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Single magnetic domain precipitates of Fe/Co and Fe and Co in Cu matrix produced from (Fe–Co)/Cu metastable alloys

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Abstract

Structural and magnetic properties of nanocrystalline Fe₂Co and (Fe₂Co)_{0.30}Cu_{0.70} alloys prepared by high energy ball milling have been studied basically by x-ray, Mössbauer spectroscopy and magnetization measurements. For the Fe₂Co alloy case, the Mössbauer measurements indicate that the sample with 160 hours of milling has two magnetic components with the same average hyperfine parameters: one magnetic crystalline component associated with the bcc Fe₂Co phase and another component attributed to the small particles of the same bcc Fe₂Co phase (SP-Fe₂Co). (Fe₂Co)_{0.30}Cu_{0.70} alloys have been prepared by milling in two different ways: (1) starting from the mixture of Fe₂Co milled alloy and pure Cu powders (sample I) and (2) milling of the elemental powder mixture of Fe, Co and Cu (sample II). The x-ray diffraction and bulk magnetization results of samples I and II indicate the formation of a (Fe₂Co)_{0.30}Cu_{0.70} supersaturated solid solution, with features of a ferromagnetic material and T_c at about (420 ± 1) K. High temperature magnetization measurements of the (Fe/Co)Cu milled materials show particle precipitation effects. Heat treatment at 675 and 875 K of the final milled materials leads to different results: in the sample I case to the precipitation of single magnetic Fe/Co particles into the Cu matrix, and in the case of sample II the precipitation of single magnetic particles of Fe and of Co into the Cu matrix.

1. Introduction

Mechanical alloying (MA) induced by the milling technique has been applied to produce alloys at low temperatures, i.e. temperatures lower than those of the melting points of the initial components. The possibility of alloy formation in systems that show a negative heat of mixing among the chemical elemental powders is explained by an interdiffusion reaction

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of the components that occurs during the formation of the alloys in the milling process. On the other hand, in the case of positive heat of mixing the alloy formation process occurring with milling is not well understood, and some phenomenological models have been suggested to explain it (Niessen *et al* 1983, Yavari *et al* 1992). From the experimental point of view a large number of works applying MA have been reported in the literature (Monteiro *et al* 1998, Uenishi *et al* 1991, Yavari *et al* 1992) for systems with a positive heat of mixing, and the results show an increasing of the solubility range of the elements compared to that found in the equilibrium phase diagram (EPD), usually leading to a supersaturated solid solution phase. Thus, metastable phases may be produced by milling in an extended composition range, even in those cases where a positive heat of mixing among the elements is expected, i.e. for the cases where the chemical elements do not present compounds or solid solution in the EPD. High energy milling has also been applied to obtain amorphous phases starting from the elemental powders (Passamani *et al* 1999), or from stable compounds (Larica *et al* 1998, Passamani *et al* 1995). In the former case, the compound is energetically destabilized by a chemical disorder introduced in the ordered structure during the milling process. Summarizing, for binary systems the MA by milling method has been widely used to produce amorphous or supersaturated solid solutions, and the thermodynamics of the process may be understood by semi-empirical models (Niessen *et al* 1983, Yavari *et al* 1992).

In the present work, studies of Fe/Co and of Fe/Co/Cu alloys were performed using high energy milling to prepare alloys. It is known that Fe–Co has a negative value for the heat of mixing (Niessen *et al* 1983), while Fe–Cu (Yavari *et al* 1992) and Co–Cu (Kuhrt and Schultz 1992) have positive values. In the reported magnetic phase diagram of the Fe–Co system obtained by milling (Kuhrt *et al* 1992), the alloy with the highest saturation magnetic moment (M_s) is found for a composition around two atoms of Fe for one of Co, i.e. the composition that will be labelled Fe_2Co in the present work.

In order to study the magnetic properties of magnetic particles of Fe/Co in non-magnetic matrices, it is convenient to select a solid solvent with particular features such as to permit precipitation of the Fe/Co particles after heat treatments. The ternary Fe–Co–Cu system may be a suitable candidate to form metastable alloys and also to produce precipitation of magnetic particles of Fe/Co in the non-magnetic Cu matrix after a heat treatment. The Cu composition of 70 at.% was chosen since this composition value may prevent rapid growth and magnetic contact among the particles precipitated after heat treatment. In the present work, samples of Fe_2Co and $(\text{Fe}_2\text{Co})_{0.30}\text{Cu}_{0.70}$ metastable alloys have been prepared by ball milling in order to study the changes in their microstructures and magnetic properties. Studies of the formed alloy properties were done by x-ray diffractometry (XRD), differential scanning calorimetry (DSC), electron scanning microscopy (ESM), magnetization measurements and Mössbauer spectroscopy (MS). The stable phase formation and magnetic precipitates obtained by heat treatment of the samples were also studied by these techniques.

2. Experimental conditions

Two series (I and II) of the $(\text{Fe}_2\text{Co})_{0.30}\text{Cu}_{0.70}$ alloy were obtained from high purity chemical elemental powders of Fe, Co and Cu (99,999%). Series I was prepared in two steps: first by milling the elemental powders of Fe and Co for 160 hours, at the composition of the $\text{Fe}_{0.67}\text{Co}_{0.33}$ binary alloy, here labelled as Fe_2Co . In the second step Cu powder was added at a defined composition and milled for 210 hours. In series II, the chemical elemental powders of Fe, Co and Cu were mixed at a defined composition and milled up to 20 hours. The total mass of each final product was about 10 grams. The milling has been performed in a Spex 8000 machine, with the materials sealed under high purity Ar atmosphere in a hard steel vial

with ball to mass ratio 6:1 for the Fe₂Co and 4:1 for the (Fe₂Co)_{0.30}Cu_{0.70} alloys. Some experimental results in other systems (Passamani *et al* 1999, Xia and Baggio-Saitovitch 1996) have shown that a homogeneous alloy can be reached for very short milling times when the milling starts from the elemental powder and the Spex 8000 machine is used. Samples were collected at selected milling times and stored in liquid nitrogen for later analysis. The sample manipulation was done inside a glove box under high purity Ar atmosphere to prevent the oxidation and contamination with other gases. The final (Fe₂Co)_{0.30}Cu_{0.70} ternary alloys were labelled as samples I and II. Parts of these samples were heat treated at 675 and 875 K under a flux of ultra-high purity argon. These temperatures were selected from differential scanning calorimetry (DSC) analysis.

X-ray diffraction patterns (XRD) of all collected samples at 300 K were obtained with Cu K α radiation in a Rigaku diffractometer; the calibrated was made with a standard Si single crystal and the uncertainty is $\pm 0.02^\circ$.

