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Mössbauer study of alloy $Fe_{67.5}Ni_{32.5}$, prepared by mechanical alloying

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Abstract We present the study of effect of the particle size on the structural and magnetic properties of the $Fe_{67.5}Ni_{32.5}$ alloy, prepared by mechanical alloying (MA). After milling the powders during 10 hours they were separated by sieving using different meshes. The refinement of the X-ray patterns showed the coexistence of the BCC (Body Centered Cubic) and the FCC (Face Centered Cubic) phases in all samples with lattice parameters and crystallite sizes independent of the mean particle size. However, big particles presented bigger volumetric fraction of BCC grains. The Mossbauer spectra were fitted with a broad sextet corresponding to the ferromagnetic BCC phase, a hyperfine magnetic field distribution and a broad singlet which correspond to the ferromagnetic and paramagnetic sites of the FCC phase, respectively. Hysteresis loops showed a magnetically, soft behavior for all the samples, however, the saturation magnetization values are smaller for the original powder and for the powders with small, mean, particle size due to the dipolar magnetic interaction and the smaller mean magnetic moment, respectively. These effects were proved by Henkel plots that were made to the samples.

Keywords Mechanical alloying · X-Ray diffraction · FeNi alloys · Mössbauer spectrometry and particle size

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1 Introduction

Fe-Ni melted alloys, especially those near the Invar composition (around 36 at. % Ni) present relevant magnetic, electrical and chemical properties, which can be used to produce pieces that are able to with stand high temperatures, materials for storing large amounts of magnetic information, high strength steels, materials with low thermal expansion coefficient, among others [1, 2].Some works concerning Fe-Ni system had shown that there is a big region of composition, in which the BCC and the FCC phases coexist and the limits of this coexistence depend on the preparation method and the thermal treatment used [3–6]. Valderruten et al. [7] prepared $Fe_{100-x}Ni_x$ samples by Mechanical Alloying (MA) A with $40 \leq x \leq 22.5$. They found that all the samples show the coexistence of the BCC and the FCC phases, in addition, they put forward a new method for adjusting the Mössbauer spectra of this type of samples with two hyperfine magnetic field distributions (HMFD) and a singlet. The HMFDs correspond to the FCC (Taenita) and BCC (Tetrataenita) ferromagnetic phases. The paramagnetic site corresponds to those low- spin Fe sites of the FCC phase,according to some experimental and theoretical reports [8–10].Concerning Fe–Ni Invar alloys calculations based upon first principles have shown that there are several magnetic states and that the energy and volume barriers between each state are very low. Thus, some mixings of the magnetic states, high-spin and low-spin states, are expected to occur with increasing temperature and pressure [11–13].

The aim of this work is to report the effect of the particle size on the magnetic and structural properties of the $Fe_{67.5}Ni_{32.5}$ Invar sample, produced by mechanical alloying. Similar studies had been reported for $Fe_{50}Al_{50}$ and $Fe_{50}Mn_{10}Al_{40}$ disordered alloys [14, 15] but, in our understanding, no one work of this type had been reported for the Fe-Ni system.

2 Experimental design

Iron and nickel powders of high purity (more than 99.9 %) were mixed with the stoichiometry $Fe_{67.5}Ni_{32.5}$, and then MA in a high energy planetary ball mill Fritsch Pulverisette 7 at 280 rpm in an argon atmosphere. Hardened stainless steel vials of 50 ml of volume and balls of the same material with 10 mm of diameter were used. A ratio 20:1 mass –ball: mass - powder and a milling time of 10 hours were used. The obtained powder was sieved in meshes number 18, 35, 60, 120, 230, 400, and 500, in order to obtain powders of mean particle size greater than 1 mm, and between 1 mm and 500 μm, 500 and 250 μm, 250 and 125 μm, 125 and 63 μm, 63 and 38 μm, 38 and 25 μm, and < 25 μm, respectively. The obtained powders were measured in a Transmission Mössbauer Spectrometer by using a radioactive Co-57/Rh source. The spectra were fitted by using the MOSFIT program [16]. A foil of α-Fe was used as calibration sample. The XRD analysis, to establish the structure, the lattice parameter and the mean crystallite size, were performed at room temperature for all samples using aX'Pert MRD of PanAnalytical diffractometer with the Cu-Kα radiation and the patterns were refined by the Rietveld method combined with Fourier analysis to describe the broadening of the lines using the Maud program [17] and [23]. This provided the average values of the lattice parameter, crystallite size and volumetric fraction.

