Structure and magnetic properties of Fe-rich nanostructured Fe$_{100-x}$Ni$_x$ powders obtained by mechanical alloying

A. Djekoun $^a$, N. Boudinar $^a$, A. Chebli $^a$, A. Otmani $^a$, M. Benabdeslem $^a$, B. Bouzabata $^a$

J. M. Greneche$^b$

$^a$Laboratoire de Magnétisme et de Spectroscopie des Solides, Faculté des Sciences, Université Badji Mokhtar, B.P 12, 23000 Annaba, Algérie

$^b$Laboratoire de Physique de l’Etat Condensé, UMR CNRS 6087, Université du Maine 72085 Le Mans Cedex 9, France

Received 1 January 2009; received in revised form 31 July 2009; accepted 31 August 2009

Abstract

Fe$_{100-x}$Ni$_x$ alloys (x = 22, 26, 30, 50 at%) were prepared by mechanical alloying (MA) of elemental powders in a high-energy planetary ball mill type Fritsch (Pulvérisette P7). Scanning electron microscopy (SEM), X-ray diffractometry and Mössbauer spectroscopy were used to study the mixing at nanometric scale. It is observed a gradual formation of mixture of phases as fcc ($\gamma$) and bcc ($\alpha$) with a nanoscale grain size. In addition, as the average grain size is decreased with a progressive enlargement of peaks of X-ray diffraction. The Mössbauer Spectroscopy confirmed the ferromagnetic ordering and was used to calculate the distribution of hyperfine fields. Mössbauer spectra analysis has shown the presence of magnetic bcc-phase and paramagnetic $\gamma$-phase (i.e.taenite), not detected by X-ray diffraction for Fe$_{78}$Ni$_{22}$ system.

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PACS: 75.50.Bb; 61.46.Df; 61.10Nz, 68.37.Lp; 76.80.+y;

Keywords: Nanostructure; Mechanical Alloying; Scanning electron microscopy; Mössbauer spectroscopy; FeNi

1. Introduction

In recent years, nanocrystalline materials have been the subject of scientific interest because of their attractive properties often superior to those of conventional polycrystalline materials. A number of synthesis techniques have been developed to produce these novel materials such as mechanical alloying.

During the last years the mechanical alloying technique has been found to be very effective in producing powders with interesting properties. By this means it is possible to synthesize alloys or composite materials with highly dispersed components far away from thermal equilibrium state like amorphous or nanocrystalline materials [1].

* Corresponding author. Tel.: +0-000-000-0000 ; fax: +213 38 87 84 45.
E-mail address: abdel_djekoun@yahoo.fr.
Furthermore, the powder route is a way to combine elemental or prealloyed components to materials which are generally not receivable by conventional technique due to e.g. the immiscibility of their components.

In most cases mechanical alloying leads to material transformation of the crystalline structure by solid state reactions. During mechanical alloying, powder particles are subjected to severe plastic deformation and are repeatedly deformed, cold welded and fractured. As a consequence, some reactions that normally take place only at high temperatures can be realized during mechanical alloying even at room temperature.

Fe–Ni system has attracted considerable attention as a basis for a number of alloys with special magnetic and mechanical properties. Severe plastic deformation of these alloys in various kinds of high-energy mechanoactivators enables one to obtain alloys with new structures and properties. Therefore, several studies were performed, where structure and properties of mechanically alloyed (MA) Fe–Ni alloys were investigated [2–8]. Recent studies of MA binary alloys showed that the single-phase concentration ranges extend significantly as compared with those for alloys produced by conventional techniques [4,8–13].

For the Fe–Ni system also this tendency takes place, but the results obtained by different researchers although similar in general do not coincide completely [2,4,7]. In particular, it was observed that the concentration ranges of the BCC and FCC single-phase solid solutions depend on the milling intensity and shift to low nickel concentration at an increase in the milling intensity [2,4].

In this study, iron-nickel powders were mechanically processed to produce micron-sized particles with nanosized grains. Mixtures of pure elemental of iron and nickel powders of Fe100–xNi(x = 22, 26, 30, and 50 at %) composition were mechanically alloyed in argon atmosphere and structural evolution has been observed by a scanning electron microscopy and characterized by X-rays diffraction and Mössbauer spectroscopy. The diffraction patterns were fitted using the Maud program. The procedure combines Rietveld and Fourier transform to describe broadened Bragg peaks, allowing thus the lattice parameter and the grain size of the different phases to be estimated.

The as-milled samples, characterized by Mössbauer spectroscopy, contain a mixture of magnetic \( \alpha \) (BCC) and paramagnetic \( \gamma \) (FCC).