⁵⁷Fe Mössbauer spectra of the collected samples were measured with ⁵⁷Co:Rh radioactive sources in a conventional transmission geometry at room temperature for different milling times. The isomer shift (IS) values of our data were taken relative to α -Fe at RT; however, the Mössbauer spectra shown in the figures are presented relative to the source.

Magnetization measurements as a function of temperature have been performed, at temperatures up to 900 K, with a Cahn Instruments Faraday balance. During these measurements the samples were kept under Ar atmosphere. Magnetization against applied magnetic field curves were obtained with a vibrating sample magnetometer (VSM) at room temperature, in a maximum field of 12 kOe.

The alloys' final compositions have been checked by electron scanning microscopy using energy dispersive x-ray spectroscopy (EDS) analysis. The results show percentages of Fe content similar to the initial composition and no impurities have been detected in the samples. After the milling procedure, all the balls have the same form and size as those of the initial ones.

3. Results and discussion

3.1. Fe₂Co alloy

The results of the Fe₂Co alloy will be initially shown in order to study the formation of (Fe₂Co)_{0.30}Cu_{0.70} alloy. Figure 1(a) presents the Fe₂Co x-ray diffraction patterns as a function of milling time. The diffraction pattern obtained for the sample before milling displays the Bragg peaks corresponding to the bcc alpha iron (α -Fe) and to the fcc and the hcp reflections peaks of the Co polycrystalline structures. At 49 hours of milling the diffraction pattern shows basically three Bragg peaks at about the angular positions of the bcc crystalline structure of α -Fe, shifted to lower angles, and there is no evidence of the Co peaks. Up to 111 hours of milling, the Bragg peaks of the bcc structure shift to lower angles, then remaining unchanged for longer times. At 160 hours, the formed Fe₂Co alloy has Bragg lines at angular positions close to the results of Bayliss (1990) for Fe/Co alloys obtained from the conventional method, but with broader line widths. These results give us an indication that during the milling process the Co atoms substitute those Fe atoms, forming a bcc Fe₂Co homogeneous alloy, as also reported by Cohen *et al* (1999). The lower limit grain size (D_c) of the observed alloy is of the order of 10 nm, as calculated with the Scherrer formula (Guinier 1994). This D_c value of 10 nm is less than a half compared with those of the crystalline initial components, as displayed in figure 1(b). From this figure, it can also be observed that for milling times longer than 49 hours the crystalline grain size keeps roughly the same, indicating that our experimental procedure would not produce amorphization of the Fe₂Co alloy.

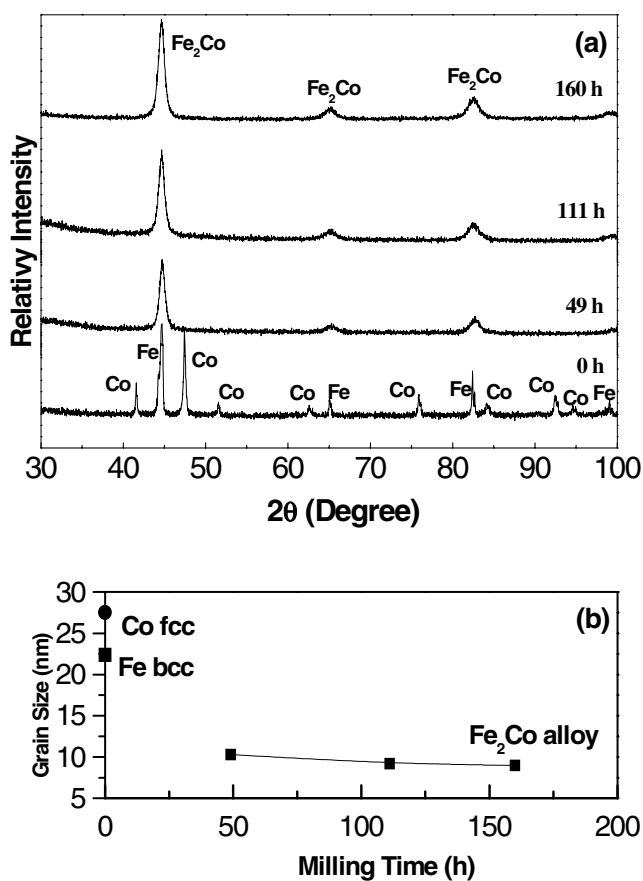


Figure 1. (a) X-ray diffraction patterns of the Fe₂Co milled alloy as a function of milling time; (b) behaviour of crystalline grain sizes obtained from the fitting of the main peak of the Fe, Co and Fe₂Co as a function of milling time. The lines that connect the experimental points are guides for the eyes.

Magnetization as a function of applied magnetic field obtained at 300 K for Fe₂Co alloys milled at different times are shown in figure 2. From this figure, it can be observed that for 49 hours of milling the saturation magnetization is roughly a half of those obtained in the alloys milled for 111 and 160 hours. Similar magnetization curves at 300 K were obtained for the samples milled for 111 and 160 hours. This lead us to conclude once again for the total reaction among Fe and Co atoms forming the Fe₂Co phase for milling times equal and longer than 111 hours.

The room temperature Fe₂Co Mössbauer spectra as a function of milling time are shown in figure 3. The Mössbauer spectra present a magnetic splitting with broad line widths characteristic of granular materials produced by milling. The fittings of these spectra were performed with a combination of a distribution of hyperfine magnetic fields (B) plus a crystalline sextet. In the distribution component a linear correlation between the IS and B values was considered, to take into account the small asymmetry observed in the Mössbauer absorption line located at the higher positive velocity range. Thus, the Mössbauer spectrum of 49 hours sample was carried out with one magnetic crystalline component slightly broad, with hyperfine parameters values of IS $\approx 0.05 \text{ mm s}^{-1}$ and $B \approx (35.0 \pm 0.2) \text{ T}$, associated with a bcc

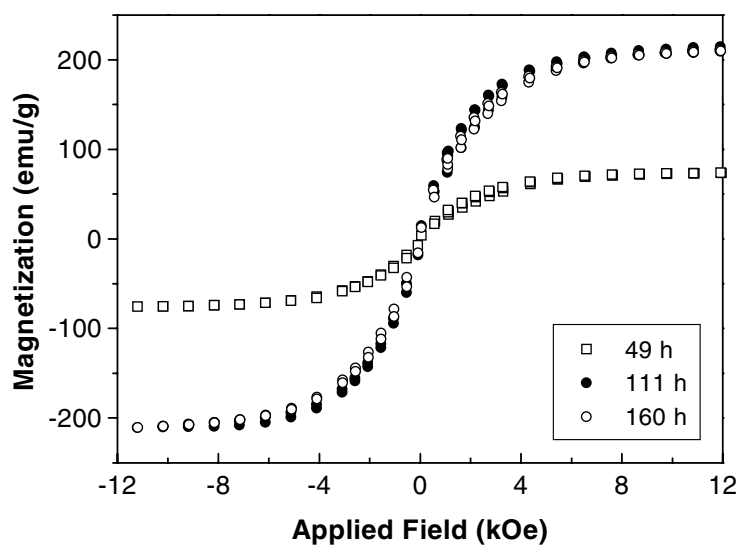


Figure 2. Magnetization as a function of applied external field measured at 300 K for the milled Fe_2Co alloy.

