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X-ray diffraction and Mössbauer studies of nanocrystalline Fe–Ni alloys prepared by mechanical alloying

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Abstract

Mechanical alloying is a powder metallurgy processing technique involving cold welding, fracturing, and rewelding of powder particles in a high-energy ball mill. Mechanical alloying is a non-equilibrium process for materials synthesis. It has been used to obtain nanocrystalline binary Fe–Ni system.

Elemental powders of iron and nickel (Fe–50 at.% Ni) have been mixed in a planetary mill. The structural effects of mechanical alloying of powders were investigated by scanning electron microscopy, X-ray diffraction analysis and Mössbauer spectroscopy.

It is observed a gradual formation of mixture of phases as fcc (γ) with a nanoscale grain size. In addition, as the average grain size is decreased with a progressive enlargement of peaks of X-ray diffraction, a paramagnetic phase appears after 48 h of ball milling detected by Mössbauer spectroscopy.

Keywords: X-ray diffraction; Mössbauer spectroscopy; Fe–Ni alloys

1. Introduction

Mechanical alloying, which is a dry and high-energy milling process, has attracted considerable interest in recent years owing to the wide range of materials, often with non-equilibrium structures, with can be synthesised: amorphous, quasicrystalline and nanocrystalline phases, extended solid solution, alloys of immiscible elements, all sorts of compounds and composites [1–6].

Although the precise mechanism of the mechanical alloying process is thought to involve the repeated fracture and welding of powder particles during ball-powder–ball and ball-powder–container collisions. Alloying takes place then by interdiffusion across welded interfaces of grain powders.

In this work, we have attempted a preparation of the Fe–Ni compound, using powders of pure crystalline metals as starting materials and high-energy ball milling as the processing technique. The material was investigated by means of microstructural observations by scanning electron microscopy, X-ray diffraction and Mössbauer spectroscopy.

2. Experimental

Pure elements, Fe (99.9%) and Ni (99.8%), with respectively −200 and −100 mesh, powders were separately weighted and mixed to get the desired composition. The mixed powder was sealed in a cylindrical vial under an argon atmosphere with stainless steel balls. Mechanical alloying was performed in a planetary ball mill (Fritsch "Pulverisette 7") at room temperature. X-ray diffraction patterns were recorded using Cu Kα ($\lambda_\alpha = 1.541$ Å) radiation. Scanning electron microscopy has been used for morphology and microstructure observations. Mössbauer spectra were taken at 300 K in a transmission geometry with conventional constant acceleration spectrometer, using a radioactive ^{57}Co source diffuse into a rhodium matrix.

3. Results and discussion

X-ray diffraction (XRD) patterns recorded for the Fe–50 at.% Ni powder mixture after various milling times are shown in Fig. 1. With increasing milling times, all diffraction lines broaden, indicating a continuous decrease in grain size and the introduction of lattice strain. The

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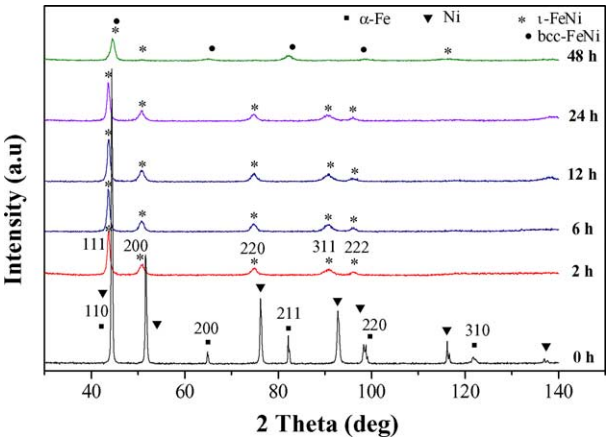

Fig. 1. X-ray diffraction patterns of 50% Fe–50% Ni alloys synthesised in high-energy milling.

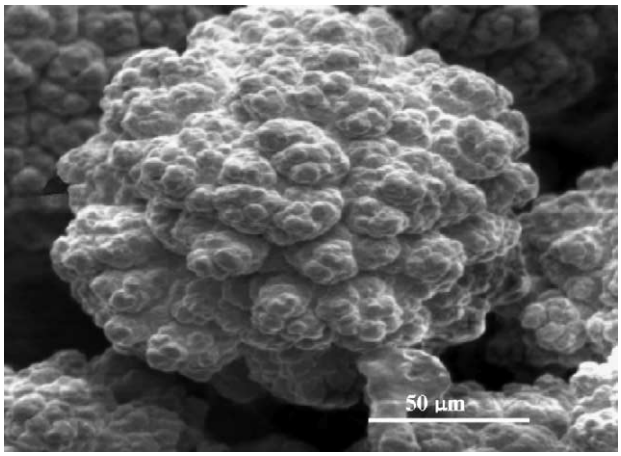

Fig. 3. SEM micrograph of unmixed (Fe, Ni) powder.

