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# Structural and hyperfine study of the $FeNi_3$ nanostructured alloy

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In this work the structural and hyperfine properties of the $FeNi_3$ alloy are investigated by X-ray diffraction and Mössbauer spectrometry, respectively. The samples were obtained after 10 hours of milling in a high energy planetary mill. This sample was sintered at 770°C during 72 hours, and then mechanically alloyed during 0.5, 1, 2, 4, 8, 12, 24 and 40 hours. The system presents a single $FeNi_3$ fcc phase in which the lattice parameter is constant (3.557 Å) and the crystallite size decreases with the milling time from 59 to 17 nm. Two components were necessary to fit the Mössbauer spectra, one paramagnetic component (doublet) associated with the low-spin $\gamma$-Fe–Ni phase ($\gamma$LS), and a hyperfine magnetic field distribution associated with the Ni-rich fcc phase. The $\gamma$LS phase is present throughout milling time except between 0 to 2 hours where the ferromagnetism increases. The magnetic behavior depends only on structural ordering of the samples. From the shape of the hyperfine magnetic field distributions was determined that the ferromagnetism increase when the structural order increases.

*Keywords:* Alloys Fe-Ni; mechanical alloying; X-rays diffraction; Mössbauer spectrometry.

En este trabajo se realizo el estudio estructural e hiperfino de la aleación $FeNi_3$ por medio de difracción de rayos-X y espectrometría Mössbauer, respectivamente. Las muestras fueron obtenidas después de 10 horas de molienda en un molino planetario de alta energía. Esta muestra fue sinterizada a 770°C durante 72 horas, y luego aleada mecánicamente con tiempos de molienda de 0, 0.5, 1, 2, 4, 8, 12, 24 y 40 horas. El sistema presenta únicamente la fase $FeNi_3$ fcc con un parámetro de red constante (3.557 Å) y el tamaño de cristalito decrece con el tiempo de molienda de 59 a 17 nm. Dos componentes fueron necesarias para el ajuste de los espectros Mössbauer, una componente paramagnética (doblete) asociado con la fase $\gamma$-Fe–Ni de bajo espín ($\gamma$LS), y una distribución de campo magnético hiperfino asociada con la fase fcc rica en níquel. El comportamiento magnético depende únicamente del ordenamiento estructural de las muestras. De la forma de las distribuciones de campo magnético hiperfino se determinó que el ferromagnetismo incrementa cuando el orden estructural de la aleación incrementa.

*Descriptores:* Aleaciones Fe-Ni; aleamiento mecánico; difracción de rayos-X; espectrometría Mössbauer.

PACS: 75.50.Bb; 71.20.Lp; 76.80.+y

## 1. Introduction

Fe-Ni alloy system has been the subject of several studies due to their special structural and magnetic properties as well as for their application in a wide range of compositions. For example, Invar, Permalloy and $FeNi_3$ alloys.

$FeNi_3$ alloy exhibit particular interest in the study of the Fe-Ni alloys, due it is ordered below a critical temperature of 765 K. In the ordered state $FeNi_3$ has the well known $AuCu_3$ structure, which corresponds to $L_{12}$ FCC phase (*Pm3m* space group), with Fe atoms located in the corners and Ni atoms at the center of the faces. The structural order-disorder transition has been studied directly by using X-rays diffraction (XRD) [1-4], and indirectly by techniques such as dilatometry, calorimetry or by measurements of their mechanical, electrical or magnetic properties [5,6]. Takahashi et al. have found superlattices in the ordered alloy and the order was obtained by heat treatment with temperatures between 682 and 764 K and quenched into iced water [2].

The aim of the present paper is to study the effect of milling time on the structural and hyperfine properties of this system. Initially, the alloy was prepared by mechanical alloying (MA) and then sintered, and subsequently it was MA at different milling times. The study was conducted by XRD and Mössbauer spectroscopy (MS).