Fe_2Co solid solution, and a second component fitted with a distribution of magnetic hyperfine fields having average hyperfine parameters similar to the previous magnetic component but, in this case, attributed to small particles of bcc Fe_2Co alloy, named here as SP- Fe_2Co . The relative absorption area of the distribution component, at 49 hours of milling, is about 27%. For longer milling times no significant change is observed in the shape of the Mössbauer spectra except for the increase of relative absorption area associated with SP- Fe_2Co phase to 35%. The model of the components used to fit the Mössbauer spectra was based on the high temperature Mössbauer measurements, where an oxidation effect was observed, even under ultra-high vacuum conditions ($\approx 10^{-5}$ Torr), for the magnetic distribution component. These results taken at high temperature help us to separate the different particle size components that contribute to the Mössbauer spectra. The model adopted to fit the Mössbauer spectra will be published elsewhere by Passamani *et al.*

The behaviour of the relative absorption area, the isomer shift (IS) and the magnetic hyperfine field (B) of each component as a function of milling time are shown in figures 4(a), (b) and (c), respectively. The B values displayed in figure 4(c) relative to the SP- Fe_2Co phase correspond to the most probable ones. The IS (figure 4(b)) of each component remains constant, while a significant change is observed in the relative area (figure 4(a)) and in B (figure 4(c)) for times longer than 49 hours. The relative absorption area of the SP- Fe_2Co phase increases with milling as expected due to the sample preparation process. On the other hand, the behaviour of B with milling time goes in the same direction as observed by the magnetization versus applied external field measurements i.e., the B values increase at about 1.5 T from 49 to 111 hours of milling and remain roughly constant for longer milling times. Thus, the above results corroborate the previous conclusion that the bcc Fe_2Co phase is completely formed for milling times of 111 hours.

3.2. Series I— $(\text{Fe}_2\text{Co})_{0.30}\text{Cu}_{0.70}$ alloy

Figure 5 shows the x-ray diffraction patterns as a function of milling time for the series I ($(\text{Fe}_2\text{Co})_{0.30}\text{Cu}_{0.70}$ alloy) produced by adding the nanostructured Fe_2Co alloy in 70 at.% of Cu.

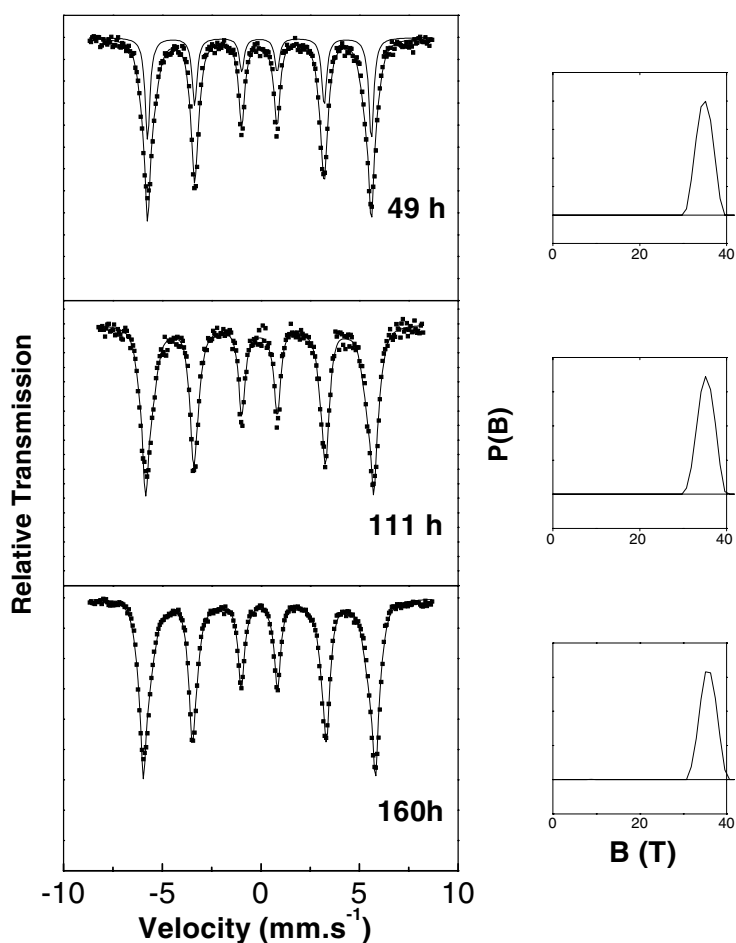


Figure 3. Room temperature ^{57}Fe Mössbauer spectra of the Fe_2Co milled alloy as a function of milling time.

The sample with 3 hours of milling displays the Bragg reflection lines corresponding to those peaks of the Cu and Fe_2Co phases. The two phases are well defined in the x-ray patterns up to 30 hours of milling. However, for milling times longer than 30 hours the Bragg lines associated with the Fe_2Co phase disappeared, indicating that a ternary alloy may be formed. The x-ray patterns of the material milled for longer than 70 hours remained similar, showing basically the reflection Bragg peaks of an fcc crystalline structure of a Fe/Co/Cu solid solution. The observed broadening of the Cu(111) Bragg peaks during the first 20 hours of milling is mainly due to the Cu grain size reduction, as estimated by the Scherrer formula (Guiner 1994) and shown in figure 6(a). From the analysis of the x-ray patterns as a function of milling time, it was observed that the angular positions related to Cu peaks were shifted to lower angles, indicating an increasing of lattice parameter of the Cu matrix, due to the diffusion of Fe and Co atoms into the Cu matrix (figure 6(b)).

Mössbauer spectroscopy has been performed in all $(\text{Fe}_2\text{Co})_{0.30}\text{Cu}_{0.70}$ milled alloys, at room temperature. It was observed that the signal to noise ratio for all samples milled for longer than 30 hours was unfavourable, leading to a loss of the transmission Mössbauer signal.

