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X-ray diffraction and mossbauer spectrometry investigations of invar nanoparticles produced by mechanical alloying

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Abstract

Fe-Ni ultra-fine particles were prepared by mechanical alloying and phase transformation during mechanical alloying was studied. Results show that phase transformation tendency is different during mechanical alloying of Fe-Ni powders with different nickel content. Fe-64%Ni (INVAR) nanocrystalline powders of were prepared by mechanical by mechanical alloying from powder mixture of elemental Fe and Ni in a planetary ball mill Fritsch Pulverisette 7 in argon atmosphere. X-ray diffraction and Mössbauer spectroscopy were used to investigate structure and phase constitution of the samples. The as-milled samples contain only a single γ-fcc (phase) with an average crystallite size of the order of 14 nm, the average hyperfine field is about 31T.

Keywords: Nanostructure, X-ray diffraction, Mössbauer spectrometry.
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1. Introduction

Nanomaterials, with their unique physical and chemical properties, hold promise for applications in a wide range of sectors including electronics, photonics, telecommunications, biotechnology, medicine, aerospace, and energy [1–3]. A wide variety of techniques are being used to synthesize nanostructured metallic materials including inert gas condensation [4], electrodeposition [5], crystallization of amorphous phases [6], sputtering [7] or mechanical alloying [8]. Mechanical alloying (MA) is as an alternative technique to obtain metastable materials in powdered form [9].

MA is a high energy ball milling operation involving repeated welding, fracturing and rewelding of powders. The microstructure of alloyed powders prepared by MA is quite different from those made by other techniques. In the mechanical alloying process, alloy phase is formed by solid-state interdiffusion reaction when the individual particles are mechanically deformed by impact. High energy ball milling benefits the acceleration of alloy formation and structural refinement of powders. It leads to extended solubilities in the solid solution at low temperatures with respect to the thermodynamical equilibrium. Besides, mechanical alloying process provides more convenient, simple and economical way to synthesize nanocrystalline materials than conventional processing. Previous studies show that both mechanical alloying iron powder with carbon powder or iron nitride powder and mechanical processing iron powder in a nitrogen gas environment or an anhydrous ammonia atmosphere lead to the formation of nanocrystalline bct- Fe [10–12]. The applicability of the High-energy ball milling to process ferromagnetic materials, in particular FeNi compounds, was recently demonstrated [13]. In turn, these materials have attracted much academic and technological attention [14, 15], due to their structural, magnetic and mechanical properties. Here, we have used MA to produce nanocrystalline $Fe_{64}Ni_{36}$ alloy (INVAR) starting from the crystalline elemental powders.

In this paper, the structural, microstructural and Mössbauer spectral properties of the $Fe_{64}Ni_{36}$ compounds, synthesized by the high-energy ball-milling technique, were studied through X-ray diffraction and Mössbauer spectroscopy.

2. Experimental

Elemental Fe (<10 μm, 99.99 wt% purity) and Ni (<10 μm, 99.98 wt% purity) powders were mixed to get Fe-36wt%Ni. Then the powder mixtures, together with stainless steel balls, were sealed in the hardened steel vial under an argon atmosphere. The weight ratio of ball-to-powder was 20:1. Mechanical alloying was performed in a planetary ball mill (Fritsch Pulverisette7) different time ranging from 0.5 h to 32 h. The planetary rotation speed was about 300 rmp. In order to avoid an increase in the vial temperature, the milling procedure was periodically interrupted every 30 mn for 15 min. X-ray diffraction (XRD) with monochromatic Cu Kα radiation ($\lambda_{K\alpha}$ = 0.154056 nm) was performed to identify the phases existing in as-prepared MA powders. ^{57}Fe Mössbauer experiments were performed at 300 K in transmission geometry using a ^{57}Co source. The analysis of the Mössbauer spectra was done by using the Mosfit program [16] and the values of isomer shift are quoted relative to that of α-Fe at 300 K.