## 2. Experimental

High purity fine powders ($\geq$99.90%) of Fe and Ni were used to obtain the stoichiometric $FeNi_3$ alloy. The mixed elemental powder was milled during 10 hours in a high energy planetary mill *Fritsch-Pulverisette* 5. The milling was performed in stainless steel jars with balls of the same material inside. The vacuum inside the jars was of $4.5\times10^{-2}$ torr, and the ratio between the ball to powder mass was 20:1. Heat treatment was carried out at 770 K during 72 hours. Then, the alloy was again mechanically alloyed with milling times of 0, 0.5, 1, 2, 4, 8, 12, 24 and 40 hours. Milling conditions were the same used in the initial alloying. The structural and hyperfine properties were conducted by XRD and MS, respectively. The XRD patterns were realized in a powder diffractometer with Cu-K$\alpha$ radiation and they were refined by using the MAUD program [7]. Mössbauer spectra where taken on a conventional spectrometer with a $^{57}$Co/Rh source of 25 mCi. All the spectra were fitted with the MOSFIT program [8].

## 3. Results and discussion

Figure 1 show the XRD pattern of the sample mechanically alloyed and sintered (named 0h MA). From the refinement of the XRD pattern it was found that only the FCC $FeNi_3$ phase

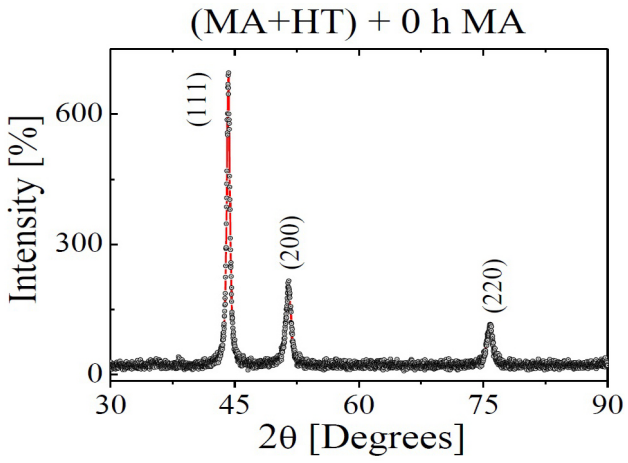


FIGURE 1. XRD pattern of the mechanically alloyed and sintered sample.

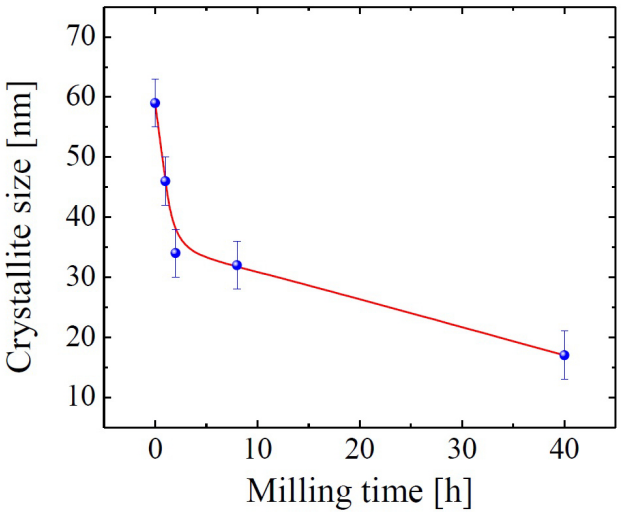


FIGURE 2. Crystallite size vs. milling time for the samples sintered and mechanically alloyed.

is present. However, as can be seen in this figure the superlattice peaks associated with the SC (single cubic) $FeNi_3$ phase does not appears (for example the (100), (110), (210) and (211) peaks). In this way the heat treatment above 770 K could not induce the ordered phase of the alloy, and the obtained is the disordered one or the FCC $FeNi_3$. The absence of structural order is attributed as due that the sample was not quenched [9], which would permit to retain the ordered phase of high temperature. MA does not induce appreciable changes in the FCC structure of the sintered alloy, the lattice parameter remains constant (3.557 Å) and is in agreement with the reported in the literature for this alloy [10,11].