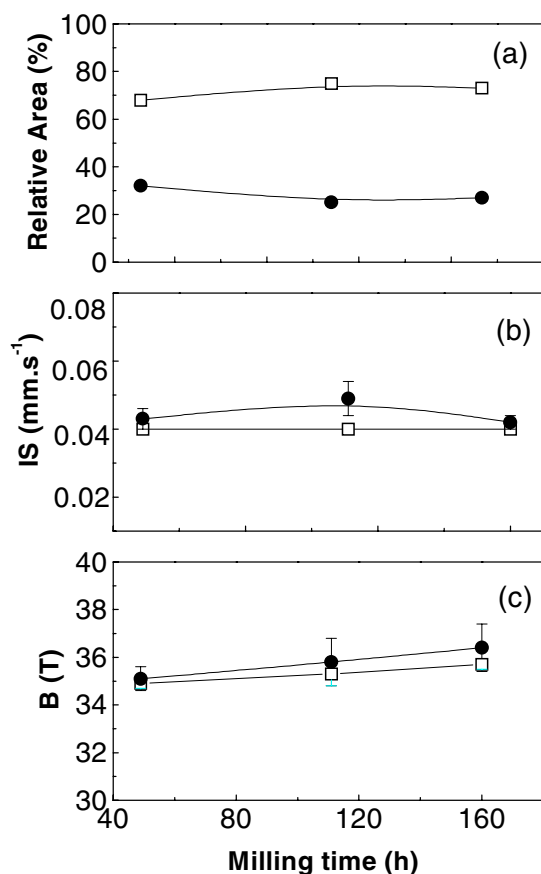


Figure 4. (a) Dependence of relative area, (b) isomer shift (IS) and (c) magnetic hyperfine field (B) of each component as a function of milling time for Fe_2Co milled alloy. Open square symbols are relative to the Fe_2Co solid solution, and full circle symbols correspond to the SP- Fe_2Co phase. The lines that connect the experimental points are guides for the eyes.

The effect is so drastic in our milled samples that it deserves some comments: (a) Cu metal has one of the highest mass absorption coefficient ($82 \text{ cm}^2 \text{ g}^{-1}$) for the 14.4 keV, that is also higher than the corresponding values for Fe ($64 \text{ cm}^2 \text{ g}^{-1}$) and Co ($66 \text{ cm}^2 \text{ g}^{-1}$) (Long *et al* 1983); (b) the microphotography of series I, not shown here, milled for long times (≥ 140 hours) indicates that the alloy particles are large, with average diameter values close to $500 \mu\text{m}$, and have irregular spherical shapes. These large particles sizes are responsible for a high effective Mössbauer absorber thickness. Thus, these facts may account for an increase of the non-resonant contribution to the Mössbauer spectrum background, leading to a strong reduction of the Mössbauer absorption lines. However, the large particle sizes (reason (b) above) could be mainly responsible for the reduction of the Mössbauer spectra transmission signal, since the Mössbauer spectra with the powder of Fe/Cu milled alloys (Monteiro *et al* 1998), were strongly enhanced with fine particle sizes obtained after sieving (100 mesh $\sim 150 \mu\text{m}$) the milled powder material. Therefore, in the present case, the large particle sizes of the samples could not be reduced by sieving the powder material. This effect was also observed for the series II, where the particles sizes in that sample are much larger.

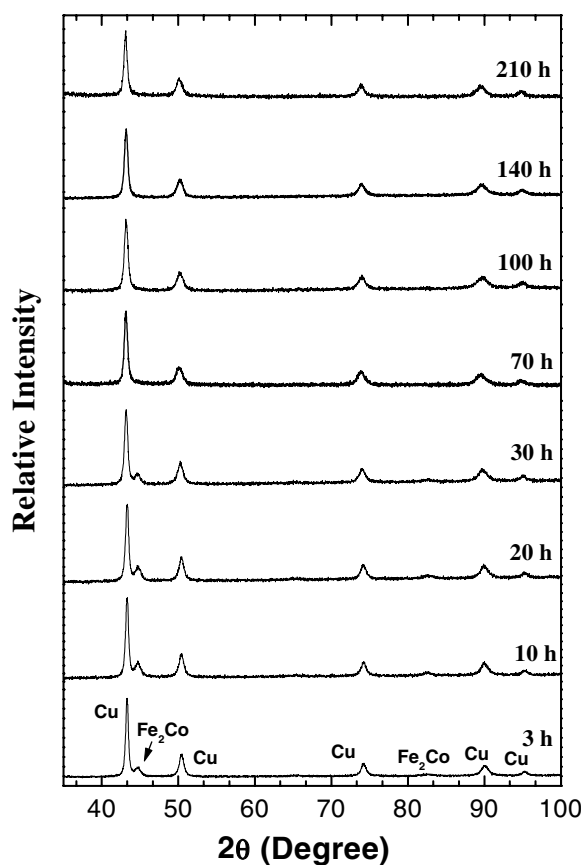


Figure 5. X-ray diffraction patterns of sample I as a function of milling time.

Figure 7 shows the room temperature Mössbauer spectrum of sample I milled for 30 hours. It shows a considerable low signal to noise ratio, giving a maximum effect of only 0.2%. This spectrum has been fitted with components associated with Fe_2Co phases plus one paramagnetic component (34%) that is associated to the substitution of Fe atoms into the Cu matrix, as already suggested by the lattice parameter behaviour of Cu as a function of milling time (figure 6(b)).

The magnetization of series I, at 300 K, as a function of an applied magnetic field is shown in figure 8, for different milling times. From 3 hours up to 30 hours of milling the magnetization values reduce, while the magnetic hysteresis increases with milling time. The reduction of the magnetization values in the 30 hour sample is consistent with the paramagnetic component observed in the corresponding Mössbauer spectrum. On the other hand, the increasing magnetic hysteresis with milling time can be associated to the formation of magnetic clusters at the beginning of the alloy formation process. Milling times longer than 30 hours lead to an increase of magnetization values and the disappearance of the hysteresis effect.

Magnetization thermal cycle measurements were performed in two different temperature ranges. Figure 9(a) displays the measurements up to 525 K of series I milled for times of 30, 70 and 210 hours. In figure 9(b) the temperature cycle is extended to 875 K. As can be