3. Results

3.1. XRD analysis

Fig. 1 presents the X-ray diffraction patterns of Fe-36Ni powders milled for different time. For the convenience of comparison, the XRD pattern of un-milled powder is also presented, showing that it is composed of α-Fe (b.c.c.) and Ni (f.c.c.). For unalloyed samples milled for 30 mn and 1h 30 mn, both the peaks of Fe and Ni element were prominent and have been slightly broadened, leading to the products of unalloyed Fe–Ni mixtures. It was observed that the characteristic Fe lines decreased gradually and decay after 3 h and only the reflections corresponding to fcc phase are present with the peaks slightly shifted towards lower angles. This proves that Fe atoms dissolve in the nickel lattice entirely, and single phase γ-FeNi solid solution was formed and the shift towards the lower angle is due to the expansion of the lattice on Fe-Ni. The XRD pattern for 12 h exhibits a significant broadening of the peaks due to the refinement of grain size and the increase of internal strain. After 24h of milling the iron oxide phase FeO was detected. Valderruten et al. [17] obtained

the mixture of α-FeNi and γ-FeNi phases for $Fe_{1-x}Ni_x$ samples with $0.225 \leq x \leq 0.400$, confirmed also by Djekoun et al. at 48 h of milling time for $Fe_{50}Ni_{50}$ [18].

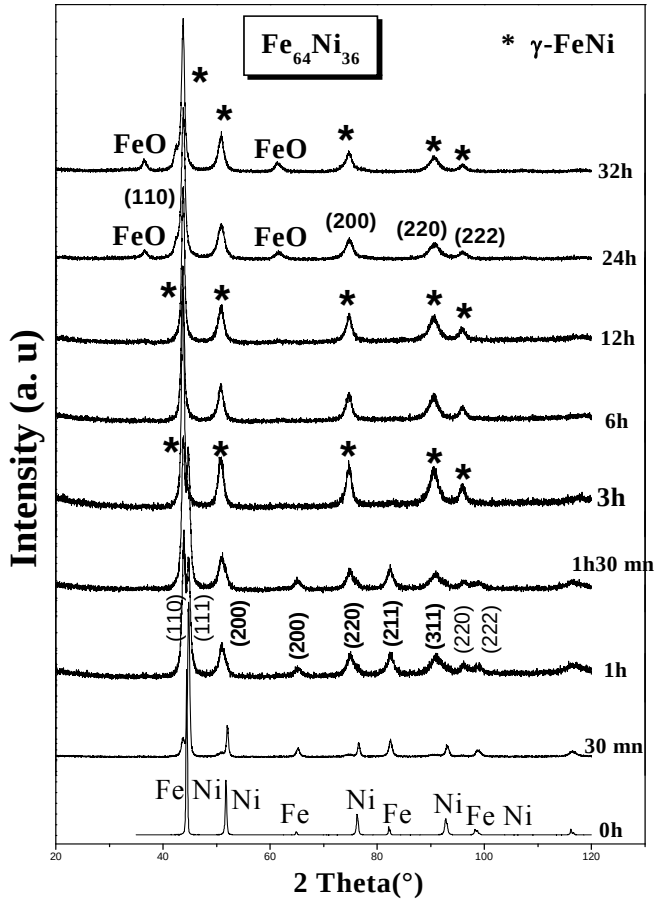


Fig. 1: X-ray diffraction patterns of $Fe_{64}Ni_{36}$ powders synthesised in high-energy mill as a function of milling time.

Fig. 2 presents the evolution of crystallite size D and lattice strain ε as a function of the milling time for nanocrystalline mechanically alloyed Fe-36% Ni. As can be seen in Fig. 2, during the early stage of milling the crystallite size decreases rapidly in the beginning of milling and becomes gradually smaller with increasing milling time with a final value of about 14.50 nm. The lattice strain ε increases from 0.40% to 0.64% when the milling time increases.