increasing milling time causes the Fe lines in the diffraction pattern to increase in width and shift toward the smaller angle region. XRD (marked 0 h milled) shows reflections corresponding to bcc Fe and fcc Ni metals. After 2 h of milling the reflection peaks (2 0 0), (2 1 1) corresponding to the bcc α-Fe disappear and only the reflections corresponding to fcc phase are present with the peaks slightly shifted towards lower angles. This shows the formation of fcc solid solution of Ni and Fe and the shift towards the lower angle is due to the expansion of the lattice on Fe–Ni alloy formation. The characteristic Ni lines gradually decrease in amplitude and decay after 48 h milling. This effect proves that Ni atoms dissolve in the iron lattice entirely. We observed a formation of mixture of phases as fcc Fe–Ni solid solution γ(Fe, Ni) (called taenite) and bcc Fe–Ni. In addition, the disappearance of almost all diffraction lines in 48 h of milling indicates that the milled powder grains (crystallite size) have been significantly refined.

Fig. 2 shows the variation of Fe–Ni crystallite average size versus milling time determined from the broadening

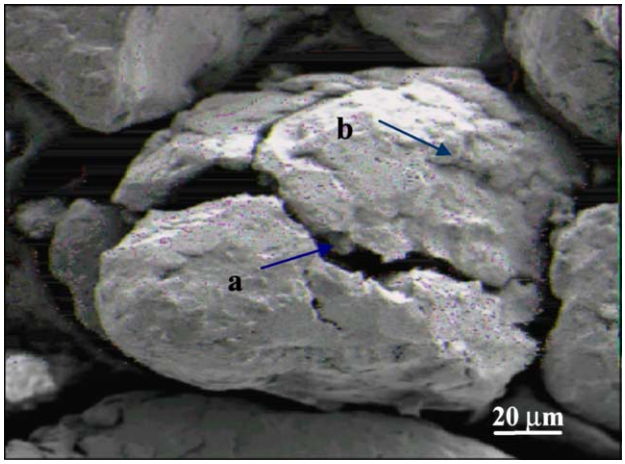

Fig. 4. SEM micrograph of (Fe, Ni) powders shows fracture (a) and cold welding (b).

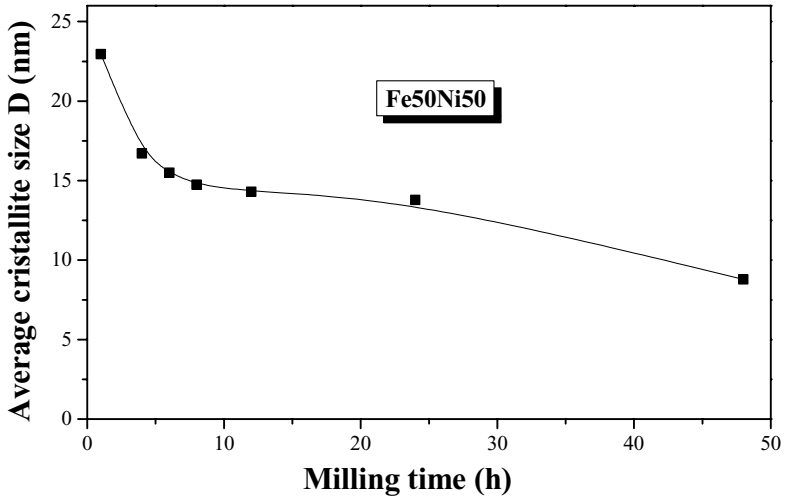

Fig. 2. Crystallite size of the Fe–Ni powders as function of milling time.