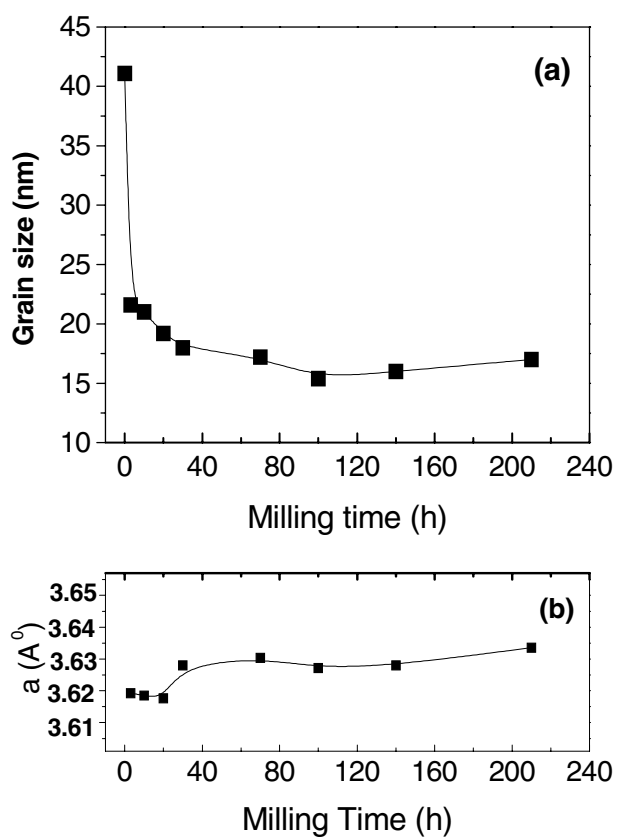


Figure 6. (a) Behaviour of grain crystalline sizes associated with the main peak of fcc phase as a function of milling time; (b) lattice parameters of the fcc phase as a function of milling time. The lines that connect the experimental points are guides for the eyes.

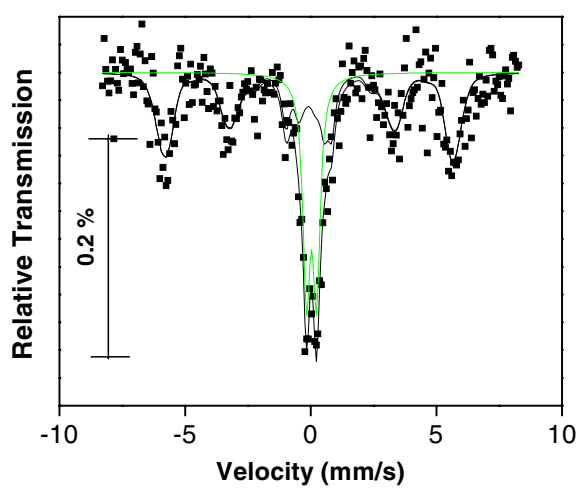


Figure 7. ^{57}Fe Mössbauer spectrum at 300 K of series I milled for 30 hours.

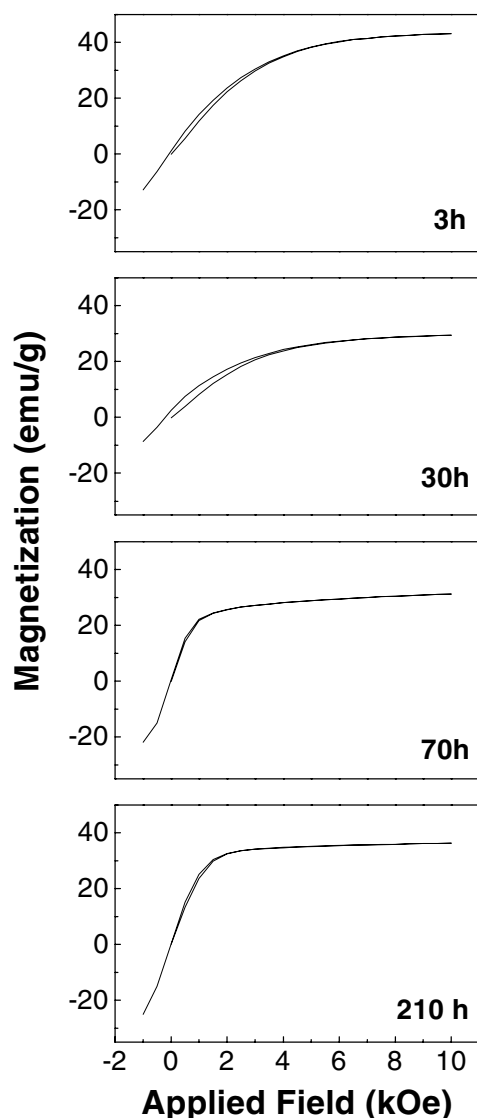


Figure 8. Magnetization as a function of applied field measured at 300 K for series I milled for different milling times.

seen from figure 9(a), no important effect is observed associated to precipitation or segregation of new phases. In this temperature range, no magnetic transition is observed for the sample milled for 30 hours, because a significant magnetic contribution from the Fe_2Co phase is still present, as indicated by high temperature Mössbauer results, which has a T_c value above 825 K (Passamani *et al* 2000). For the sample with 210 hours of milling, the magnetization as a function of temperature curves show a behaviour typical of a ferro/paramagnetic transition with T_c at about (420 ± 1) K, defined in this work as a maximum in the derivative of the magnetization curve.

The magnetization versus temperature curves, for temperatures up to 875 K, are shown in figure 9(b). In the case of the sample milled for 30 hours, the magnetization curve shows a

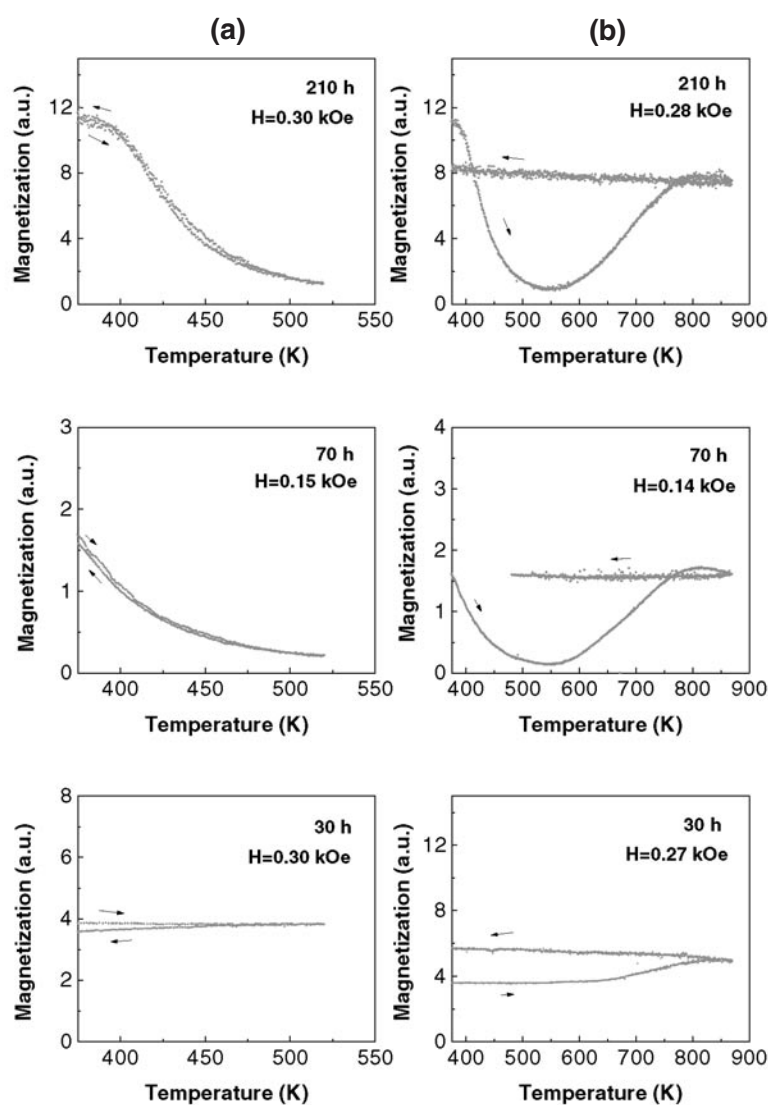


Figure 9. (a) Magnetization as a function of temperature, for series I for different times of milling, for temperatures up to 525 K, and (b) magnetization curves for the same series at temperatures up to about 875 K.

