Co in a Cu lattice. An itinerant electron is indicated.

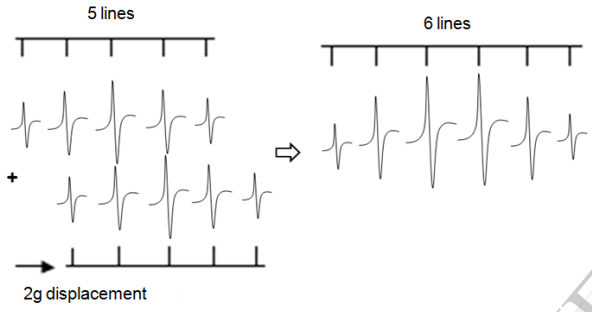



**Figure 8.-** Schematic overlapping of hyperfine lines of resonance from EPR spectra due to a partly covalent bonding of Co in a Cu lattice. The expected 2g displacement is indicated. Such an overlapping produces six lines of resonance in the experimental pattern.

The experimental EPR spectra support the development of a solid solution in the sNps. The six lines of resonance can be explained by the above discussed effects. They can only happen when Cu atoms neighbor Co atoms at random. There is an hyperfine coupling (nucleus-spin) with a high molecular magnetic moment. It is due to the presence of ferromagnetic Co dissolved in the Cu structure that produces a molecular moment ($I_{Cu-Co} = 2$) and 2l + 1 lines of resonance [21]. Additionally the level of covalent bonding leads to a displacement of a second set of five lines giving rise to the six lines in the experimental EPR spectrum. EPR results are similar for the two different volume fractions under investigation (i.e. 5 and 2.3 %).

## 4. - Concluding Remarks

In the present work it is shown that it is possible to synthesize alloyed Cu-Cu sub-nanoparticles by inducing a chemical reduction reaction of mixed metallic chlorides. NaCl added in excess has shown effective results as a dispersant medium since average particle sizes have been kept below 10 nm. The method offers the possibility to be extended to other systems where alloyed particles are desired. The nanoparticle size depends on the milling time with a slight tendency to decrease as the milling time is increased.

The nanoparticles in Cu-Co mixtures develop a solid solution according to X-ray diffraction and EPR measurements. The chemical composition of the nanoparticles is proportional to the added amounts of reagents. The results of characterization by EPR shows the spin properties into of a CuCo sNps in solid solution on the basis in the rules of quantum mechanics, in this direction, the presence of free radical in Cu causes an interaction with neighboring Co, which allows to visualize the formation of the solid solution through hyperfine interaction between them.



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