Hysteresis loops were performed using the VSM facility of a Physical Properties Measurement System (PPMS) and finally the Thamm Hesse curves were done to determine the magnetic dipole behavior.

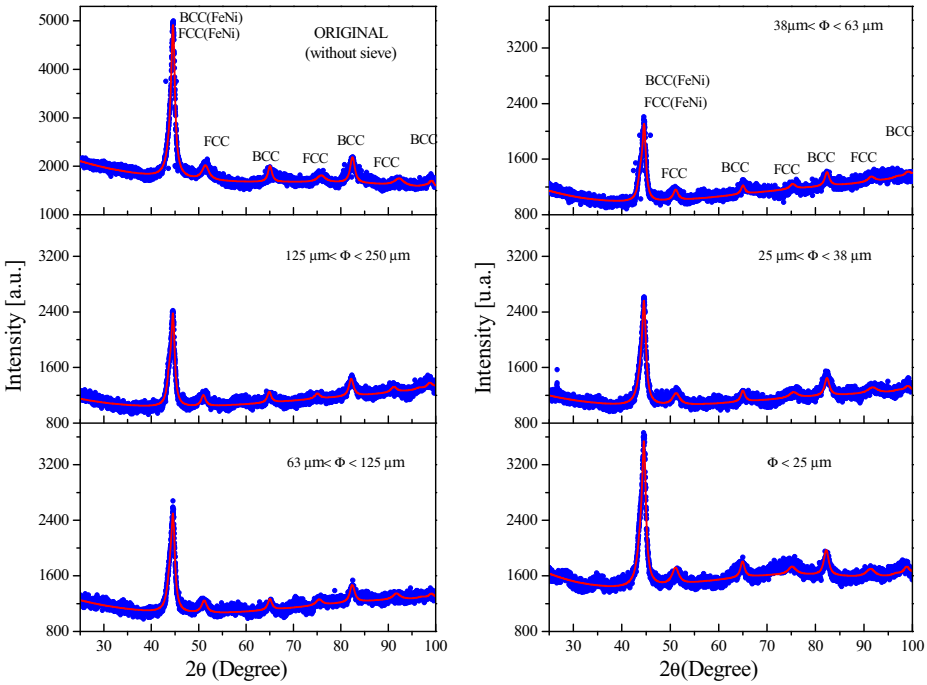

Fig. 1 XRD patterns of $Fe_{67.5}Ni_{32.5}$ samples with different mean particle size

3 Results and discussion

3.1 XRD results

As it is illustrated in Fig. 1, XRD patterns of some of the obtained samples show the same Bragg peaks. They can be attributed to the BCC and FCC crystalline phases. The coexistence of both phases in all the studied samples can be noted. The structural parameters of these phases are shown in Table 1.

It can be observed from these results that lattice parameter for both, BCC ($\sim$ 2.864Å) and FCC ($\sim$ 3.561Å) phases, remains nearly independent of the particle size. The mean crystallite size value of the BCC phase ($\sim$ 14 nm) is higher than that of the FCC phase ($\sim$ 8nm), and both are independent of the particle size. These crystallite sizes indicate that our Fe-Ni particles are nanostructured and if we compare these crystallite sizes (supposing a mean size of 10 nm for both structures) with the particle size range, it can be proved that the mean number of crystallites inside the particles varies nearly from 10^{11} up to 10^{19} for the smallest and biggest particles, respectively. These big quantities of crystallites inside the particles indicate that they present many grain boundaries so many atoms that diffract the X-rays, incoherently. In this way, they contribute to the broadening of the background of the patterns, besides the fluorescence of Fe atoms when they are irradiated by Cu radiation.

As it is shown in Table 1, Fig. 2, the volumetric fraction of the BCC phase and FCC phase increases and decreases, respectively, with the increase of the mean particle size. This

Table 1 Structural parameters obtained from the Rietveld refinement of the XRD patterns

Sample	Phase	Lattice parameter (Å)±0, 0009.	Mean crystallite size (nm)	Volumetric fraction (%)
Original	BCC	2,859	14	67
	FCC	3,539	7	33
$125 < \phi < 250\ \mu$m	BCC	2,871	14	74
	FCC	3,578	11	26
$63 < \phi < 125 < \mu$m	BCC	2,860	13	68
	FCC	3,557	9	32
$38 < \phi < 63 < \mu$m	BCC	2,864	14	66
	FCC	3,566	10	34
$25 < \phi < 38 < \mu$m	BCC	2,863	13	63
	FCC	3,557	6	37
$\phi < 25 < \mu$m	BCC	2,871	13	65
	FCC	3,573	6	35