flat behaviour up to 650 K, due to the main contribution of Fe/Co phases as mentioned before. For higher temperatures an increase of the magnetization value is observed indicating that the Fe/Co/Cu solid solution, already formed at this milling time, is being transformed, producing precipitates of Fe/Co magnetic particles in Cu matrix, as will be shown later for the case of the heat treatment of the final milled materials. Samples with longer milling times show more clearly the precipitation effect that occurs in the $(\text{Fe}_2\text{Co})_{0.30}\text{Cu}_{0.70}$ supersaturated solid solution submitted to high temperature heat treatment. The precipitation model is supported by the x-ray results, performed after thermo-cycle magnetization experiments, and also in the samples heat treated at two defined temperatures, as will be discussed in the heat treated sample results section.

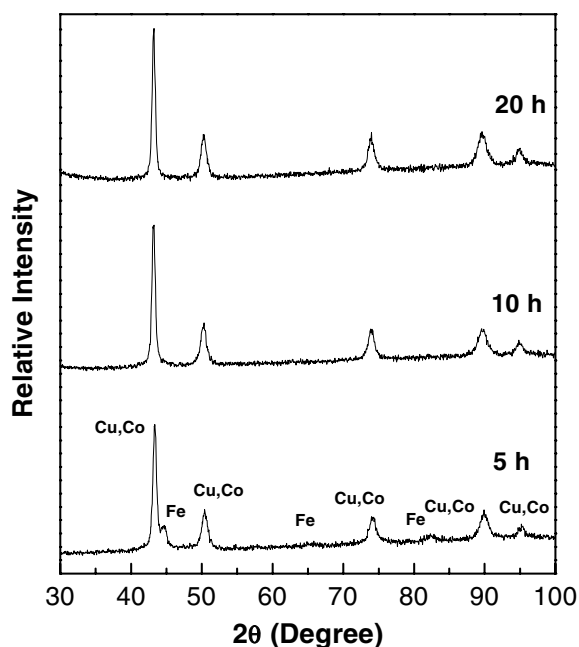


Figure 10. X-ray diffraction patterns of series II as a function of milling time.

Therefore, the results presented for the series I show that: (1) the $(\text{Fe}_2\text{Co})_{0.30}\text{Cu}_{0.70}$ supersaturated solid solution is formed for times longer than 70 hours; (2) for temperatures below 550 K, the magnetization curve of the 210 hour sample displays a thermal behaviour similar to a typical ferromagnetic material; (3) series I is thermally stable at temperatures up to 550 K and in the case of the 210 hour powders (sample I) the magnetic transition has been observed at (420 ± 1) K; (4) temperatures higher than 550 K lead to the precipitation of magnetic particles of the Fe/Co alloy in Cu matrix.

3.3. Series II— $(\text{Fe}_2\text{Co})_{0.30}\text{Cu}_{0.70}$ alloy

Series II, as mentioned in the section of experimental conditions, results from the milling of the mixture of the elemental powders, at a defined composition. Figure 10 displays the x-ray diffraction patterns of series II milled for 5, 10 and 20 hours. The x-ray diffraction pattern of the 5 hours milled sample shows Bragg peaks relative to those of α -Fe and the peaks of fcc Cu very close to the most intense peaks of Co, leading to asymmetric lines. Therefore, even at this short milling time one could not distinguish the Cu and Co phases by x-ray diffraction due to the line broadening by the grain refinements. However, analysing the most intense Bragg peak at about fcc Cu, it seems to have a small shift to lower angles with milling time. For milling times longer than 5 hours, the bcc Fe Bragg peaks are not observed in the x-ray patterns. The angular positions of the fcc phase observed for the powder milled for 20 hours are very close to those observed in sample I. The estimated grain size (D_c) of the final milled powder (sample II) is about 14 nm, a similar value to that observed in sample I.

EDS analysis performed at different sample regions confirms that sample II has a composition very similar to the nominal one, indicating a homogeneous distribution of Fe and Co atoms in the Cu matrix.

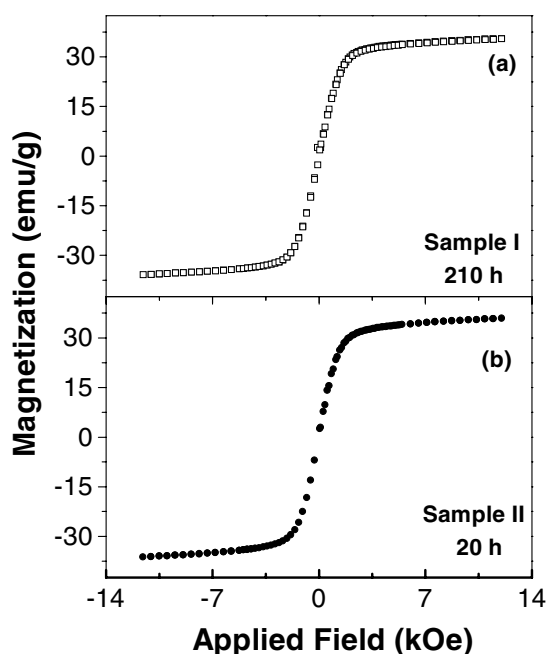


Figure 11. Magnetization as a function of applied field measured at 300 K for samples I (a) and II (b).

The behaviour of the magnetization measurements as a function of applied magnetic field, for different milling times of series II, is similar to the series I case, already presented. Figures 11(a) and (b) display the hysteresis curves, obtained at 300 K, of samples I (210 hours) and II (20 hours), respectively. As can be seen from these figures the curves are very similar and they show similar magnetization values at the highest magnetic fields and also similar coercivity effects.

