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Synthesis and characterisation of nanostructured FeCo alloys

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Nanocrystalline $Fe_{(1-x)}Co_x$ ($x = 0.12, 0.5, 0.6$) mixtures have been prepared by mechanical alloying using a planetary ball mill under several milling conditions. The alloying process between the elemental powders and the microstructure changes of the prepared samples have been investigated using X-ray diffraction (XRD) and ^{57}Fe Mössbauer spectrometry. The XRD patterns refinement on the mechanical alloying products according to the Rietveld method (Maud software) reveals the allotropic transformation of Co from fcc to hcp form and the progressive dissolution of Co into the α-Fe lattice as a function of both Co concentration and milling conditions. The grain size values of the obtained powders reaches a nanometer scale of about 10 nm.

Mössbauer results show that the beginning of the solid state reaction between Fe and Co elemental powders depends on the milling conditions. After 24 h of milling, the average hyperfine magnetic fields values of $Fe_{88}Co_{12}$, $Fe_{50}Co_{50}$ and $Fe_{40}Co_{60}$ mixtures are consistent with a disordered and an ordered FeCo solid solution, respectively.

1. Introduction

In recent years, a great deal of attention has been devoted to the mechanical alloying process used to prepare nanostructured materials. It has been shown that the milling conditions could influence the microstructure of the milled compounds, the end product of the milling treatment and the path to the later state [1].

The FeCo nanocrystalline materials represent a topic of growing interest in the field of magnetic materials because of their enhanced physical properties compared to those of materials with a more conventional grain size [2]. The Co content effect on the FeCo alloys structure has been proved. Thus, it was found that FeCo is a substitutional alloy with a bcc structure from pure Fe to about 80 at.% Co, it is fcc for 90 at.% Co [3].

In this work, the milling conditions effects on the microstructure of the nanostructured FeCo alloys are studied by XRD and Mössbauer spectrometry.

2. Experimental details

Elemental Fe and Co powders with high purity were used as the starting materials and mixed at the desired compositions (12, 50 and 60 at.% Co) in a planetary ball mill (Fritsch Pulverisette 7). The milling process was carried out at: (i) $V_1 = 750$ rpm for the $Fe_{88}Co_{12}$ (sample A) and $Fe_{40}Co_{60}$ (sample B) mixtures with five balls (Φ12 mm) and a ball to powder weight ratio $R_1 = 35/1$; (ii) $V_2 = 400$ rpm for the $Fe_{50}Co_{50}$ mixture (sample C) using three balls (Φ15 mm) and a ball to powder weight ratio $R_2 = 20/1$. In both cases, the stainless steel vials were sealed under Ar atmosphere inside a glove box.

The powder mixtures were characterized by a Siemens D501 X-ray diffractometer using Cu K_α radiation. XRD patterns refinement has been performed using MAUD program based on Rietveld method [4]. Mössbauer spectra were recorded at room temperature in a transmission acceleration geometry mode with a ^{57}Co source in a Rhodium matrix. The Mössbauer spectra were fitted with the Mosfit program [5].

3. Results and discussions

The XRD patterns of $Fe_{(1-x)}Co_x$ powder mixtures milled for several times are presented in Fig. 1. It can be easily seen that for the initial powders mixtures, Bragg peaks of elemental Fe and Co are observed. Upon milling, the broadening of the XRD peaks and the reduction in their intensities are attributed to the grain refinement and to the strain accumulation induced

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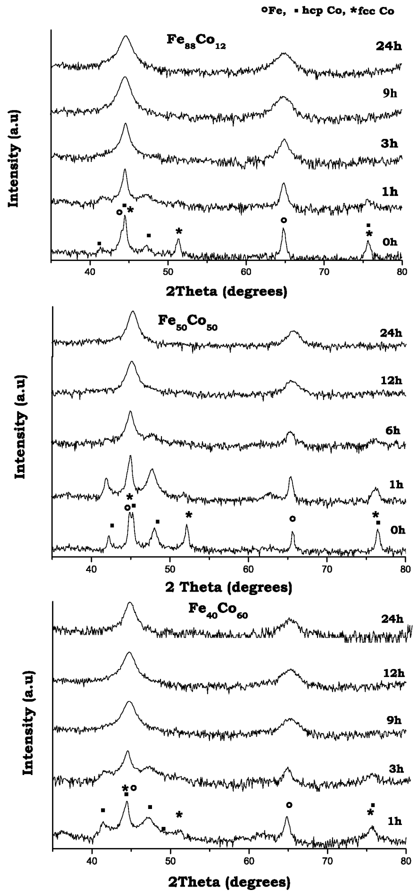

Figure 1 X-ray diffraction patterns of $Fe_{(1-x)}Co_x$ powder mixtures milled for different milling times.

during the milling process. In fact, the Rietveld refinement results show that during the first 6 h of milling, the crystallite size decreases rapidly to the nanometer range. Further crystallite size reduction proceeds slowly and the final average grain size is in the order of 10–12 nm. Simultaneously, the internal strain increases rapidly and remains nearly constant upon further processing.