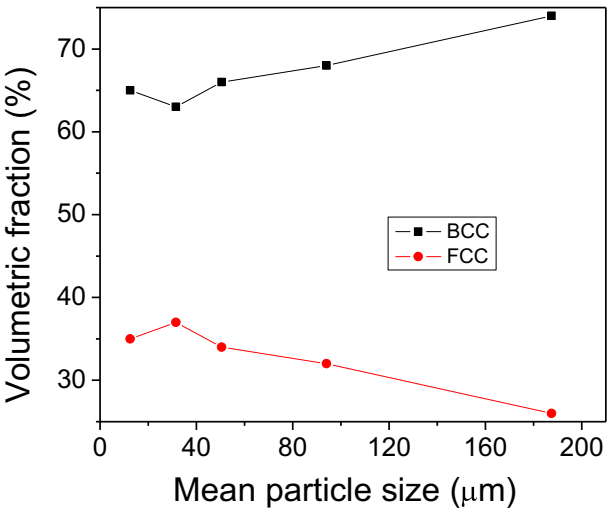

Fig. 2 Volumetric fraction of the BCC and FCC phases vs. mean particle size

result indicates that the grains of the BCC phase are the majority and that they present a bigger tendency to the agglomeration, compared with those of the FCC phase.

3.2 Mössbauer spectroscopy results

Figure 3 shows the Mössbauer spectra recorded at room temperature (RT) of $Fe_{67.5}Ni_{32.5}$ powders milled for 10 h. In this case all the spectra were fitted with a broad paramagnetic site (singlet) with spectral area < 3 %, a broad sextet with a mean spectral area of ∼ 29 %, and a broad hyperfine magnetic field distribution (HMFD) with a mean spectral area of

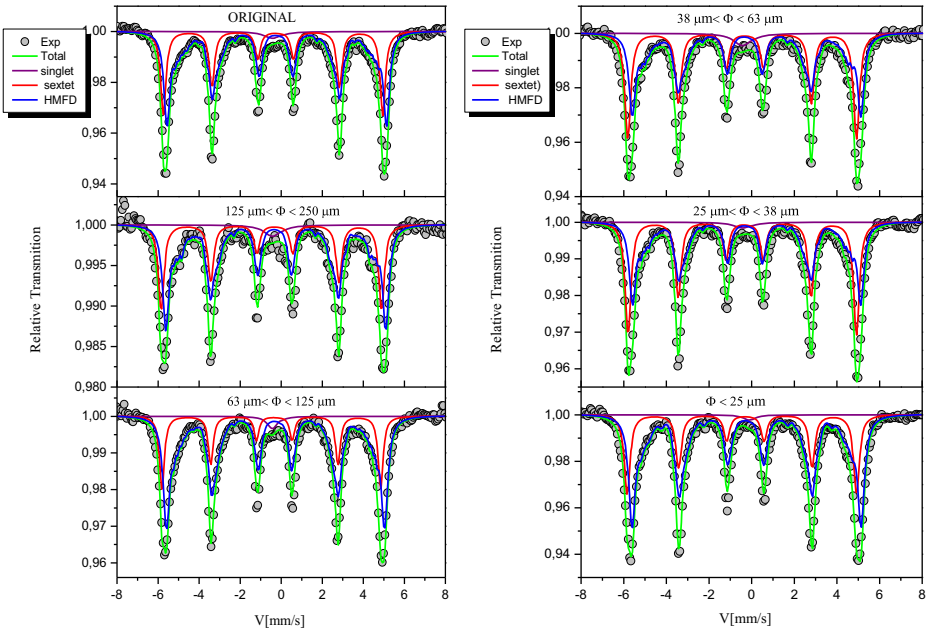

Fig. 3 Fitted room-temperature of the Mössbauer spectra of samples $Fe_{67.5}Ni_{32.5}$ with different mean particle size

$\sim$ 68 %. These three contributions agree with the disordered character of the sample and with the XRD results if we associate the broad sextet to the Fe sites of the BCC (Fe-Ni) phase, and the broad singlet and the HMFD to the Fe sites of the FCC (Fe-Ni) phase. The singlet is consistent with those Fe sites in the FCC phase which are very rich in Fe atoms as neighbors (remembering that Fe in FCC phase is paramagnetic). In the FCC ferromagnetic phase, fitted with a broad HMFD and taking into account former results [3–9], sites of Fe with small number of Ni neighbors were taken; they were associated to low- spin sites, and sites of Fe sites rich in Ni atoms as neighbors or high- spin sites.

