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Evidence of small crystallites in milled Fe/Co alloy observed by Mössbauer spectroscopy

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Structural and magnetic properties of nanocrystalline $Fe_{0.67}Co_{0.33}$ alloy prepared by high energy ball milling have been studied by x-ray diffraction and Mössbauer spectroscopy. The x-ray diffraction pattern of the sample milled for 160 hours indicates the existence of a single bcc phase. On the other hand, Mössbauer measurements, at different temperatures, show that the milled sample has two magnetic components with the same average hyperfine parameters. One sextet component is associated with large crystallites of bcc $Fe_{0.67}Co_{0.33}$ alloy, stable in vacuum up to 825 K and the other component is attributed to small crystallites of $Fe_{0.67}Co_{0.33}$, alloy having sizes in the range from 10 to 18 nm.

1. Introduction

In the last decade, mechanical alloying by the milling method has been applied intensively to produce non-equilibrium phases of systems with a positive heat of mixing [1]. Thus, states such as amorphous [2], quasicrystalline [3] and nanocrystalline [4] have been obtained by milling mixture of elemental powders to produce binary and ternary alloys [5].

In general, the crystalline materials produce by milling method present a large number of defects, strains and reduced crystalline grains and particles sizes. It has been recently reported, that Mössbauer spectroscopy used for analyze milled materials, indicates the existence of two components to fit the spectra obtained from alloys where the x-ray diffraction pattern shows a single crystalline phase: one component is associated to the part of the material that keeps the "bulk" hyperfine parameters of the crystalline phase and the second component attributed to the contribution from very small crystallites [5, 6]. Usually, the latter component has its average hyperfine parameters similar to those of the former component, but with broader magnetic hyperfine field distribution. The reported small crystallites to "bulk" ratio obtained from the Mössbauer relative absorption area is approximately 1 : 3. The attribution of components model used to fit the Mössbauer spectra of single crystalline phase materials obtained by milling has been based on the improvement of the fit and on the similarity among the hyperfine parameters of the components. To our knowledge the attribution made to the observed components needs additional experimental evidences.

Since it is well known that Fe/Co alloys are stable up to the respective melting point of the elements, at about 1500°C [7], in the present work it has been applied milling to produce $Fe_{0.67}Co_{0.33}$ alloy, x-ray diffraction and Mössbauer spectroscopy to characterized the different "phases" of the formed alloy. The idea is to use x-ray diffraction to display the existence of a single crystalline phase of Fe/Co alloy. The Mössbauer spectroscopy analysis of this alloy, measured at different temperatures, indicates that the two components of the spectra are related with the crystallite sizes.

2. Experimental conditions

$Fe_{0.67}Co_{0.33}$ alloy was obtained from high purity chemical elemental powders of Fe and Co (99.99%). The alloy was prepared by milling the mixture of the elemental powders for times up to 160 hours. The total mass of the produced alloy was about 7 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. The powder manipulation was done inside a glove box under high purity Ar atmosphere to prevent the oxidation and contamination with other gases.

X-ray diffraction patterns (XRD) were obtained for all milled samples with the Cu-K_α radiation, at room temperature (RT).

^{57}Fe Mössbauer spectra of the collected samples were measured with ^{57}Co : ***Rh*** radioactive sources in a conventional transmission geometry at 4.2 K (sample of 160 hours of milling) and at RT (samples of 49, 111 and 160 hours of milling). High temperature measurements were performed using an Austin furnace coupled with a ultra high vacuum pump, giving a residual pressure value better than 10^{-5} Torr during the experiments. Mössbauer spectra of the $Fe_{0.67}Co_{0.33}$ alloy milled for 160 hours were taken as a function of temperature with the ^{57}Co : ***Rh*** source being kept at RT. Each spectrum was measured during 24 hours at the specified temperatures, followed by another run at RT. The center shift

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(CS) values of our measurements were taken relatively to α-Fe at RT and are not corrected for second order Doppler effect. However, the Mössbauer spectra shown in the figures are presented relative to the source.

The final composition of the alloy has been checked by scanning electron microscopy using x-ray energy dispersive (EDS) analysis, and the results show that the Fe content in the milled sample is the same of the initial nominal composition. No contramination with Cr has been observed in the sample milled for 160 hours.