High temperature thermo-cycle magnetization measurements for the series II are shown in figure 12. These results are also similar to those of series I, showing a T_C of (421 ± 1) K for the sample with 20 hours of milling and the precipitation effects for high temperature measurements. On the other hand, as seen in the figures 9(b) and 12 for samples with long milling times, on cooling from the high temperatures the magnetization values around 800 K are lower than those on heating. This behaviour may be associated to a formation of magnetic particles with multidomains.

Therefore, by combining the results of x-ray, EDS and magnetization under fields and temperatures it can be concluded that samples I (210 hours) and II (20 hours) are a $(\text{Fe}_2\text{Co})_{0.30}\text{Cu}_{0.70}$ supersaturated solid solution. It is important to mention that Mössbauer spectroscopy has also been performed in milled materials of series II and the same effect as described for series I (the loss of Mössbauer transmission signal) was observed. In series II the particles are much larger than those observed in series I. The large particle size effect observed in series I and II may be understood due to the non-utilization of process agent controls like methanol or acetone that sometimes are used in some works for rich Cu and Ag milled alloys to reduce the particle size. The procedure was not used in our case to avoid contamination of the samples, an effect observed in some reported works.

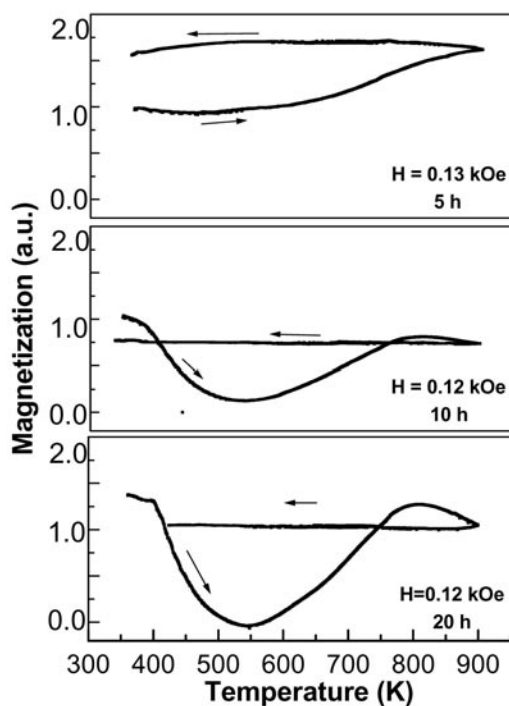


Figure 12. Magnetization as a function of temperature for series II at different milling times.

3.4. Heat treatment at high temperatures of the final milled materials of samples I and II

This section presents the results of the heat treatment of samples I and II, performed under a flux of high purity Ar atmosphere, in order to study the formation of the magnetic particles precipitated in the non-magnetic matrix. Figure 13 shows the x-ray diffraction patterns of samples I (210 hours) and II (20 hours) treated at 675 and 875 K. The temperatures were selected based on the DSC and the high temperature magnetization analyses. No oxide phases were observed in the x-ray patterns.

The x-ray diffraction patterns of the samples I and II heat treated at 675 and 875 K are very similar, showing basically the Bragg peaks at the angular positions of Cu metal plus new reflection lines at angular positions of bcc phase. The angular position of the most intense bcc Bragg peaks of samples I and II heat treated at 875 K are also shown in figure 13, as an inset plot. Fittings of the bcc Bragg peaks with Lorentzian lines were performed in order to obtain their angular positions. According to the results of Fe–Co phase reported by Bayliss (1990), the x-ray patterns indicate bcc Fe/Co precipitates in sample I. In the sample II case, the high temperature formed precipitates produce Bragg peaks at pure polycrystalline Fe metal positions. Also, in sample II some asymmetry can be observed around higher angle fcc-Cu positions. Therefore, as mentioned before, the angular positions of Co lines are very close to those of Cu and this asymmetry in Cu lines, may indicate the formation of pure Co metals precipitates. Therefore, the heat treatments lead to the formation of a bcc Fe/Co alloy particle in sample I and bcc Fe and fcc Co phases in sample II. In both cases the particles were dispersed in the Cu matrix. From the analysis of x-ray results, using the Scherrer formula, the grain size values (D_c) of these precipitates were estimated and are shown in table 1.

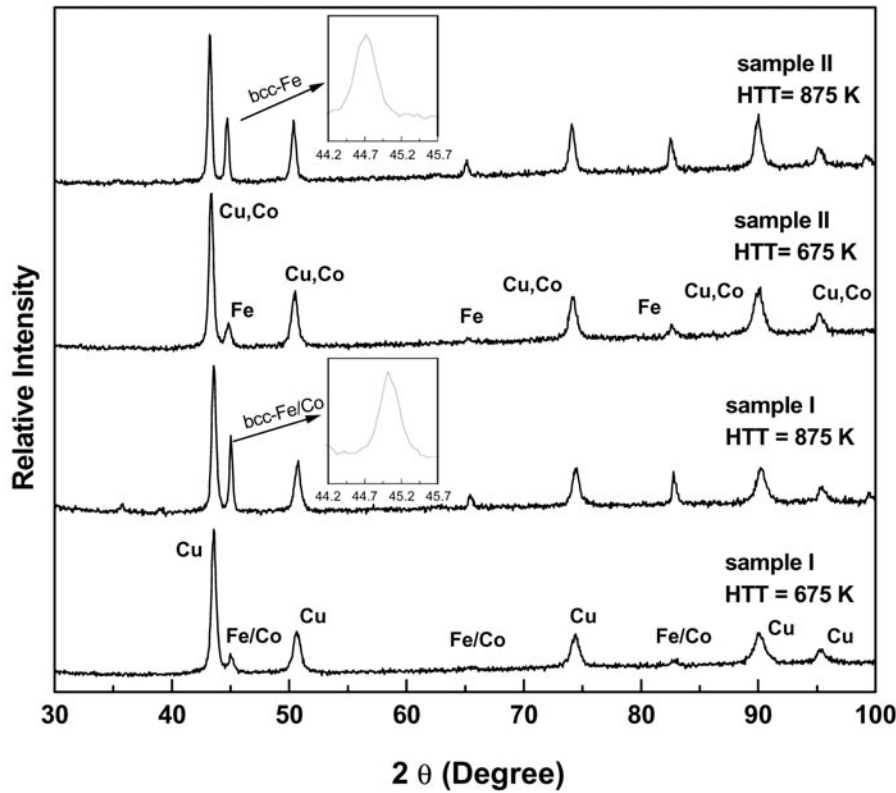


Figure 13. X-ray diffraction patterns of samples I and II treated at 675 and 875 K.

Table 1. Crystalline grain sizes (D_C), estimated from the most intense Bragg peaks of fcc Cu; bcc Fe, and Fe/Co phases, for different heat treated samples; particles diameters (D_P) calculated from the coercivity field values. In the case of sample II, D_P were calculated supposing a pure contribution of Fe or Co particles. The symbol HTT means heat treatment temperature.

