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Mössbauer and x-ray study of mechanically alloyed Fe–Ni alloys around the Invar composition

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Abstract

$Fe_{100-x}Ni_x$ powders ($22.5 \leqslant x \leqslant 40$ at.%) mechanically alloyed (MA) for 10 h were characterized by x-ray diffraction (XRD) and transmission ^{57}Fe Mössbauer spectrometry (TMS). In all of this composition range, the nanostructured alloys consist of two crystalline phases, body-centred cubic (BCC) and face-centred cubic (FCC). The Mössbauer spectra were fitted by means of a new fitting model involving two hyperfine magnetic field distributions (HMFDs), and a narrow singlet. One HMFD corresponds to the ferromagnetic BCC grains (tetrataenite), and the other to the ferromagnetic FCC grains (taenite), and the narrow singlet to paramagnetic FCC grains (antitaenite or superparamagnetic FCC grains). The Ni content dependence of the hyperfine field at ^{57}Fe nuclei of the FCC phase gives evidence for some jump at about 32.5 at.% Ni, attributed to Invar anomaly.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The Fe–Ni system has attracted the attention of researchers because it originates the formation of a great number of alloys with special thermal and magnetic properties [1–7]. Indeed, atomic volume, elastic modulus, heat capacity, magnetisation and Curie temperature show anomalous behaviour. This system presents two crystalline phases, body-centred cubic (BCC) for Fe rich alloys and face-centred cubic (FCC) for Ni rich alloys while both coexist for intermediate compositions. The composition limits of these phases depend on the preparation method and the heat treatment. When conventional techniques are used to produce equilibrium alloys the single phase ranges are very restricted, but when mechanical alloying (MA) is used to prepare them these single phase ranges extended significantly [8–14], and they shift to a low Ni concentration when the milling intensity increases [8, 15, 16]. Annealing the MA samples of the Fe–Ni system produces a further extension of the FCC single phase concentration compared to that of as-milled alloys as a result of the thermal suppression of the austenite into martensite transformation [17]. Recently, studies have been reported concerning the variation of the structural and magnetic properties during the martensitic transformation [18, 19] and about the dependence of this transformation with the concentration and milling time [20].

Many of the papers related to Fe–Ni equilibrium alloys are devoted to the study of samples around the Invar composition (65–70 at.% Fe). The Invar effect which was discovered by Guillaume in 1897 results from the anomalously low thermal expansion phenomenon observed over a large temperature range on FCC FeNi alloy containing 35 at.% Ni [21]. In addition, atomic volume, elastic modulus, heat capacity and magnetic properties exhibit anomalous behaviour for such a composition, stimulating numerous experimental and theoretical studies and thus providing large scientific debates to explain the Invar effect. Indeed, around this composition the lattice parameter shows expansion from 3.572 up to 3.583 Å (0 K) when Ni changes from 20 to 38 at.% and from 3.572 up to 3.588 Å at 300 K (room temperature (RT)) when Ni changes from 20 to 42 at.% Ni [1]. For these samples, unusual paramagnetic behaviour was reported giving rise to some controversial interpretations. Nakamura [1] suggested that the single line and the six-line patterns obtained from Mössbauer spectrometry (MS) originated from paramagnetic and ferromagnetic regions, respectively. It was also reported

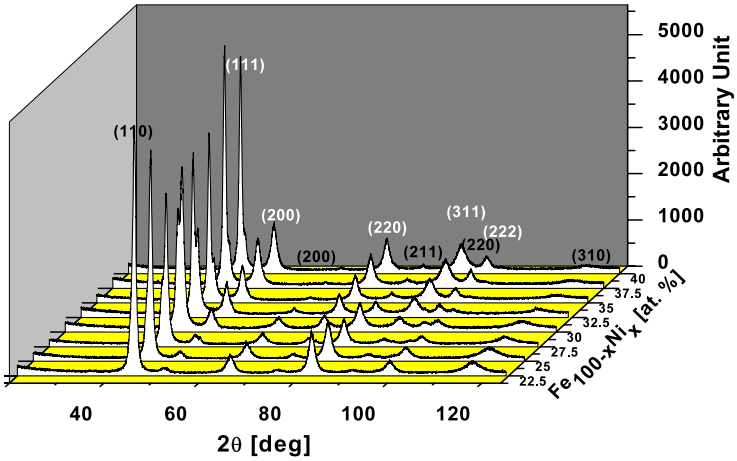

Figure 1. XRD patterns (plotted on a linear scale) for $Fe_{100-x}Ni_x$ samples alloyed for 10 h.