3. Results and discussion

Fig. 1 presents the $Fe_{0.67}Co_{0.33}$ x-ray diffraction patterns as a function of milling time. The diffraction pattern, of the zero hour sample, displays 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 sample diffraction pattern shows basically three Bragg peaks with angular positions of the bcc crystalline structure of α-Fe, slightly 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 reached the largest shift and then remain unchanged for longer milling times. The obtained milled $Fe_{0.67}Co_{0.33}$ alloy has Bragg lines at angular positions close to that reported for bcc Fe/Co phase [8], but with slightly broader line widths. These results give us, at least, two indications: (1) the pure bcc phase of $Fe_{0.67}Co_{0.33}$ alloy has been formed for milling time equal and longer than 111 hours; (2) the milling process leads to grain refinement, producing the smallest crystalline grain size of about 15 nm, as estimated from Scherrer equation.

The RT Mössbauer spectra of $Fe_{0.67}Co_{0.33}$ alloy as a function of milling time are shown in Fig. 2. For the 49 hours milling time sample, the Mössbauer spectrum presents a magnetic splitting with broad line width and asymmetric outer lines, indicating that it should be analyzed with more than one magnetic component. The fitting of this spectrum was carried out with two magnetic subspectra: one magnetic crystalline component with line width slightly broad ($\Gamma = 0.40$ mm/s) and hyperfine parameters values of $CS \approx 0.04$ mm/s and $B_{hf} \approx 35$ T associated to large crystallites (LC) of bcc $Fe_{0.67}Co_{0.33}$ alloy. A second magnetic component was fitted with a distribution of magnetic hyperfine field: the obtained average hyperfine parameters values are similar to the previous magnetic component. This latter component was attributed to small crystallites (SC) of the bcc $Fe_{0.67}Co_{0.33}$ alloy in reasonable accordance with reported results of the literature [5, 6]. Therefore, the components observed in the RT Mössbauer spectra of the present milled samples are due to large and small crystallites and are named here as LC-$Fe_{0.67}Co_{0.33}$ and SC-$Fe_{0.67}Co_{0.33}$, respectively. These terms will be used now on to distinguish the bcc $Fe_{0.67}Co_{0.33}$ phase with different crystallite sizes. The model used to fit the Mössbauer spectra of the $Fe_{0.67}Co_{0.33}$ milled alloy and its crystallite sizes attribution have been based on the high temperature Mössbauer measurements where oxidation effects give further supported to the fitting model concerning the identification of the magnetic components. Backing to the results shown in Fig. 2, it can be seen that by increasing the milling time, from 49

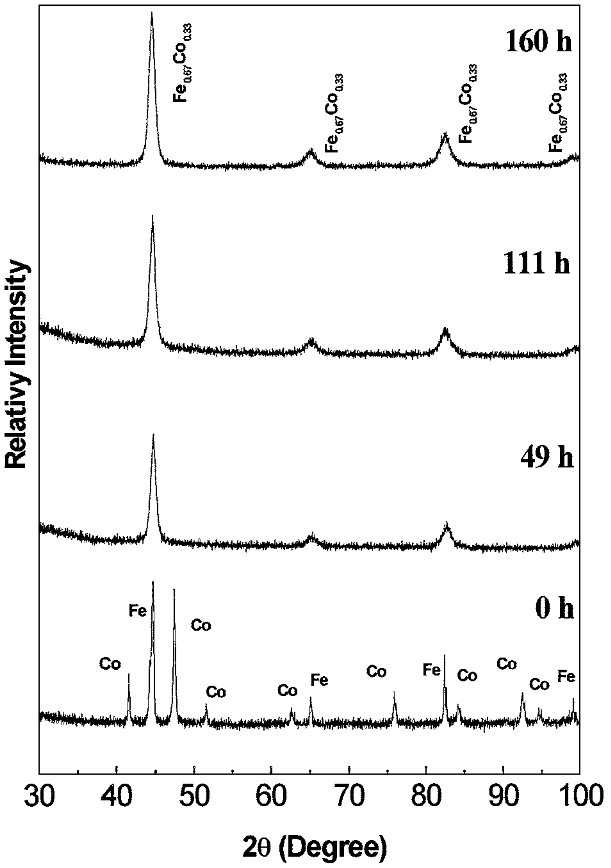

Figure 1 X-ray diffraction patterns of the $Fe_{0.67}Co_{0.33}$ milled alloy as a function of milling time.