HTT (K)		Sample I	Sample II	Sample II
		Fe/Co (Å)	Fe (Å)	Co (Å)
675	D_C	138	123	—
675	D_P	145	198	77
875	D_C	161	242	—
875	D_P	170	734	80

Magnetization measurements as a function of applied magnetic field, at 300 K, are shown in figure 14(a) for samples I and II heat treated at 675 and 875 K. Figure 14(b) is an amplification of the inner part of the hysteresis curves shown in figure 14(a). These results show that the values of the coercivity fields (H_c) have increased for the heat treated samples when compared with the results of the untreated case (see figure 11). Assuming, the well known behaviour of H_c with the volume of the magnetic particles (Cullity 1972), it can be concluded that our magnetic precipitates, at least for low heat treatment temperature, may work as single magnetic particles. Therefore, we can estimate the sizes of spherical particles, which contribute to the

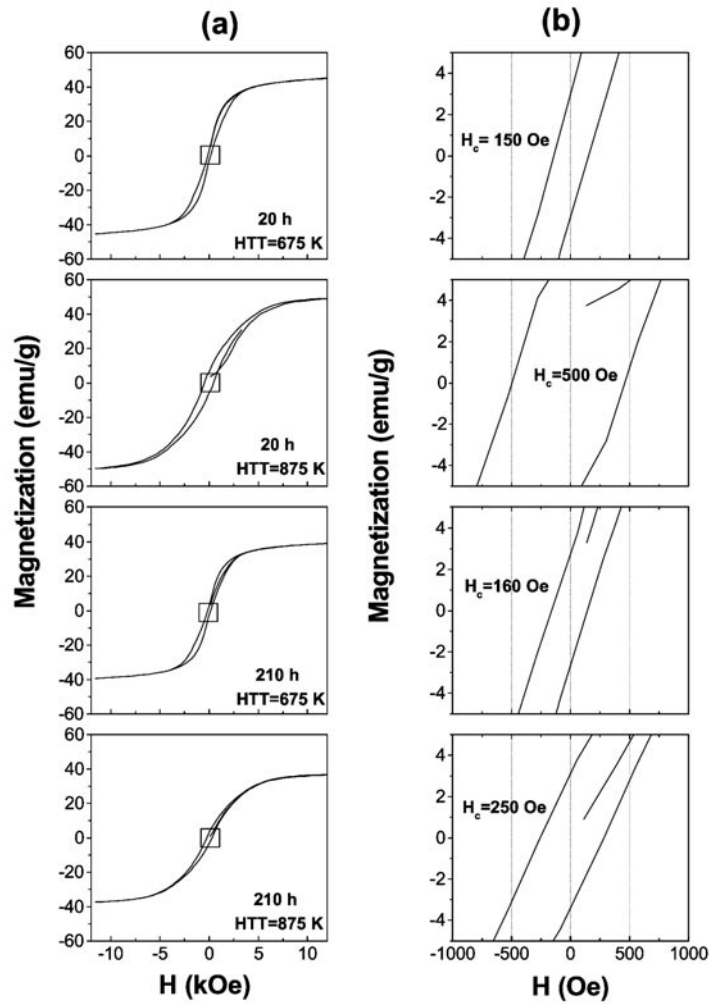


Figure 14. (a) Magnetization curves as a function of applied magnetic field for samples I and II treated at 675 and 875 K; (b) amplification of the inner parts of the hysteresis magnetization curves of samples I and II treated at 675 and 875 K.

magnetization curves of the two samples from the coercivity fields (Cullity 1972):

$$H_C = \frac{2KV}{\mu} \left[1 - 5 \left(\frac{k_B T}{kV} \right)^{\frac{1}{2}} \right] \quad (1)$$

where K is the anisotropy energy per unit volume, V is the volume and μ is the magnetic moment of the magnetic particles. As suggested by the $M \times H$ experimental results the magnetic particle forms a single domain and therefore μ can be expressed by

$$\mu = V \left(\frac{N_A}{V_c} \mu_c \right) \quad (2)$$

where N_A is the Avogadro number, V_c is the volume of molar Fe or Fe/Co alloy and μ_c is $2.2 \mu_B$ for the iron moment and $2.4 \mu_B$, estimated from the B , for the Fe/Co moment. Assuming that the particles on average have a spherical shape and we may take for the constant K values

for Fe and Fe/Co bulk (Wijn 1991, Cullity 1972), the particle diameters are estimated and are shown in table 1. In the analysis of sample II, we have assumed that the main contribution of coercivity fields comes from Fe or Co particles. The estimated average sizes of our magnetic particles are in the range of those found for the single domain particles in conventional magnets (Cullity 1972).

Summarizing, by combining the results of x-rays and magnetization under applied field of treated and untreated samples I and II it can be concluded that the heat treatment promotes the precipitation of single domain magnetic particles of bcc Fe/Co alloy (sample I) and of bcc Fe and fcc Co magnetic particles (sample II) dispersed in Cu matrices. The magnetic precipitates have an average diameter of 150 Å, which is in accordance with the value observed for a single domain in conventional magnetics (Bean *et al* 1959 and Cullity 1972).

4. Conclusions

The present work shows significant results about the magnetic properties of the Fe₂Co alloy and (Fe₂Co)_{0.30}Cu_{0.70} supersaturated solid solution obtained by high energy milling. The samples of (Fe/Co)Cu were prepared in two different ways: in series I, the Fe₂Co alloy was initially obtained by milling a mixture of Fe and Co powders and, finally, the formed alloy was added to Cu powder for further milling. Series II was obtained by milling the mixture of Fe, Co and Cu powders, at the same nominal composition as the previous one. For series I, in the first step of preparation, it was possible to observe the formation of two distinct behaviours of the bcc Fe₂Co alloy: one associated to bcc large particles of Fe₂Co alloy and another one associated to small particles of the same alloy.

For both series I and II the results of x-rays, EDS and of magnetization versus applied magnetic field and temperature lead us to conclude that the milling process induces the formation of a (Fe₂Co)_{0.30}Cu_{0.70} crystalline supersaturated solid solution. The alloys show a typical behaviour of a magnetic material with T_c at about (420 ± 1) K.

Heat treatment on the final milled materials of samples I and II promotes the precipitation of bcc Fe/Co single domain magnetic particles (sample I) and of pure Fe and Co single magnetic domains into the Cu matrix (sample II). The average sizes estimated from the coercivity fields of the heat treated samples are in the order of 150 Å. The results of heat treatment have shown that the atomic distributions of Fe and Co atoms in the Cu matrix of the supersaturated solid solution seem to be different in samples I and II, because their precipitates are different.

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