that the single line becomes broader at very low temperature due to the paramagnetic to antiferromagnetic transition. Ok and Han [22] reported a study on very fine and larger particles of γ-$Fe_{69}Ni_{31}$: the single line and the six-line Mössbauer patterns are due to the fine particles while the single line disappears for larger particles, suggesting an assignment of the single line to the superparamagnetic behaviour of the ferromagnetic or antiferromagnetic fine particles. On the basis of their own studies and those reported in the literature on Fe–Ni minerals present in different meteorites and synthetic analogue samples, Rancourt and Scorzelli proposed that the single line is attributed to antitaenite, a paramagnetic low-spin FCC γ_{LS}-Fe–Ni phase [23, 24]. According to theoretical predictions given by Rancourt [25], this antiferromagnetic low Ni content phase possesses a Fe atomic moment of $\mu_{Fe} \approx 0.5\ \mu_B$. In addition, it exhibits the same crystal structure as taenite (FCC rich Ni content) which presents a high Fe atomic moment of $\mu_{Fe} \approx 2.8\ \mu_B$ and predominant ferromagnetic interactions. The influence of the atomic disorder and of the structural type has also been investigated on the basis of theoretical calculations involving the coherent-potential approximation within the Korringa–Kohn–Rostocker band-structure model [26]. It was concluded that the magnetic ground state vanishes from $Fe_{60}Ni_{40}$ to the non-magnetic $Fe_{75}Ni_{25}$ system. In addition, re-entrant ferromagnetic phase transitions have been evidenced in the FCC phase close to the Invar composition. More recently, *ab initio* calculations of the volume dependence of thermodynamic and magnetic properties of the FCC FeNi phase allow us to conclude that the magnetic structure is characterized by a continuous transition from the ferromagnetic state at high volumes to a disordered non-collinear magnetic structure at low volumes [27].

The paramagnetic behaviour has also been reported for Fe–Ni samples prepared by mechanical alloying [8, 9, 12, 13, 17]. Kaloshkin *et al* suggested, on the basis of Mössbauer studies, that the FCC alloys with 20–28 at.% Ni are non-ferromagnetic at room temperature [17]. The studies of powders prepared by MA give evidence of a decrease of the mean hyperfine field when Ni content is about 37.5 at.%, i.e. the Invar region. This decrease is smaller than that observed in the case of in-equilibrium state samples [7].

Most of the Mössbauer studies concerning Fe–Ni alloys close to the Invar composition, give rise to spectra which were fitted by means of paramagnetic and magnetic components. But very few details are concerned with the fitting procedure. Baldokhin *et al* [8] fitted the spectra of as-milled alloys with 10 and 20 at.% Ni and the BCC structure with two sextets and a small singlet. The singlet was associated with a small amount of the paramagnetic FCC phase. The two sextets were associated to the ferromagnetic BCC phase. Mössbauer spectra of double phase alloys (22, 24, 26 and 28 at.% Ni) were fitted with two sextets and a singlet too. For single phase alloys with a FCC structure (30–50 at.% Ni) the Mössbauer spectra were fitted with a hyperfine magnetic field distribution (up to 5 hyperfine fields) [8]. For alloys with more than 50 at.% Ni Mössbauer spectra were fitted with three sextets, which were associated with three different surroundings of iron atoms in these alloys [8].

The present work aims to compare the phase composition and hyperfine properties of a set of $Fe_{1-X}Ni_X$ samples around the Invar composition and prepared by MA, to those reported in the literature, and to propose a new fitting description of Mössbauer spectra, allowing thus to distinguish the hyperfine contributions attributed to the BCC (tetraenite) and FCC (taenite) Fe–Ni phases.