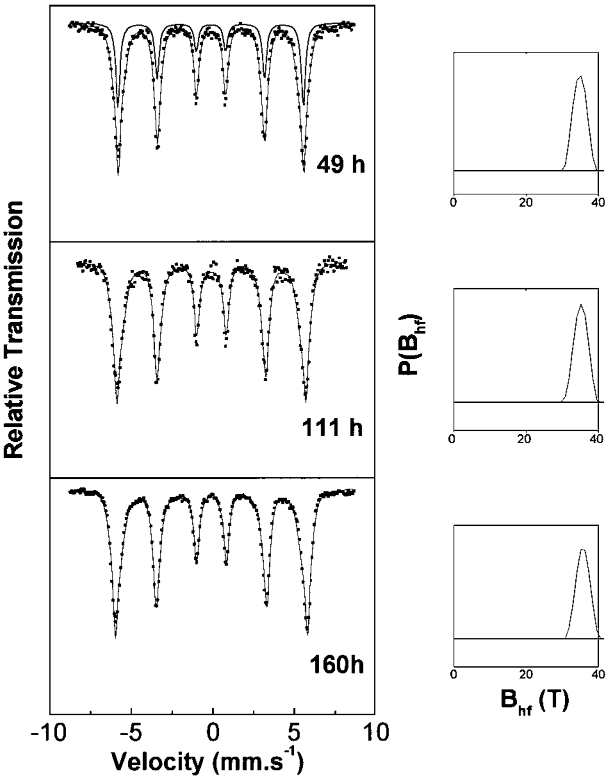

Figure 2 Room temperature ^{57}Fe Mössbauer spectra of the $Fe_{0.67}Co_{0.33}$ milled alloy as a function of milling time.

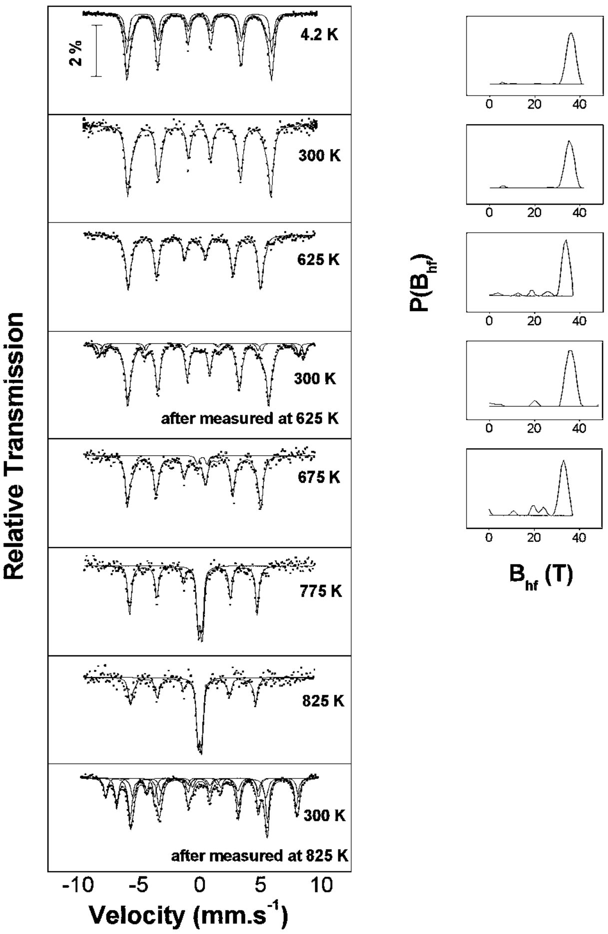

Figure 3 Temperature dependence of the ^{57}Fe Mössbauer spectra of the $Fe_{0.67}Co_{0.33}$ alloy milled for 160 hours performed in a furnace under vacuum of about 4×10^{-5} Torr. The Mössbauer spectra are displayed relative to the source.

to 160 hours, no significant change is observed in the shape of the Mössbauer spectra. However, some points must be mentioned: (1) the relative absorption area associated to SC-$Fe_{0.67}Co_{0.33}$ alloy increases with the milling time from 29 to 35%; (2) the magnetic hyperfine field values of the components also increase with milling time up to 111 hours remaining roughly unchanged for longer times and, finally, (3) the central shift values of the components do not change with milling time. The hyperfine parameters obtained from the fits of the Mössbauer spectra are shown in Table I.