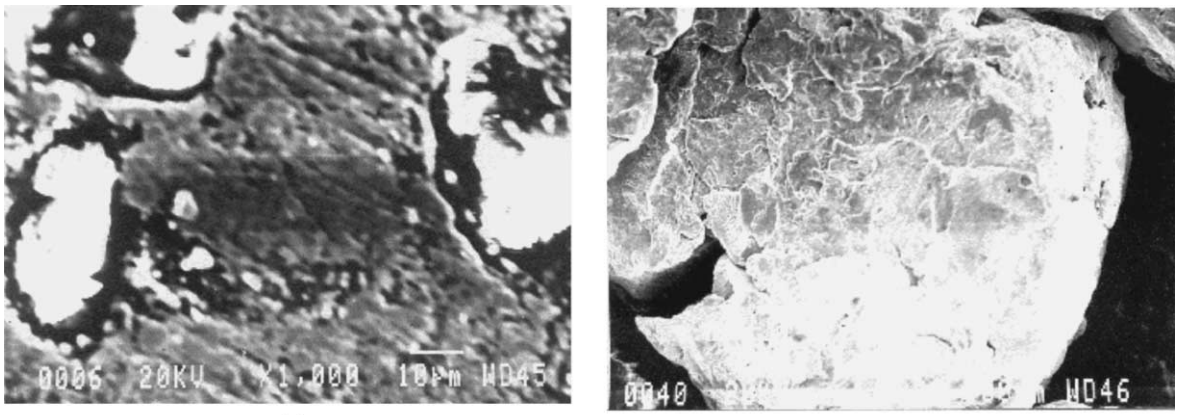

Fig. 5. SEM micrograph of (Fe, Ni) powders prepared by mechanical alloying after milling times (a) 1 h; (b) 12 h.

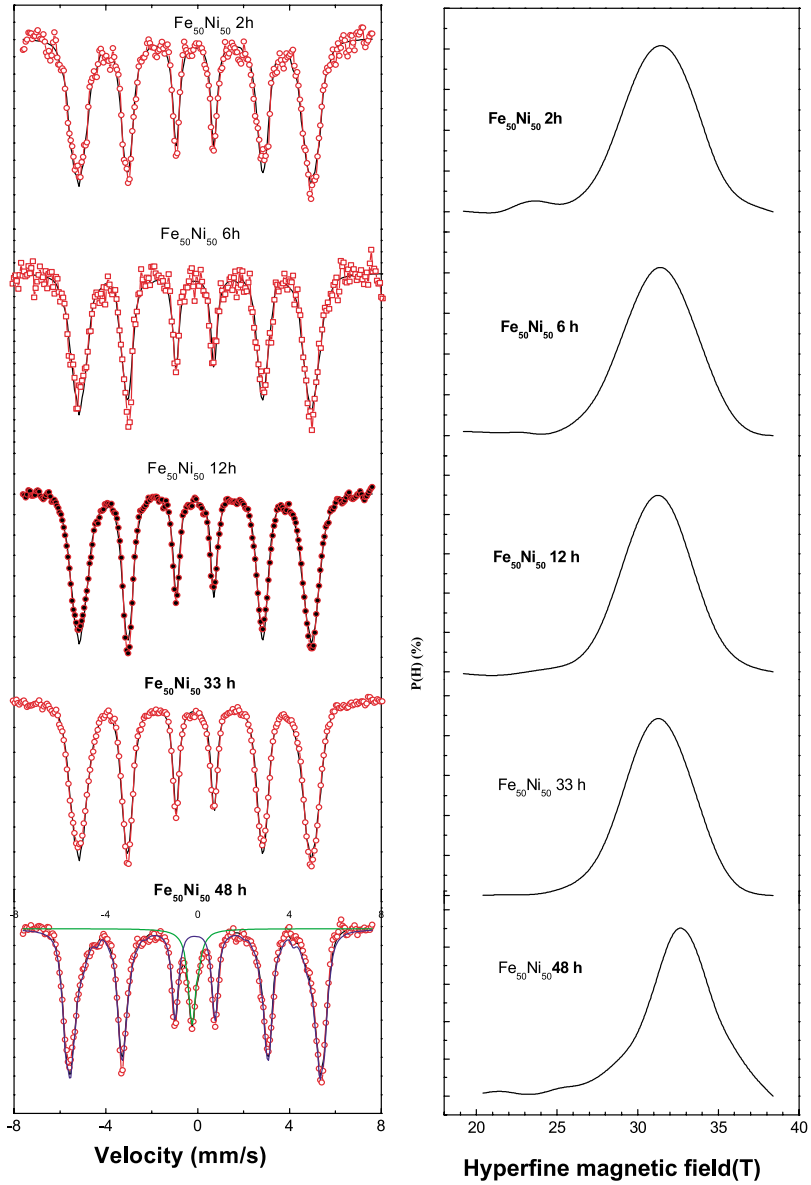

Fig. 6. Mössbauer spectra and hyperfine field distributions (HFDs) at room temperature for (Fe, Ni) powders after different milling times.