From the XRD patterns of mechanically alloyed Fe and Co mixtures under the two different milling conditions, it is clear that the disappearance of the fcc Co lines (which may be due to the allotropic transformation of Co from fcc to hcp form) occurs after 1, 3 and 6 h of milling for samples A, B and C, respectively. While, the complete vanishing of the Co lines and therefore the diffusion of Co into the Fe matrix, takes place after 3, 6 and 12 h of milling for samples A, B and C, respectively. So, one can notice that the disappearance of both fcc and hcp Co lines is Co content and milling conditions dependent. In general, high intensity and large ball to powder weight ratio can promote faster reaction rate. This is because the number of collision per unit time increase as the number of balls increases. At the same time, increase in collision frequency results in an increase in milling temperature, which in turn leads to faster diffusion process.

For the sample A, the lattice parameter deduced from the XRD patterns refinement, presents the same variation as a function of the milling time in comparison with that of the milled pure Fe [6]. This behavior may be due to the lower Co content (12%). However, for the higher Co concentrations, the lattice parameter decreases during the first 9 and 12 h of milling for samples B and C, respectively. This is evident by the slight shift of 2θ angles of the XRD peaks due to the dissolution of Co into the Fe lattice and therefore to the formation of FeCo solid solution. Because the diffusivity of Co into Fe is larger than that of Fe in Co, more Co diffuses into Fe [7]. The stationary state which is reached on further milling time is confirmed by the constant values of the lattice parameters. The above results allow us to conclude that the lattice parameters of Fe and Co mixing and of the end products is Co content dependent (Fig. 2). This result is in a good agreement with earlier studies on the FeCo powder mixtures [8].

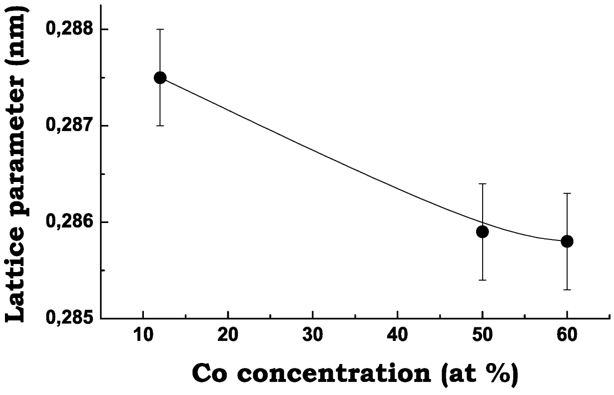

Figure 2 Lattice parameters of FeCo solid solutions versus Co content (x) in the compounds milled for 24 h.

Mössbauer spectra for the $Fe_{(1-x)}Co_x$ compounds are shown in Fig. 3 as a function of the milling time. During the first 3 h of milling, the Mössbauer spectra are consistent with a sextet having an average hyperfine magnetic field of about 33 T corresponding to unreacted Fe. On further milling time, the broadening of the Mössbauer lines and their shift towards higher hyperfine fields are attributed to the mixing of Fe and Co and consequently to the presence of Co atoms as first and second nearest neighbors of Fe atoms. In fact, it is well known that the presence of one Co atom in the vicinity of the Fe atoms increases the hyperfine magnetic field by about 0.8 T [9]. Furthermore, the beginning of lines broadening corresponding to the starting of the reaction between elemental powders depends on the milling conditions and Co content. Thus, the substitution of Fe atoms by Co ones takes place after 6, 3 and 9 h of milling respectively for samples A, B and C.

The average hyperfine magnetic field variations (Fig. 4) which describe the evolution of the inter diffusion reaction between Fe and Co, can be divided into 3 steps:

(i) A plateau, up to 3 h of milling, with a constant value of about 33 T corresponding to the unreacted Fe.

(ii) A rapid increase, between 3 and 12 h of milling, related to the mixing of the Fe and Co powders.

(iii) A plateau, above 12 h of milling, for samples A and B and a slow increase for the sample C, attributed to the FeCo solid solution formation.