2. Experimental method

Pure carbonyl Fe powder (99.9%) and electrolytic Ni powder (99.9%) were used as the starting materials. $Fe_{1-X}Ni_X$ samples with $22.5 \leqslant x \leqslant 40.0$ were alloyed under vacuum for 10 h and rotation frequencies of 280 rev min^{-1} by MA in a planetary ball mill (Fritsch 'Pulverisette 5') using hardened chromium steel vials and balls. The ball mass-to-powder mass (BM/PM) ratio was about 20:1. The final products were characterized by x-ray diffraction (XRD) using a Rigaku diffractometer with the Cu Kα radiation and Mössbauer spectrometry (MS) by collecting the spectra at room temperature (RT) and at 77 K with a conventional transmission spectrometer using a ^{57}Co (Rh) source and an α-Fe foil as the calibration sample. The XRD patterns were refined by the Rietveld method using the

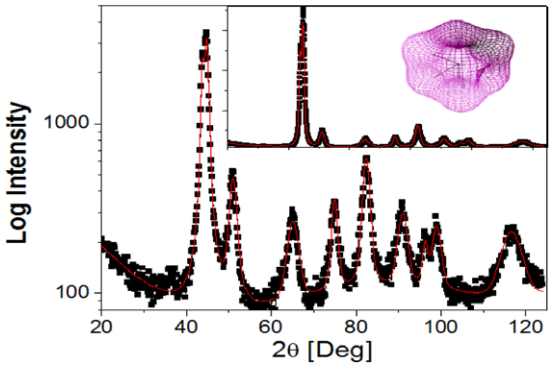

Figure 2. XRD pattern of the $Fe_{67.5}Ni_{32.5}$ sample alloyed for 10 h reported in a logarithmic scale to extend the baseline scattering. The inset gives the same pattern with a linear scale and the mean shape of structural grain.

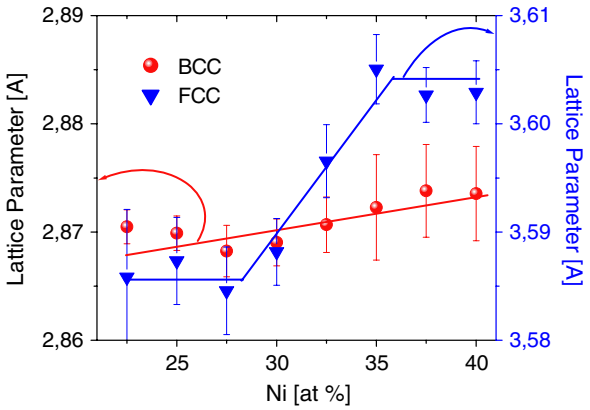

Figure 4. BCC (a) and FCC (b) lattice parameter dependence on Ni content.

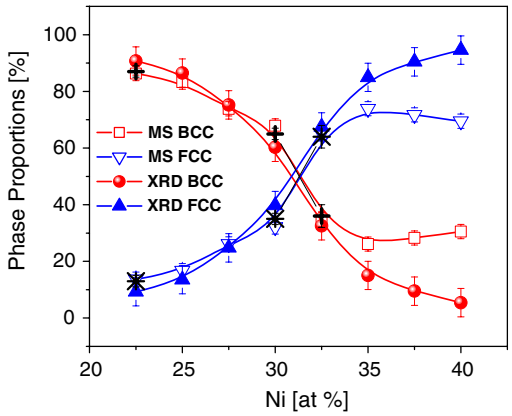

Figure 3. Phase proportions estimated from XRD patterns and RT Mössbauer spectrometry at 300 K. In addition, + and * symbols represent BCC and FCC phase proportions estimated from Mössbauer spectra at 77 K, respectively.

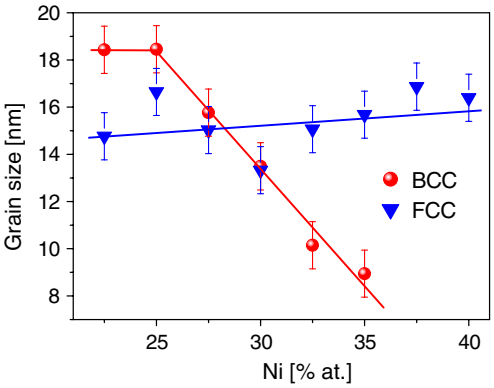

Figure 5. Grain size versus Ni content of the Fe–Ni (BCC) and Fe–Ni (FCC) phases obtained from the refinement of the XRD patterns.

MAUD program [28] and the Mössbauer spectra were fitted by using the MOSFIT program [29].

3. Experimental results and discussion

As illustrated in figure 1, XRD patterns show the same Bragg peaks, the intensities of which are Ni content dependent. They can be attributed to BCC and FCC phases: Miller indices are labelled in black and white on corresponding Bragg peaks, respectively. One observes that the intensities of Bragg peaks assigned to a FCC phase increase when the Ni content increases. Different microstructural models were proposed and a better description is obtained assuming pseudo-cubic grains for both BCC and FCC phases, as illustrated with one composition in figure 2.