Due that the alloy does not exhibit significant structural changes with the milling time, it was only performed the XRD pattern of some samples, those alloyed during 0, 1, 2, 8 and 40 hours. The structural parameters obtained from the refinement of the patterns are reported in Table I.

Crystallite size is the only parameter that changes with the milling time, and its temporal evolution is shown in Fig. 2. It can be noted that there exists a decreasing tendency in the crystallite size as the milling time increases, which indicates that MA increases internal micro tensions and in this way the brittleness of the alloy. The system is nanostructured, due the nanometric order of the crystallite size which changes from 59 to 17 nm.

TABLE I. Structural parameters obtained from the refinement of the XRD patterns of the samples alloyed for different milling time.

| **Milling time [h]** | **Phase** | **Lattice parameter** [Å] $\pm$ 0.003 | **Crystallite size [nm]** $\pm$ **4** |
|---|---|---|---|
| 0 | fcc $FeNi_3$ | 3.557 | 59 |
| 1 | fcc $FeNi_3$ | 3.558 | 46 |
| 2 | fcc $FeNi_3$ | 3.557 | 34 |
| 8 | fcc $FeNi_3$ | 3.557 | 32 |
| 40 | fcc $FeNi_3$ | 3.556 | 17 |

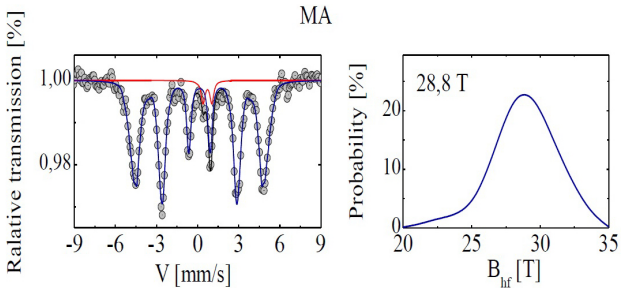


FIGURE 3. Mössbauer spectrum and its respective hyperfine magnetic field distribution for the initial MA sample.

The Mossbauer spectrum and its corresponding hyperfine magnetic field distribution (HMFD) for the sample mechanically alloyed before heat treatment, is shown in Fig. 3. The refinement of the spectra was realized using two magnetic components, a doublet with $\Delta Q$ = (0.63 $\pm$ 0.05) mm/s and $\delta$ = (0.48 $\pm$ 0.02) mm/s, and a HMFD with mean HF value of 28.8 T. The paramagnetic component has been reported previously by various authors. Ok and Hand associate this with FCC fine particles which behave as superparamagnetic [12], while Rancourt and Scorzelli attribute this paramagnetic component to the low-spin $\gamma$-Fe-Ni phase ($\gamma$LS) or antitaenite, which are FCC Fe-rich grains [13-15]. In current paper the doublet is attributed to the $\gamma$LS phase for two reasons: i) the particle sizes of the system are not as small as for the existence of superparamagnetic behavior [12]. ii) The nature of the MA technique allows obtaining disordered samples, and then it is possible to have FCC Fe-rich grains. The HMFD includes magnetic fields between 19 and 33 T, and its most probable magnetic field agrees with its mean value. The Gaussian shape and the broad of the distribution indicate the disordered character of the sample.

The most representative Mössbauer spectra (and their respective HMFDs) in the temporal evolution of the system are shown in Fig. 4. For 0 hours, the alloy remains disordered

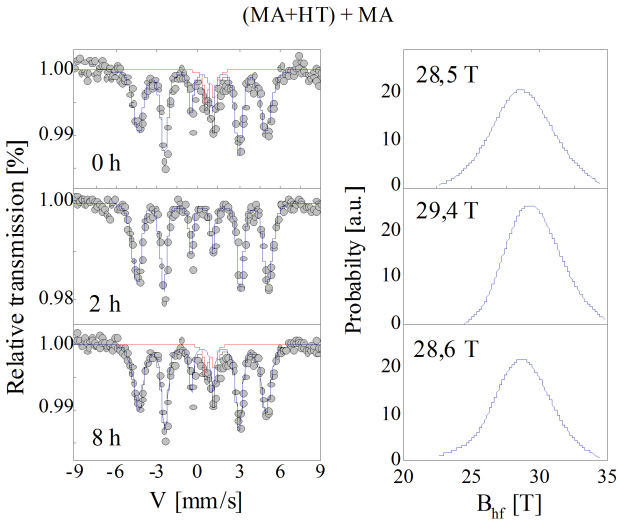


FIGURE 4. Mössbauer spectra and their respective hyperfine magnetic field distributions for MA, sintered and MA sample at different milling times.