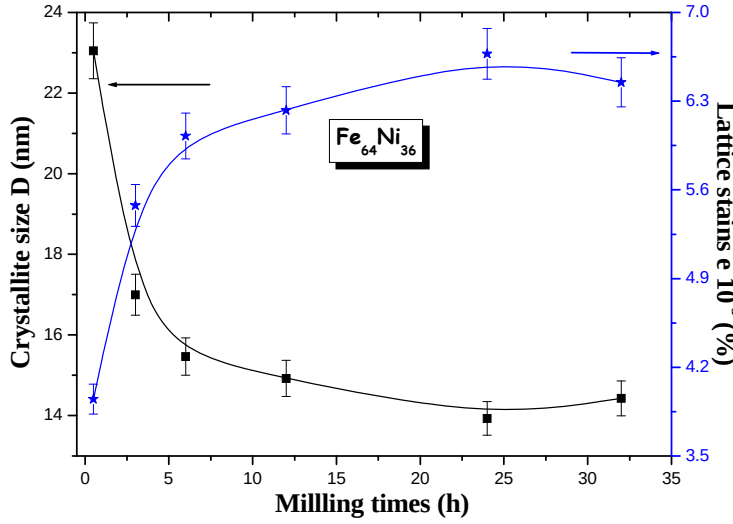


Fig. 2: Average crystallite size D and mean level of internal strains e versus milling times for $Fe_{64}Ni_{36}$

In the case of $Fe_{65}Ni_{35}$ alloy Pekala et al. [19] have found that a final crystallite and the mean lattice strain level size reached 10 nm and 0.66%, respectively, after 200 h of milling. Shiyne et al. [20] have proved that the average grain size attained the minimum value of 12 nm, while the average lattice strain increased up to 0.49% for $Fe_{25}Ni_{75}$ structure after 120 h of milling. We calculate the lattice parameters, *a*, of the present samples in terms of the (111) peak data and draw the results in Fig. 3. It can be seen that the lattice parameter

of the samples increase with increasing milling time from 0.35021 nm to 0.35816 nm after 32 h of milling. The increase of lattice parameter with milling time is due to the disordering of the alloy as was suggested by Oleszak and Shingu [21] in the case of FeAl alloy. It is interesting to note, for comparison, that for mechanical alloying $Fe_{65}Ni_{36}$, Jartych et al. [22] found a lattice parameter equal to 0.35906 and 0.35911 nm for γ-FeNi phase prepared by low and high-energy milling processes, respectively, after 50 h of milling using a planetary ball mill. Tcherdyntsev et al. [23] obtained a value of 0.3590 nm after 1h of milling with a planetary ball mill.

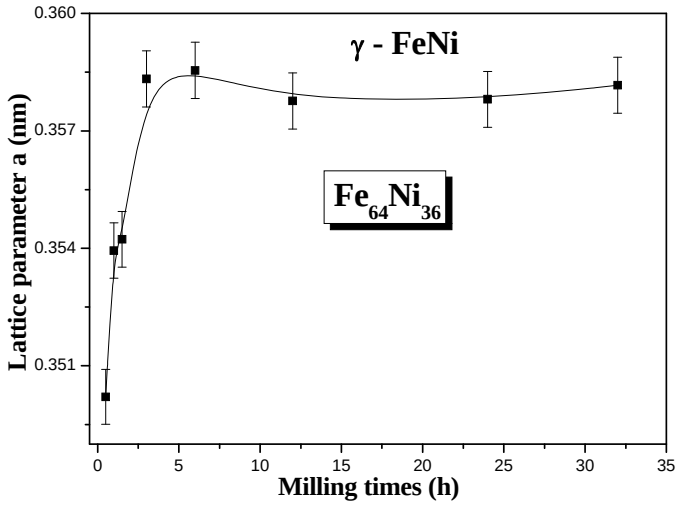
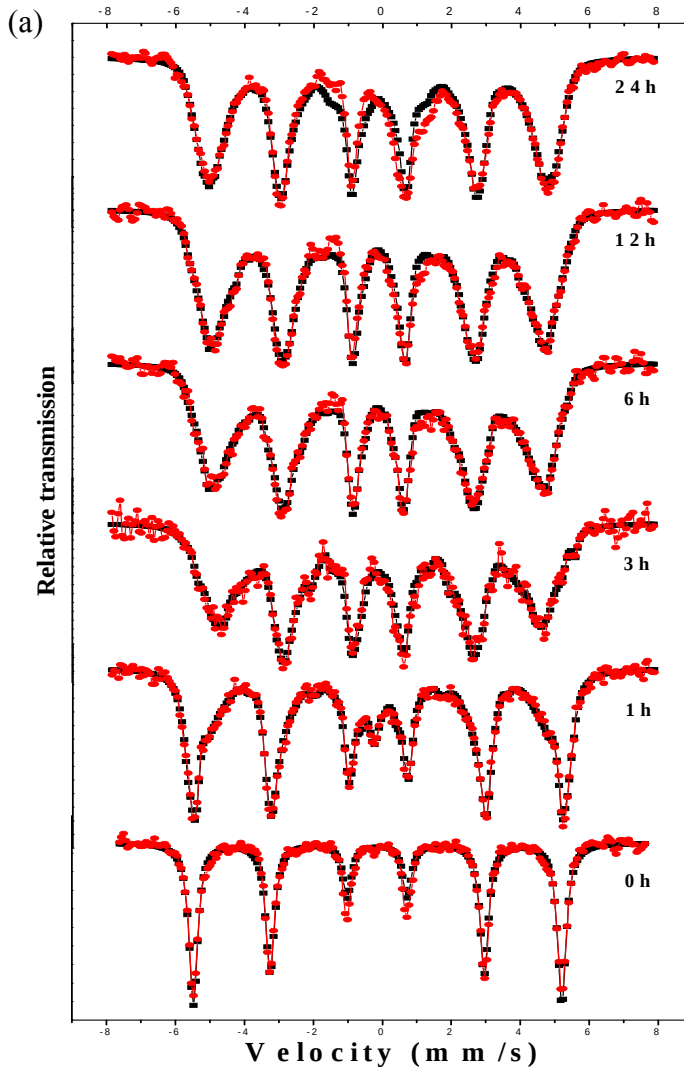