In addition, the logarithmic scale gives evidence for a good agreement for the wings of the Bragg peaks: it also allows to conclude that the grain boundary contribution does not exceed about 10–12 at.% for these milled powders, thus suggesting a highly dense nanostructure (grain boundaries of about 0.7–0.8 nm thick) [30].

Figure 3 shows the behaviour of the volumetric percentage of the two detected phases estimated from x-ray diffraction analysis as a function of the Ni concentration. The coexistence of the two phases in all of the studied composition range can be noted whereas the proportion of FCC increases as the Ni content increases. It is important to mention that the MA process increases the coexistence range of these two phases, as previously reported [2, 4, 8, 9, 13], compared with those prepared by melting in this composition range.

As illustrated in figure 4, the mean lattice parameter of the BCC phase remains nearly constant at around 2.872 Å, a value slightly higher than that of pure BCC–Fe. This feature is well supported by both the very similar radius of the Fe (1.26 Å) and Ni (1.24 Å) atoms and the lower density of the BCC phase. On the contrary, one observes three regimes of the mean lattice parameter of the FCC phase: a first plateau at about 3.585 Å, then an increase up to a second plateau at about 3.605 Å, with values much larger than those of pure FCC Ni, whatever the Ni content is. These changes can be explained by combination effects of the radius values, the atomic disorder and the high density of FCC packing. On the other hand, the present values are higher than those reported for melted and ordered alloys obtained by different preparation techniques. This increase was reported by Nakamura [1] for melted Fe–Ni alloys around this composition region and this anomaly is typical of Invar behaviour.

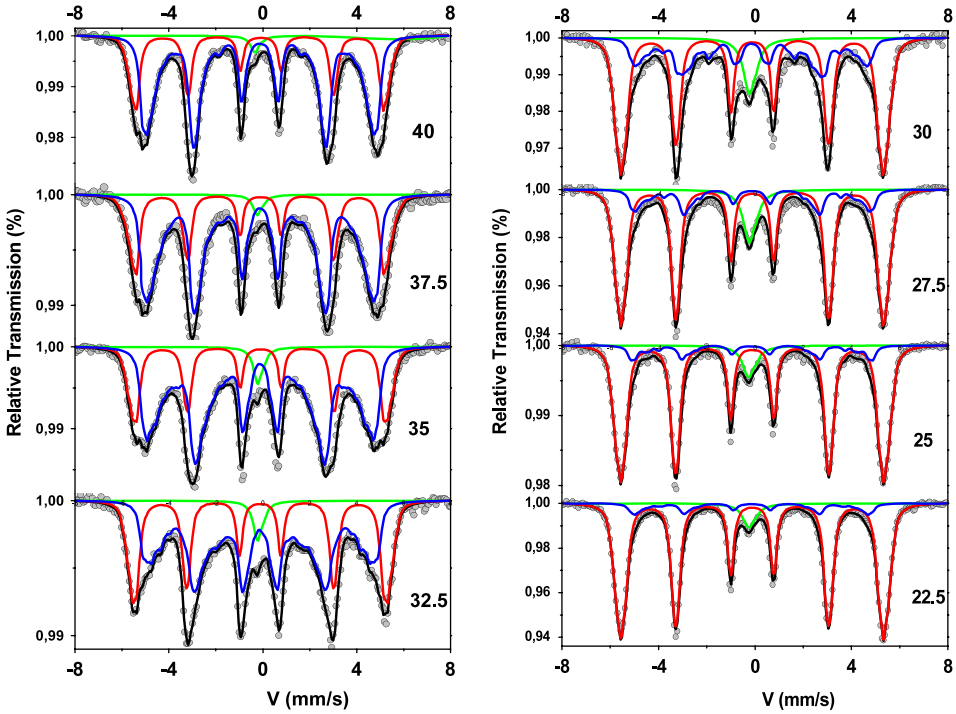

Figure 6. RT Mössbauer spectra of the MA $Fe_{100-x}Ni_x$ samples milled for 10 h.