For the stationary state, the obtained values of about 35 T for samples A and C and 34.28 T for sample B

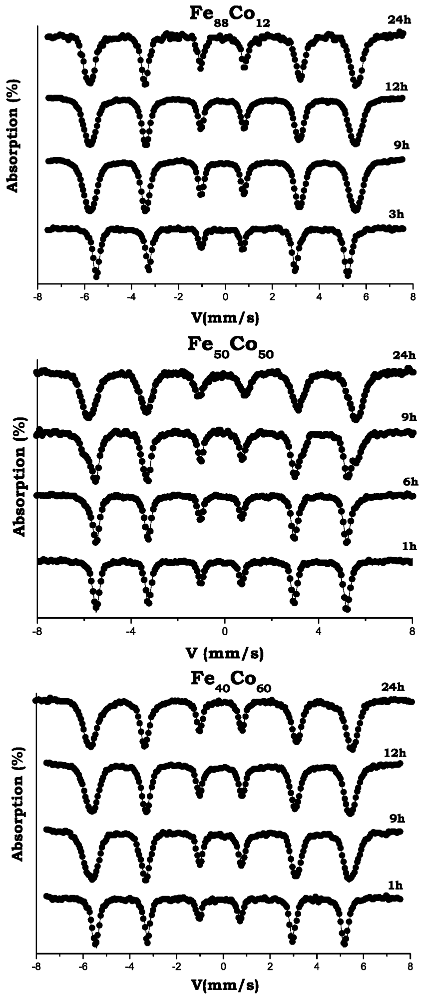

Figure 3 Mössbauer spectra for $Fe_{(1-x)}Co_x$ powder mixtures milled for different milling times.

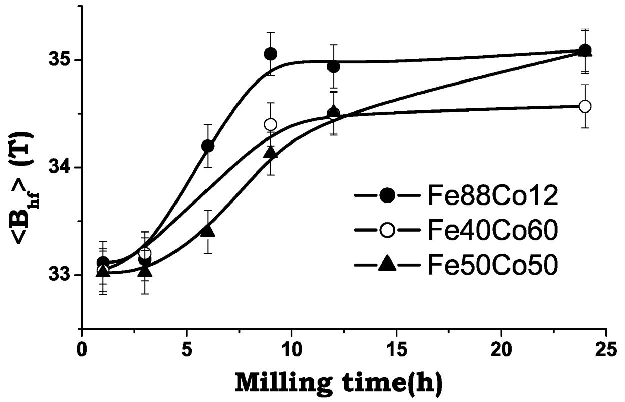

Figure 4 Evolution of average hyperfine magnetic fields of $Fe_{(1-x)}Co_x$ mixtures with the milling time.

are similar to those reported in the literature for the disordered and the ordered FeCo alloys respectively [10]. One can suppose that the differences observed in the behavior of the average hyperfine magnetic field in the case of samples B and C is due to the effect of the Co concentration, since they are milled in the same conditions. While, the difference between samples (A, B) and C can be assigned to both the kinetic of the milling reaction (Vi and Ri, $i = 1, 2$) and the Co concentration. It is obvious that when milling intensity is increased either by increasing the weight of the ball and/or the density of the ball materials or by increasing the speed of collision, more energy will be transferred to the powder particles and more energy will be dissipated in the form of heat which is crucial for the formation of solid solution.

4. Conclusion

The Fe-Co alloys powders were prepared by mechanical alloying process with high-energy ball milling. The XRD patterns show that the Co transforms from fcc to hcp structure in the early stage of milling. On further milling time, the Co dissolves into the Fe bcc lattice leading to the formation of the FeCo solid solution where the crystallite size reaches a nanometer scale.

The lattice parameter and the average hyperfine magnetic field of the end products are Co content dependent. Mössbauer results further show that the starting time of the reaction between Fe and Co powders depends on both milling conditions and Co concentration.

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References

1. P. POCHET, E. TOMINEZ, L. CHAFFRON and G. MARTIN, *Phys. Rev.* B **52** (1995) 4006.
2. G. HERZER, *J. Magn. Magn. Mater.* **157/158** (1996) 133.
3. CH. KUHRT and L. SCHULTZ, *J. Appl. Phys.* **71** (1992) 1896.
4. L. LUTTEROTTI, *MAUD, CPD Newsletter (IUCr)* **24** (2000).
5. F. VARRET and J. TEILLET, unpublished Mosfit program, Université du Maine (France).
6. H. MOUMENI, S. ALLEG and J. M. GRENÈCHE, private communication 2002.
7. LANDOLT-BÖRNSTEIN, New Series, in “Diffusion in Solid Metals and Alloys,” edited by H. Mehrer, Group III (1990) Vol. 26, p. 127.
8. X. L. DONG, Z. D.ZHANG, S. R. JIN and B. K. KIM, *J. Magn. Magn. Mater.* **210** (2000) 143.
9. I. VINCZE, I. A. CAMPBELL and A. J. MEYER, *Solid State Commun.* **15** (1974) 1495.
10. H. HAMDEH, B. FULTZ and D. H. PEARSON, *Phys. Rev.* B **39** (1989) 11233.

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