The Table 2, show the hyperfine interactions parameters of $Fe_{67.5}Ni_{32.5}$ alloy at room temperature, where, the fit with a broad sextet associated to the BCC phase, presents a nearly constant hyperfine field value of 33 T; it is independent of the particle size. This type of fit contrasts with the previous work reported by Valderrutem et al. [7] for this system, in which they used a HMFD to fit the fields of the Fe sites inside the BCC phase. However, taking into account that they obtained a very narrow HMFD, centered around 33 T for this phase, we prefer to use only one broad sextet for the BCC contribution. The average hyperfine field of HMFD associated with the FCC phase that was obtained in the current work has a nearly constant value of 31.4 T, it is also independent of the particle size, and this value is consistent with Restrepo et al. [2] results for nanocrystalline Fe-Ni melted alloys, and with the result of Valderruten et al. [7] for a MA alloy with this composition.

3.3 Magnetic characterization results

Finally, Fig. 4 shows the hysteresis cycles obtained for three powders: original (without sieve), 63 μm $<$ Φ $<$ 125 μm, and Φ $<$ 25 μm, (see) and these cycles permit to

Table 2 Hyperfine interactions parameters obtained for the samples of $Fe_{67.5}Ni_{32.5}$ alloy with various mean particle size

Sample	δ ($mm.s^{-1}$) $\pm$ 0.02	Γ(mm.s^{-1}) $\pm$ 0.02	QS(mm.s^{-1}) $\pm$ 0.02	HMF(T)	Area (%)	Phase
Original	−0, 039	0,5			2	Singlet
(Without sieved)	0,029	0,157	−0, 128	33,027	35	Sextet
	0,088		−0021	31,24	63	HMFD
	−0, 041	0,5			3	Singlet
$125 < \phi < 250\mu$	−0, 033	0,166	−0, 171	33,164	33	Sextet
	0,03		−0, 018	31,006	64	HMFD
	−0, 074	0,3			2	Singlet
$63 < \phi < 125 < \mu$	−0, 082	−0, 142	−0, 147	32,907	25	Sextet
	0,004		−0, 021	31,148	73	HMFD
	−0, 041	0,5			3	Singlet
$38 < \phi < 63 < \mu$	−0, 02	0,168	−0, 127	33,123	43	Sextet
	0,33		−0, 011	30,988	54	HMFD
	−0, 006	0,5			2	Singlet
$25 < \phi < 38 < \mu$	0,011	0,165	−0, 011	33,082	45	Sextet
	0,07		−0, 01	31,661	53	HMFD
	0,226	0,315			1	Singlet
$\phi < 25 < \mu$m	−0, 05	0,164	−0, 164	33,22	30	Sextet
	0,036		−0, 023	31,79	69	HMFD

[δ :] Isomer Shift, QS: Quadrupole Splitting, HMF: Hyperfine Magnetic Field A: Relative Area, Γ: Width at half maximum.

classify the samples as magnetically soft with coercive fields lower than 30 Oe. It can be noted that with particle size between 63 and 125 μm presents the bigger saturation magnetization while those with size lower than 25 μm and without sieving presents small saturation magnetization values.

In order to understand the behavior of the obtained cycles, the normalized difference of the magnetization ΔM vs. H curves (or Henkel plots [21]) were calculated according to the method proposed by Thamm and Hesse [22] and they are shown in Fig. 5.It can be noted that for the original sample (Fig. 5a) the predominant interaction is the one that produces negative δM_{nor} values for all the range of applied field, and this is the dipolar magnetic interaction between the moments of the particles. The higher dipolar interaction among particles explains the lower saturation magnetization values of this sample. The powders with smaller particle sizes (see Fig. 5b and c) the ΔM vs. H curves have negative values for small applied fields indicating that the predominant interaction (for zero and small applied fields) is the dipolar one. As the external field increases the modulus of the δM_{nor} values decreases showing that the external field competes with the dipolar interaction, increasing in this way the magnetization. Then the curves present a positive maximum for bigger applied fields, this fact indicates that at these fields the values of the dipolar magnetic field between the