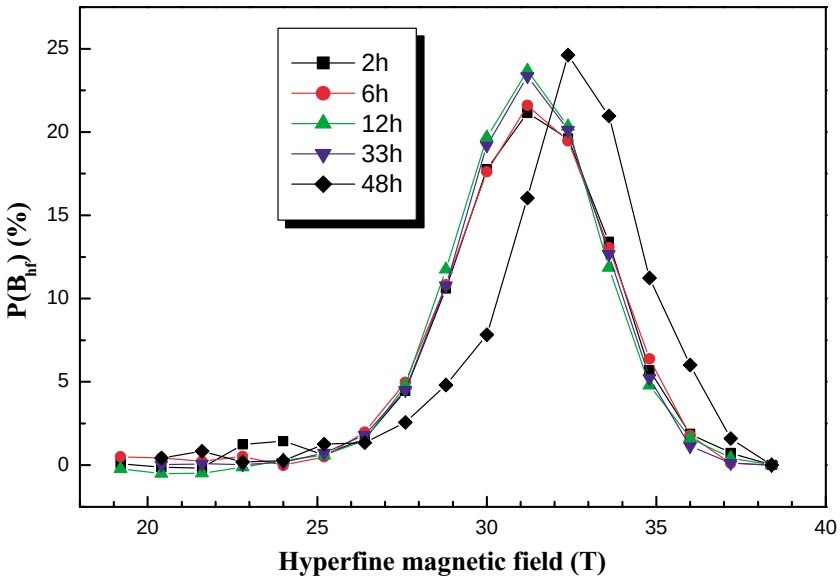

Fig. 7. Hyperfine magnetic field distributions of (Fe, Ni) powders after different milling times.

of the X-ray lines [7]. As can be seen in Fig. 2, during the early stage of milling the crystallite size decreases dramatically. The average crystallite size becomes gradually smaller with increasing milling time with a final value of about 8 nm. This value is smaller than the 45 nm [8] and 16.5 nm [9] for the iron–nickel ultra-fine particles obtained by a gas-condensation method, with the same composition.

Microstructural aspects of the powders as a function of milling time are presented in Fig. 3. Initially, one can see that unmixed (Fe–Ni) powders are spherical (Fig. 3). As a result of intensive fracture and cold welding as shown in Fig. 4, composite particles are formed (milling 1 h). Powders have lamellar, multilayer structure and are elongated in shape (Fig. 5a) typical of materials prepared by mechanical alloying for ductile or brittle elements [10,11]. By increased milling times, the mechanical alloying progress and the refinement of the structure continues. At this stage these lamellar structures disappear as shown in Fig. 5b.

The Mössbauer measurements allowed us to observe the alloy formation at every stage of the milling process. The room temperature Mössbauer spectra taken at different times are shown in Fig. 6. Between 2 and 33 h of milling, the Mössbauer spectrum shows the presence of a magnetic sextet and a distribution of hyperfine fields with a most probable hyperfine value $H_p = 31.2$ T (Fig. 6), with asymmetric intensities with very broadened lines, typical for Fe–Ni disorder alloys in the composition range 35–50% Ni, can be attributed to Fe–Ni γ-phase (Ni-rich taenite). After the mixing time 48 h, the Mössbauer spectrum at room temperature exhibits 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 attributed to a Fe–Ni solid solution with a concentration of about 30 at.% Ni. This agrees with results obtained for the formation of Fe–Ni phase by a gas method with the same composition [9]. On the other hand, Ping and Rancourt [12] worked recently with splat-quenched Fe–Ni alloys in the composition range of 5–70 at.% Fe, Mössbauer spectra at room temperature were used to confirm the absence of any α phase (bcc phase) and they found that for 30 at.% Ni the spectrum consists of a single line well defined ascribed to dynamic effects.

The fitting of the spectra resulted in the hyperfine magnetic field distributions, $P(B_{hf})$, shown in Fig. 7. They are relatively broad because of the high lattice strains, defects and high density of the grain boundaries in the milled alloy. We observe that the maximum of the distribution $H_i = 33.6$ T is slightly shifted to the larger magnetic field for the 48 h milled alloy.

4. Conclusion

Mechanical alloying has been applied for alloys synthesis from Fe–Ni powder mixture. This process occurs in two steps: First a lamellar structure is formed. By increased milling time, the refinement of the structure continues. At this stage, the lamellar structure disappears. The Mössbauer spectrum at room temperature shows the coexistence of Fe–Ni phases with different composition, a magnetic phase corresponding to a disordered Fe–Ni γ-phase and a paramagnetic phase attributed to a Fe–Ni solid solution due to the (Ni-poor) Fe–Ni (∼30% Ni).

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