Fig. 3 shows the Mössbauer spectra of the 160 hours sample as a function of temperature, from 4.2 up to 825 K. The spectrum at 4.2 K is similar to that obtained at 300 K, but with the expected higher magnetic hyperfine field values. At 625 K, the magnetic hyperfine field distribution curve (at right side of the Fig. 3) show values higher than those obtained at lower temperatures ($T < 625$ K), indicating that new effect has occurred in the sample at about this temperature. On the other hand, the spectrum at 300 K, obtained after the Mössbauer measurement at 625 K, shows the LC and SC initial components plus two new magnetic components (called here as A and B), having its hyperfine parameters close to those of the α-Fe_2O_3 and $CoFe_2O_4$ [9], indicating a partial transformation of the initial magnetic components. However, since the LC sextet component has at, and above, 775 K similar relative area of about 65% as obtained at 300 K for the as-milled sample and, as reported by Asano *et al.* [10], the bcc Fe/Co alloy has a higher order-disorder magnetic transition temperature, the doublet observed at 775 K is attributed to the A and B components in the paramagnetic state. The results indicate that oxidation process has taken place mainly in the SC-$Fe_{0.67}Co_{0.33}$ particles during the high temperature Mössbauer measurements. As shown by Schuele *et al.* [9], the blocking temperatures, indicated by the Mössbauer data of $CoFe_2O_4$ oxide particles, are in the range from 650 K to 793 K for size values between 18 nm to 10 nm, respectively which may indicate that the SC-$Fe_{0.67}Co_{0.33}$ particle sizes are in the same range, if it is to consider that the oxidation process would roughly preserve the particle sizes. At 300 K, the spectrum of the same sample, after measured at 825 K, has basically the same three magnetic components: the sextets, attributed to the LC-$Fe_{0.67}Co_{0.33}$, the A and the B components. Therefore, during the thermal cycle, the relative area of the crystalline sextet remains nearly constant, at about 65%, while the component initially fitted with the magnetic hyperfine field distribution has been gradually transformed into the A and B oxides (Fig. 5c). The oxidation process of the SC-$Fe_{0.67}Co_{0.33}$ phase, occurring even under vacuum of about 10^{-5} Torr, can be understood as due to the particles high surface to volume ratio. Thus, high temperature measurements produce oxidation of the small crystallites of the $Fe_{0.67}Co_{0.33}$ alloy (SC-$Fe_{0.67}Co_{0.33}$), reassuring the presence of the large and stable bcc crystallites of $Fe_{0.67}Co_{0.33}$ alloy (LC-$Fe_{0.67}Co_{0.33}$). Fig. 4 shows the x-ray diffraction patterns of the as-milled $Fe_{0.67}Co_{0.33}$ sample (Fig. 4a) and of the same sample annealed at 825 K (Fig. 4b). This figure also help us to understand the oxidation effect that occurred basically in SC-$Fe_{0.67}Co_{0.33}$ phase, since the x-ray pattern of the annealed sample displays Bragg peaks of the bcc $Fe_{0.67}Co_{0.33}$ alloy (Fig. 4b) narrower than those observed for the as-milled sample (Fig. 4a). It is also evident, in the x-ray pattern of the annealed sample, the presence of the mentioned Fe oxides ($CoFe_2O_4$ and Fe_2O_3) Bragg peaks. However, there are no evidence of pure Fe and Co segregated phases and of Co oxides.

TABLE I Hyperfine parameters of $Fe_{0.67}Co_{0.33}$ alloy milled for different times, obtained from the fittings of the Mössbauer spectra

	LC component			SC component		
Milling time (h)	B_{hf} (T)	CS (mm/s)	Area (%)	$\langle B_{hf}\rangle (T)$	$\langle$CS$\rangle$ (mm /s)	Area (%)
49	35.0 ± 0.3	0.04 ± 0.01	73	35.0 ± 0.3	0.03 ± 0.01	27
111	36.0 ± 0.3	0.03 ± 0.01	69	36.0 ± 0.3	0.05 ± 0.01	31
160	36.3 ± 0.3	0.05 ± 0.01	65	36.4 ± 0.3	0.04 ± 0.01	35

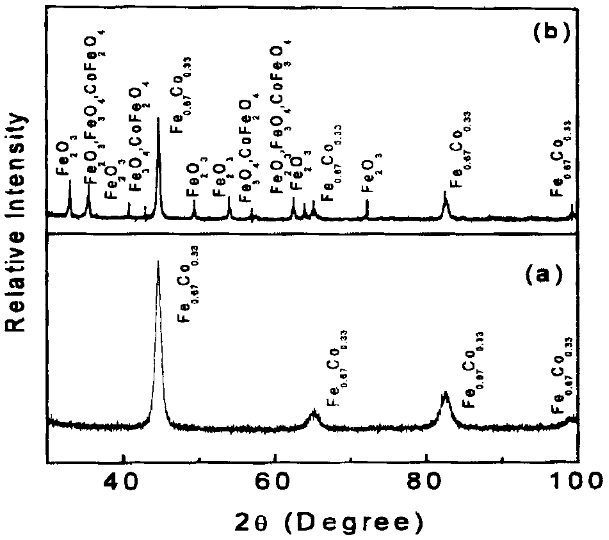

Figure 4 X-ray diffraction patterns of the $Fe_{0.67}Co_{0.33}$ alloy (a) milled for 160 hours (as-milled) and (b) the same sample after annealed at 825 K.