2. Experimental techniques

Elemental Fe (99.998%) and Ni (99.999%) powders were mixed in appropriate proportions to obtain the compositions Fe100–xNi(x = 22, 26, 30, and 50 at%). The mixtures were then loaded in hardened steel vials under argon atmosphere and milled at RT in a planetary ball mill (Fritsch Pulverisette 7) using hardened steel balls, with a ball-to-sample weight ratio of 20:1. The milling intensity \( I = 8 \) corresponding to vial rotation speed of \( \approx 1124 \text{ tr/min} \) was used. After different milling times, the process was interrupted and small amounts of milled powders were taken out for analysis. Structure and magnetic properties of synthesized samples were studied after different durations of milling. X-ray investigations were performed on a D501 SIEMENS diffractometer in continuous scanning mode using CuK\( \alpha \) radiation (\( \lambda_{\alpha} = 0.154056 \text{ nm} \)). Scanning electron microscopy has been used for morphology and microstructure observations. Mössbauer spectra were taken at 300K in transmission geometry with conventional constant acceleration spectrometer, using a radioactive \( ^{57}\text{Co} \) source diffuse into a rhodium matrix. X-ray patterns were analysed by Maud program [14], which is based on Rietveld method [15].

3. Results and Discussion

Microstructural aspects of the powders as a function of milling time are presented in Figure. 5. It can be seen that different morphologies are present during the mechanical alloying stages. As a result of intensive fracture and cold welding as shown in Fig. 1 (a and b, respectively). Some of these particles present a layered structure formed of superposed Ni and Fe layers (Fig. 1c), typical of materials prepared by mechanical alloying for ductile or brittle elements as indicated by Davis et al. [16] and Otmani et al. [17]. This layered structure is gradually destroyed with increasing milling time.
X-ray diffraction patterns recorded for the Fe_{100-x}Ni_x (x = 22, 26, 30, and 50 at%) powders mixtures after various milling times are shown in Figure 2. It was observed that the characteristic Ni lines decreased gradually. With increasing milling times, all diffraction lines broaden, indicating a continuous decrease in grain size and the introduction of lattice strain. As can be seen from the figure, the as-milled samples contain a mixture of α (BCC) and γ (FCC) phases, with the former being the dominant phase. Tcherdynešev et al. [18] have shown that the samples with up to 20 at% Ni contain single bcc phase and the samples with 22, 24, 26, and 28 at% Ni contained both BCC and FCC phases. Kaloshkín et al. [19] have shown that concentration ranges of single bcc phase solid solution are larger in mechanical alloyed alloys compared with the equilibrium phase diagram.
Fig. 2. XRD patterns of Fe_{100-x}Ni_{x} (x = 22, 26, 30, and 50 at%) powdered alloys for various milling times.

Fig. 3 presents the evolution of crystallite size $D$ and of lattice strain $\varepsilon$ as a function of the milling time for nanocrystalline mechanically alloyed Fe_{30} % Ni. It was observed that the reduction of the crystallite sizes was accompanied by the increase of the lattice strain level when milling time increased. The same evolutions were observed for the others as-milled samples.
In accordance with X-ray diffraction, the RT Mössbauer spectra of as-milled samples (Fig. 4) show a magnetically split pattern resulting from the α(BCC) phase and a singlet arising from the γ(FCC) phase. Note the small amounts of the γ (FCC) phase present in the as-milled sample of the alloy with x = 22 not detected by X-ray diffraction. It is evident from Fig. 4 that the relative intensity of the γ (FCC) phase in the as-milled samples increases with increasing milling time and Ni content, in agreement with the results of Baldokhin et al. [20] and reflects the increasing tendency for the γ (FCC) phase in going towards higher Ni concentrations.

Our results agree with the published data, especially with the data reported in Ref. [2] (Fig. 5). Actually, the milling intensity has a complex effect on the final structure of alloy. Two main parameters change with increase of the intensity: on the one hand, concentration of different types of structure defects increases and on the other hand, the average temperature of the milling process increases. According to Ref. [4], the structure defects, which are caused by the MA, lead to a lesser destabilization of the FCC phase than of the BCC phase. Moreover, as it was mentioned in Ref. [2], according to the Fe–Ni phase diagram, an increase of the milling temperature will stabilize FCC and destabilize the BCC structure. That is why, in general, an increase of the milling intensity will extend the FCC concentration range and narrow the BCC concentration range (Fig. 5). As it was shown earlier [13,21,22] the MA treatment will always cause the narrowing of two-phase concentration range in the case of binary systems, because of the constraint of the simultaneous existence of several phases with different compositions. The only one phase with the lowest Gibbs energy commonly forms at low temperature MA process.
Fig. 4: Room temperature Mössbauer spectra of as-milled Fe-Ni powdered alloys vs milling time
4. Conclusion

In this work, we have prepared Fe$_{100-x}$Ni$_x$ (x = 22, 26, 30, and 50 at%) alloys by mechanical alloying technique in a high-energy planetary ball mill. The SEM images taken at different milling times allowed us to follow the morphology of the materials at different stages. The as-milled samples, characterized by X-ray diffraction and Mössbauer spectroscopy, contain a mixture of α (BCC) and γ (FCC) phases with a nanoscale grain size (determined by Maud program). According to X-ray diffraction data Fe-Ni mechanical alloying process (MA) samples contained bcc and fcc phases, but in the concentration ranges differing from those of equilibrium bulk alloys.

Acknowledgements

Anne-Marie Mercier (Laboratoire des Fluorures de l’université du Maine) is gratefully acknowledged for her help in performing X-ray diffraction experiments.

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