Fig. 3: Lattice parameter of γ-FeNi powders as a function of milling times for $Fe_{64}Ni_{36}$

3.2. Mossbauer spectroscopy

The Mössbauer measurements were done in order to monitor the process of alloy formation at every stage of milling. The room temperature Mössbauer spectra and their corresponding HFD for different milling times are shown in Fig. 4. For the unmilled sample,

the spectrum shows the presence of a typical sextet with a mean hyperfine field $\langle B_{hf} \rangle$ equal to 33 T which corresponds to the α-Fe present in the starting FeNi powder.



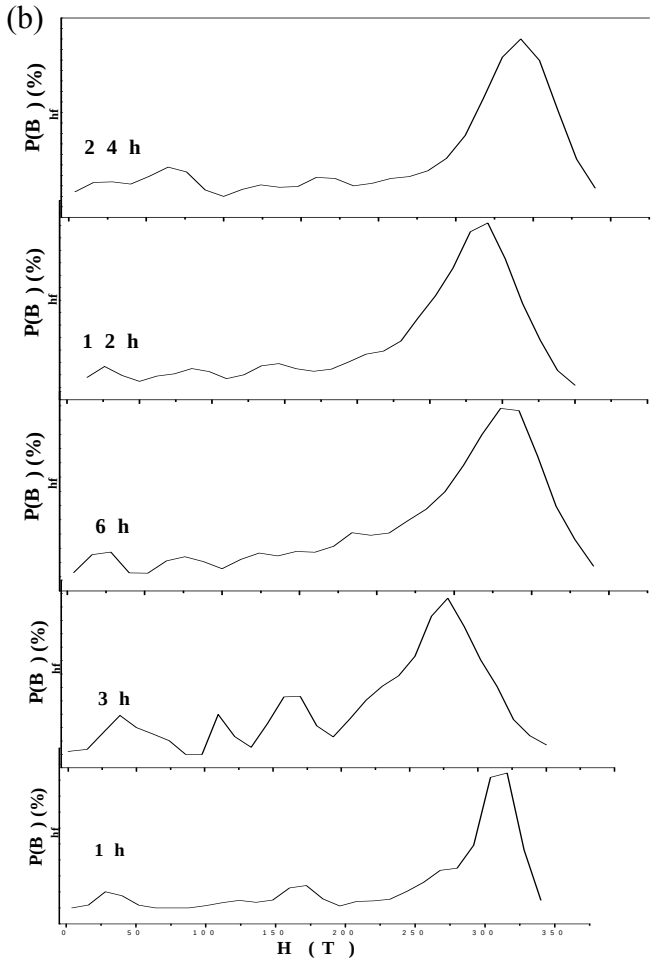


Fig. 4: (a) Room temperature Mossbauer spectra and (b) Hyperfine magnetic field distribution for $Fe_{64}Ni_{36}$ synthesized in a high-energy ball mill as a function of milling time.