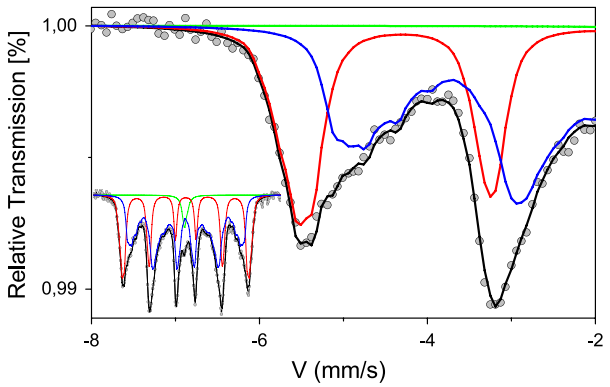

Figure 7. Zoom of peaks 1 and 2 of the Mössbauer spectrum of the $Fe_{67.5}Ni_{32.5}$ sample milled for 10 h. The inset represents the whole spectrum. One distinguishes the BCC, FCC magnetic components and the quadrupolar single line component.

Figure 5 clearly shows that the mean grain size of the BCC phase decreases from 18 down to 8 nm while that of the FCC phase remains nearly constant (15 nm) when the Ni content increases. Such behaviours are related to the fragility of the BCC grains and the ductility of the FCC phase, respectively.

The RT Mössbauer spectra which are presented in figure 6 consist of magnetic sextets with broad and asymmetrical lines and a single line for low Ni content. The spectra can be first modelled by either one singlet and one sextet with broad lines or one singlet and one hyperfine magnetic field distribution (HMFD). As those models are not greatly satisfactory because of their asymmetry, another approach is proposed, involving two HMFDs and a singlet, in addition to a small preferential orientation of the Fe magnetic moments. It is well established that the presence of Ni as first or second nearest neighbours in a BCC structural type enhances the hyperfine field and the isomer shift at the Fe site [31]. Consequently, the magnetic hyperfine structure was divided into two independent components associated with different HMFDs and different values of isomer shifts to describe the asymmetry of the lines. The best agreement is obtained when the lower limit and the higher limit of the two HMFDs is about 32 T but with a small overlap to make these distributions smooth. Finally, the single line is due to the FCC Fe–Ni paramagnetic grains with high Fe content [5, 17, 20]. To illustrate the efficiency of the present fitting model developed to describe Mössbauer spectra obtained on the $Fe_{100-x}Ni_x$ powders with $22.5 \leqslant x \leqslant 40.0$, figure 7 shows the two lowest energy peaks and the spectrum of the sample when $x = 32.5$. Let us emphasize that the hyperfine structures observed at 77 K are less resolved particularly when the Ni content increases, as illustrated in figure 8. However, the same fitting model has been applied (with a limit of 33 T) on those spectra, giving rise to the same quantitative conclusions, as shown in figure 3.

Figure 9 shows the HMFDs estimated from the proposed fitting model and after considering the texture effect. Two principal domains can be noted the high field component is attributed to the BCC Fe–Ni ferromagnetic grains (tetrataenite) [4], while the other one (lower field values) is ascribed to the FCC Fe–Ni ferromagnetic grains (taenite) [4]. The small reduction of the hyperfine field limit (32 T) in comparison to the typical value of BCC–Fe (33 T) is due to the increase of lattice parameter, i.e. reduced density, and the decrease at 300 K of the magnetic moment according to the Bethe–Slater curve [32].

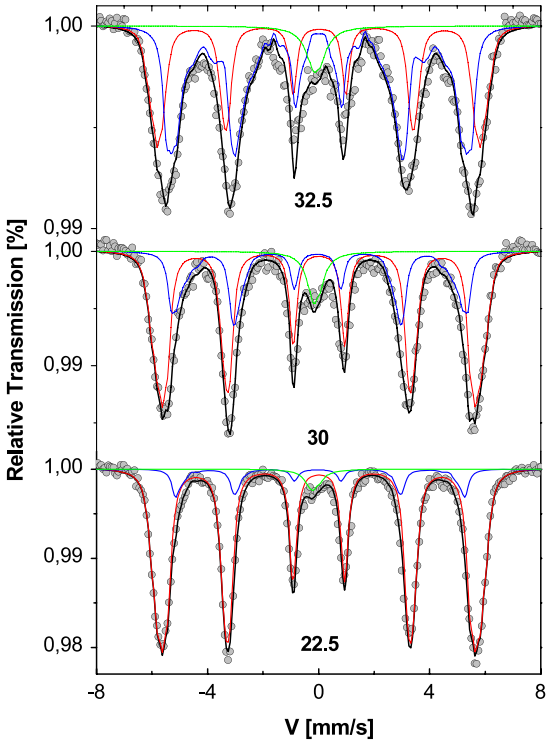

Figure 8. 77 K Mössbauer spectra of some MA $Fe_{100-x}Ni_x$ samples milled for 10 h.