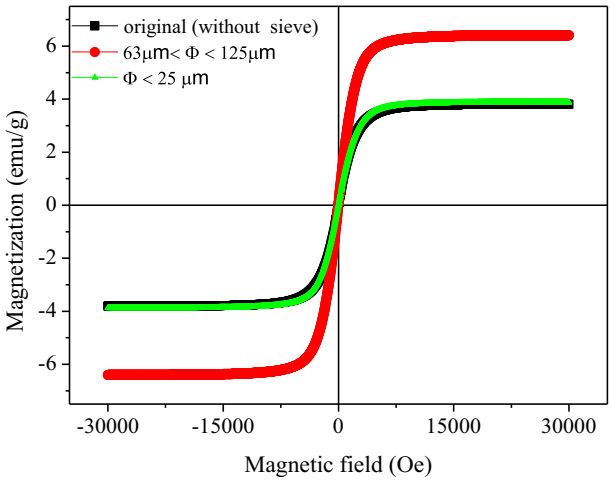

Fig. 4 Hysteresis cycles for samples with different mean particle size

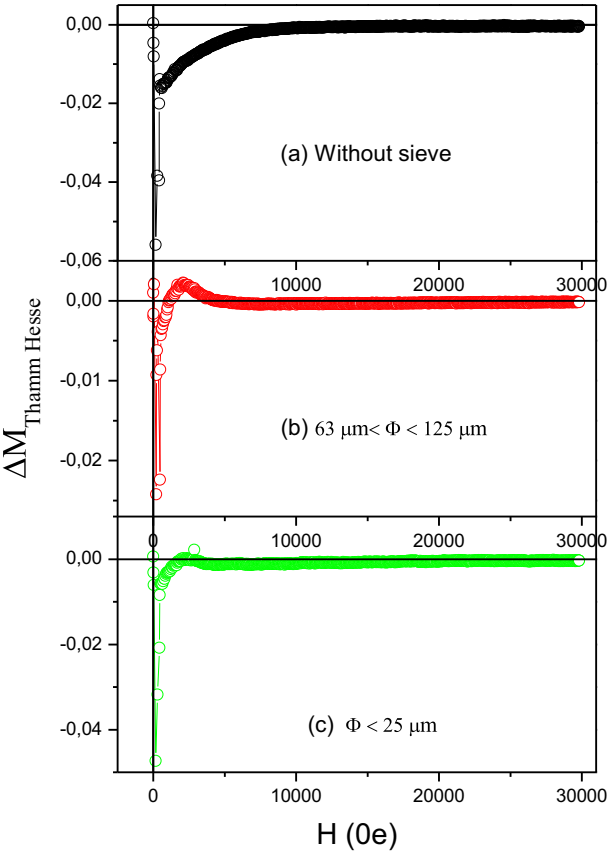

Fig. 5 Thamm and Hesse curves for samples with different mean particle size

moments of the particles compete with the magnetic external field, and there just dominates magnetic interaction which favors the magnetization. This interaction is the coupling of the internal ferromagnetic change between the ferromagnetic BCC and/or FCC grains. It can also be noted that the intensity of the peak for the powder with particle size ranged between 63 and 125 μm is bigger than that for the powder with particle size < 25 μm, in accordance with the values of the saturation magnetization observed for these powder as shown in Fig. 5.

4 Conclusions

Mechanical alloying has been used to produce the $Fe_{67.5}Ni_{32.5}$ Invar sample. The sieved samples show the coexistence of the BCC and FCC phases and behave as ferromagnetic disordered systems with a magnetically soft behavior. Separation of the original powder in different mean particle sizes produce differences in the structural and magnetic behaviors. Structural parameters, like lattice parameter and crystallite size of both detected structures, remain independent of the mean particles size; however the volumetric fraction changes, while the BCC phase increases the FCC phase decreases with the increase of the mean particle size. In respect of magnetic properties, the original powder presents a predominant magnetic dipolar interaction owing to the presence of big particles with a big magnetic moment which acts contrary to the magnetization of the sample. For powders with lower mean particle sizes the dipolar interaction remains as the predominant one between particles; but its intensity is much lower. In such way, it is enough to apply a small external field to align the magnetic moment of the particles that compete with the dipolar interaction. In this way it is possible to note the narrow coupling between the ferromagnetic BCC and/or FCC grains which favors the magnetization of the samples.

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