After milling time of 30 mn, the spectra are still characteristic for α-Fe, i.e, magnetically split patterns with six lines, confirmed by x-ray diffraction. After 1h of milling, the Mössbauer spectrum shows clearly the coexistence of Fe-Ni phases with different composition, a magnetic phase corresponding to a disordered Fe-Ni γ-phase and a

paramagnetic phase assigned to a solid solution with a concentration of about 30at.% Ni, not detected by XRD with small amount about 4.90 %, with increasing milling time this phase disappear completely. For samples milled between 3h and 12h, it can be seen that the shape of the spectra begin to change with a broadening of the spectral lines in relation to α-iron. The Mössbauer spectrum shows the presence of a magnetic sextet, with asymmetric intensities, typical for Fe-Ni disorder alloys in the composition range 35-50% Ni, can be assigned to Fe-Ni γ-phase (Ni-rich taenite). This agrees with results obtained for the formation of Fe-Ni phase by a gas condensation method [24].The singlet line attributed to a fcc iron rich paramagnetic phase, usually coexists with the ferromagnetic fcc around 50% Fe as explained by Lima et al. [25] and Scorzelli et al. [26]. This has been also observed by Djekoun et al. [19] for mechanical alloyed $Fe_{50}Ni_{50}$. Valderruten et al. [18] reported similar observations.

The fitting of the spectra resulted in the hyperfine magnetic field distributions, $P(B_{hf})$, shown in fig.5. They are relatively broad because of the high lattice strains, defects and high density of the grains boundaries in the milled alloy.

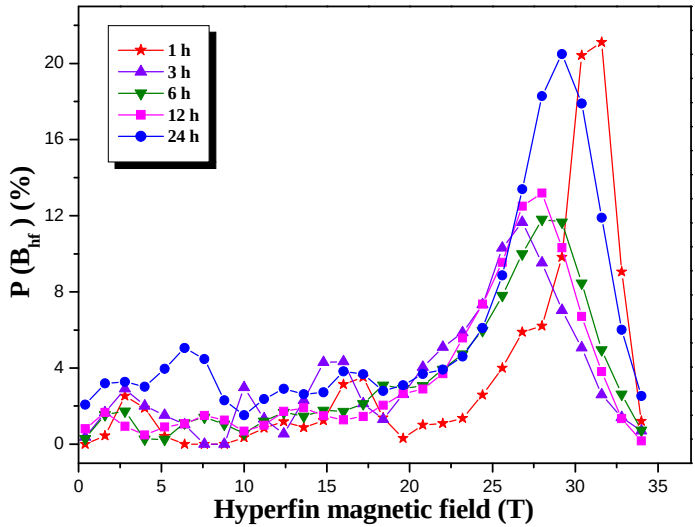


Fig. 5: Hyperfine magnetic field distribution of (Fe, Ni) powders after different milling times

4. Conclusion

Mechanical alloying has been applied for alloys synthesis from Fe-Ni powders mixture. From XRD spectra, we have followed the formation of $Fe_{64}Ni_{36}$ alloy from elemental Fe and Ni powder. The results presented in this work clearly show the great potential of this technique. High-energy ball milling of Fe and Ni powders results in the single solid solution phase γ-FeNi of $Fe_{64}Ni_{36}$ alloy formation accompanied by a grain refinement. The crystallite sizes and lattice strain level reached the saturation values of 14.50 nm and 0.64%, respectively, after 24 h of milling. For the sample milled 1h, the Mossbauer spectrum shows the coexistence of a magnetic phase and a paramagnetic phase attributed to a Fe-Ni solid solution.

5. References

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