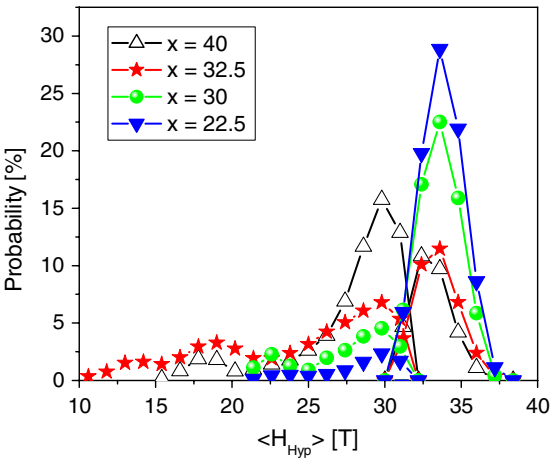

Figure 9. HMFDs obtained for the $Fe_{100-x}Ni_x$ samples with $32.5 < x < 40$. The lines are a guide for the eye.

It is important to emphasize that the proportions of BCC and FCC phases fairly agree with those estimated from x-ray diffraction as illustrated in figure 3, particularly for low Ni content. The small disagreement at high Ni content rather suggests the presence of Fe rich BCC and Ni rich FCC grains. In addition, the expected hierarchy of isomer shift values is observed.

The mean hyperfine field of the BCC phase remains rather Ni content independent at RT but that of the FCC phase reveals some jump at about 32.5 at.% Ni. This transition is illustrated in figure 10 from the total mean hyperfine field which is compared to that obtained on melted

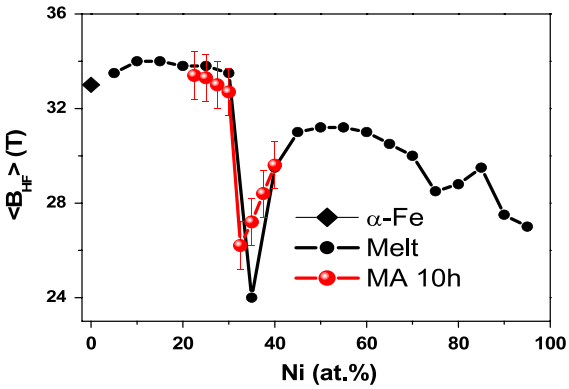

Figure 10. RT mean hyperfine field values as a function of Ni content.

FeNi alloys [7]: one observes a good agreement but the decrease is slightly lower than that reported for in-equilibrium state samples [1] and similar to that reported for MA samples [33], the small difference resulting probably from the non-homogeneous chemical disorder. One can suggest the occurrence of a small gradient of the composition within the crystalline grains (increasing Fe and Ni content from the centre towards the periphery within FCC and BCC grains, respectively). Therefore, in comparison to data reported in [7], one expects that the binomial distribution description explains the magnetic hyperfine behaviour of such nanostructured Fe–Ni powders. Another feature is concerned with the isomer shift of the FCC phase, which slightly increases with Ni content: this is consistent with the evolution observed on well ordered FeNi alloys associated to a low/high moment transition as earlier proposed [34]. Finally, the coercive field and the saturation magnetization values estimated at 300 K on present nanostructured powders slowly decrease when the Ni content increases: such results are rather consistent with those observed on FeNi alloys and confirm the presence of both BCC and FCC phases over a wider range of composition.

4. Conclusion

This new fitting model allows to better describe the Mössbauer hyperfine structure of FeNi powdered alloys and to distinguish the two BCC and FCC components. The Invar anomaly is also observed in nanostructured FeNi alloys prepared by high energy ball milling from the jump of hyperfine field corresponding to the FCC phase, at about 32.5 at.% Ni. The present description gives a better insight of the atomic diffusion mechanism of Fe into FCC Ni and of Ni into BCC Fe during the mechanical alloying process as a function of Fe and Ni contents from the hyperfine field distribution, giving rise to Fe (and Ni) in(de)creasing content gradient from the centre to the periphery of nanocrystalline FCC grains: this approach is in progress and will be discussed elsewhere.

Acknowledgments

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