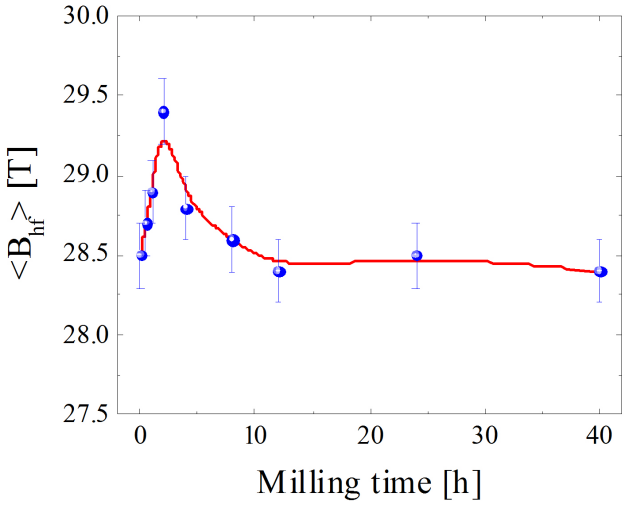


FIGURE 5. Mean hyperfine magnetic field vs. milling time for the different samples.

and preserves the magnetic phases present before the heat treatment; between 0 to 2 hours, the ferromagnetism increases and the paramagnetic component disappears; between 2 to 40 hours the paramagnetic site appears again and the ferromagnetic phase decreases lightly. The broad of the HMFDs indicates that the alloys are disordered, however, for 2 hours the alloy is lest disordered due its HMFD is lightly least broad. The results suggest that the MA induces atomic order-disorder variations in the system.

In the ordered state of the $FeNi_3$phase each iron atom had 12 Ni atoms as nearest-neighbors and 6 Fe atoms as next nearest-neighbors. Also if we take into account that in this FCC structure the nickel has higher magnetic moment than iron [16], then by MS, the largest ferromagnetic behavior is obtained when the system is ordered. This appreciation explains why ferromagnetism is increased from 0 to 2 hours and decreases between 2 to 40 hours (Fig. 5). The random nature of mechanical alloying establish that the value of the most probable hyperfine magnetic field (28.5 T), in the samples alloyed with milling times above 8 hours corresponding to iron sites with 8 nickel atoms and 4 iron atoms as nearest neighbors.

The behavior of the mean hyperfine magnetic field with respect to milling time is shown in the Fig. 5. The graphic summarized the results obtained. Between 0 to 2 hours of milling the system tends to be ordered and the mean hyperfine magnetic field is increased from 28.5 to 29.4 T. Between 2 and 8 hours the system is disordered and the mean hyperfine magnetic field decreases slightly. Above 8 hours the system not varied considerably. The magnetic behavior of the alloy $FeNi_3$ which is of the ferro-ferro type is opposite to that which presents the alloys of the ferro-diluter type. In the alloys Fe-Al the ferromagnetism is associated with the increase of the atomic disorder [17,18].

## 4. Conclusions

All the samples of the $FeNi_3$ system obtained by MA, sintered and then mechanically alloyed during different milling times show only the disordered FCC structure with lattice parameter (3.557 Å). The system is nanostructured and the mean crystallite size decreases with milling time. The ferromagnetism is exhibit by the alloys during all the milling times, however, the formation of some Fe-rich sites allow the formation of the phase ($\gamma$LS) in a small proportion (except for 0.5, 1 and 2 hours of milling). The MA induces order-disorder structural variations, particularly it was established that the increase in the ferrogmanetism is due only to an increase in the atomic order of the alloy.

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