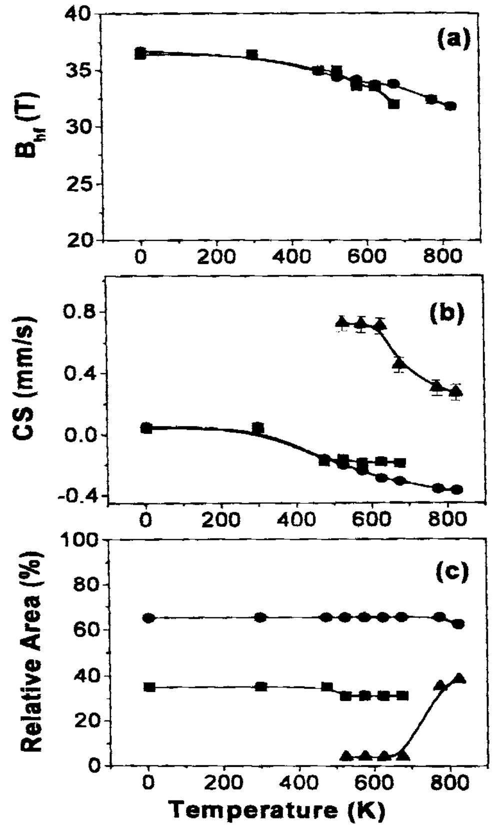

Figure 5 Behavior of the B_{hf} (a), CS (b) and the relative area (c) as a function of temperature for each component observed in Mössbauer spectra of the milled $Fe_{0.67}Co_{0.33}$ alloy. The full circle symbols are associated to the LC-$Fe_{0.67}Co_{0.33}$ (sextet), the full square to the SC-$Fe_{0.67}Co_{0.33}$ (magnetic distribution component) and the full triangle to the Fe oxides. The lines connecting the points are a guide to the eyes.

The behavior of the hyperfine parameters of each component observed in the sample milled for 160 hours, as a function of temperature, are shown in Fig. 5. The B_{hf} (Fig. 5a) and CS (Fig. 5b) values follow the expected trends, i.e. the B_{hf} and the CS values reduce with increasing temperature. The temperature behavior of the CS values is due to the second order Doppler shift contribution, which tends to negative values as the temperature increase, in those cases where the source and the absorber are set at different temperatures.

Recently, Bonetti *et al.* [11] have shown that milling pure metallic Fe yields a phase, observed by magnetization measurements, that is associated to the grain boundary of nanocrystalline iron. This reported experimental results evidences the interface component in the milled pure Fe and it could also be used as a model to explain the broad magnetic distribution component observed in the present Fe/Co alloy Mössbauer spectrum. In such case the oxidation process of the bcc $Fe_{0.67}Co_{0.33}$ alloy could be understood as due to the interface regions. However, due to the total oxidation of the broad magnetic Mössbauer component, observed after the sample heating, it is seems to be reasonable to expect that the small particles may oxidize easier than the interface regions inside of the particles.

4. Conclusion

The present results, based on the milled $Fe_{0.67}Co_{0.33}$ alloy, indicate that: (i) the Mössbauer magnetic components of $Fe_{0.67}Co_{0.33}$ alloy were associated to different sizes of the bcc $Fe_{0.67}Co_{0.33}$ magnetic particles; (ii) the A and B magnetic phases observed after high temperature heat treatments were associated to α-Fe_2O_3 and $CoFe_2O_4$, respectively; (iii) large crystallites of bcc $Fe_{0.67}Co_{0.33}$ alloy are stable in vacuum furnace at temperatures as high as 825 K; (iv) the magnetic component associated to the small crystallites of the $Fe_{0.67}Co_{0.33}$ alloy are more sensitive to any presence of oxygen at high temperatures, leading to the formation of Fe oxides even at atmosphere pressures as low as 10^{-5} Torr, mainly due to the higher surface to volume ratio and the presence of residual gas in the furnace; (v) the Mössbauer doublet observed above 650 K is associated to superparamagnetic particles of $CoFe_2O_4$ and α-Fe_2O_3 which may indicate that the alloy SC component have particle sizes in the range of 10 to 18 nm.

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