Investigating the martensite-austenite transformation on mechanically alloyed FeNi solid solutions

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Abstract. The martensite-austenite transformation on $Fe_{70}Ni_{30}$ and $Fe_{75}Ni_{25}$ nanostructured solid solutions has been investigated by neutron thermo-diffraction experiments carried out between 300 and 1000 K. We observe that the difference between the temperatures at which the martensitic transformation starts (A_i) and finishes (A_f) exceeds 250 K, being five times larger than that of the as-cast coarse-grained conventional alloys. The main reason for this striking phenomenon is the drastic microstructural changes produced during the severe mechanical milling process, giving rise to a large reduction of the crystalline mean size (below 20 nm) and the generation of a considerable microstain (reaching 1%).

1. Introduction

Mechanical alloying technique has been largely used for the synthesis of metastable Fe binary metastable alloys [1], either in amorphous [2] or nanocrystalline states [3,4], even in the case of solid solutions with almost vanishing miscibility of the elemental constituents [5,6]. Moreover, these alloys have attracted great interest because very often they exhibit anomalous magnetic behaviour, such as the invar anomalies observed in Fe-Cu [7]. In particular, $Fe_{100-x}Ni_x$ solid solutions obtained by means of mechanical alloying or ball milling is one of the most studied Fe-binary systems during the last two decades [8-13]. The crystal structure of these compounds depends on the relative percentage of Fe and Ni in the composition, being face centred cubic (FCC) for $x \geq 35$, body centred cubic (BCC) for $x \leq 20$ and a mixture of both BCC and FCC for intermediate nominal compositions [8,10]. The microstructure of these powder materials at the sub-micrometer length scale consists of agglomerated grains with mean crystalline sizes below 20 nm, favouring the formation of heterogeneous and highly disordered grain boundaries [14-16]. The reduction of the mean crystalline size makes more relevant the role played by the grain boundaries in the macroscopic physical-chemical properties, which in many cases largely differ from those of coarse-grained alloys with the same composition [17-21].

On the other hand, it is well known that BCC FeNi alloys, the martensitic phases, prepared by conventional annealing undergo the so-called MA transformation (BCC→FCC) on heating. The initial, A_i, and final, A_f, temperatures have been chosen as those corresponding to the existence of 10 and 90% of the FCC (austenitic) phase in the powder sample, respectively. The difference, $\Delta T = A_f - A_i$, is composition-dependent and does not exceed 50 K in any case [22]. Moreover, on cooling from

high temperatures, the reverse structural transformation (FCC→BCC) takes place with an important hysteresis in temperature.

Previous thermomagnetic measurements have revealed that this MA transition is observed also in FeNi mechanically alloyed samples [8,23,24]. However, most of the studies concerning the MA structural transformations, have been carried out by using room temperature RT) x-ray diffraction and Mössbauer spectroscopy on samples that have been previously annealed at high temperatures and then cooled down to RT [25-27].

On the other hand, powder neutron thermo-diffraction is considered as a fundamental tool for *in situ* studies of the temperature dependence of nuclear and/or magnetic structure in metastable systems [28]. Hence, in the present paper we report a detailed structural analysis of MA transformation on $Fe_{70}Ni_{30}$ and $Fe_{75}Ni_{25}$ powder samples together with the temperature-induced microstructural relaxation taken place in the martensitic phases of these as-milled alloys during heating up from RT to 1000 K.

2. Experimental details

Powders of elemental Fe, with maximal particle size of 60 μm and purity of 99.95%, and Ni, with average particle size of 7 μm and purity of 99.9%, were milled in a high-energy ball mill (Retsch PM/400) during 50 h under controlled Ar atmosphere. The structural characterization was performed using "in situ" neutron thermo-diffraction experiments at the POLARIS time of flight diffractometer (ISIS Facility, UK) in the temperature range from RT to 1000 K. The samples were heated under vacuum at a heating rate of 2 K/min and each diffraction pattern was collected every 5 min. The Rietveld refinement of the diffraction patterns was performed using the FullProf Suite package [29] on patterns measured on the detector bank C (that with the higher experimental resolution) of POLARIS instrument. The interplanar distance range, from 0.3 to 3.2 Å, allows us to fit at least 35 reflections for BCC and/or FCC crystal structures. Nevertheless, a reduced d-space range (0.75-2.25 Å) is showed on the diffraction figures of the article in order to better appreciate the profile of the Bragg peaks.

3. Results and discussion

The figure 1 shows the neutron thermo-diffractograms of the $Fe_{70}Ni_{30}$ and $Fe_{75}Ni_{25}$ samples collected during the heating up from room temperature. In the as-milled state a mixture of both BCC and FCC phases is present in the powder samples (see fig. 2), with an approximate 78(1) and 81(1)% of BCC phase, respectively (see fig. 3). The MA structural transformation of the majority BCC phase takes place approximately between 600 and 850 K, where the Bragg reflections associated with the FCC (BCC) phase increase (decrease) their intensity. The Bragg reflections of the BCC phase disappear at high temperatures (above 850 K). This progressive transformation is better observed in Figure 1. In addition, a continuous sharpening of the BCC Bragg peaks, due to the temperature induced microstructural relaxation of the as-milled BCC nanostructure, is also observed along the similar temperature range. Moreover, the BCC and FCC phases in the as-milled samples seem to have roughly the same composition as indicated by their almost equal values for the respective lattice parameters.

On the other hand, Figure 3 displays the relative phase percentages and the microstructural analysis obtained from the fits of the neutron diffraction patterns of $Fe_{70}Ni_{30}$ and $Fe_{75}Ni_{25}$ samples, respectively. The mean maximum strain and the mean crystalline size for the BCC phase have been determinate by line-profile analysis using a linear combination of spherical harmonics and Stephens´ formulation [30]. It is worth noting the following features: (*i*) the MA transformation spreads out in temperature on both samples for more than 250 K, being five times larger than the values observed on coarse-grained conventional alloys [22]; (*ii*) an interconnection between the martensitic transformation and their microstructural relaxation can been established. Hence, the microstructure of the metastable as-milled solid solutions, characterized by a large maximum strain (~1%) and a small crystalline size (< 20 nm), is responsible for a large broadening of the Bragg peaks (see figures 1 and 2). Concerning the huge enlargement of the temperature range for the MA transformation, it could be related to both the high concentration of crystalline defects and the presence of extended grain boundaries.
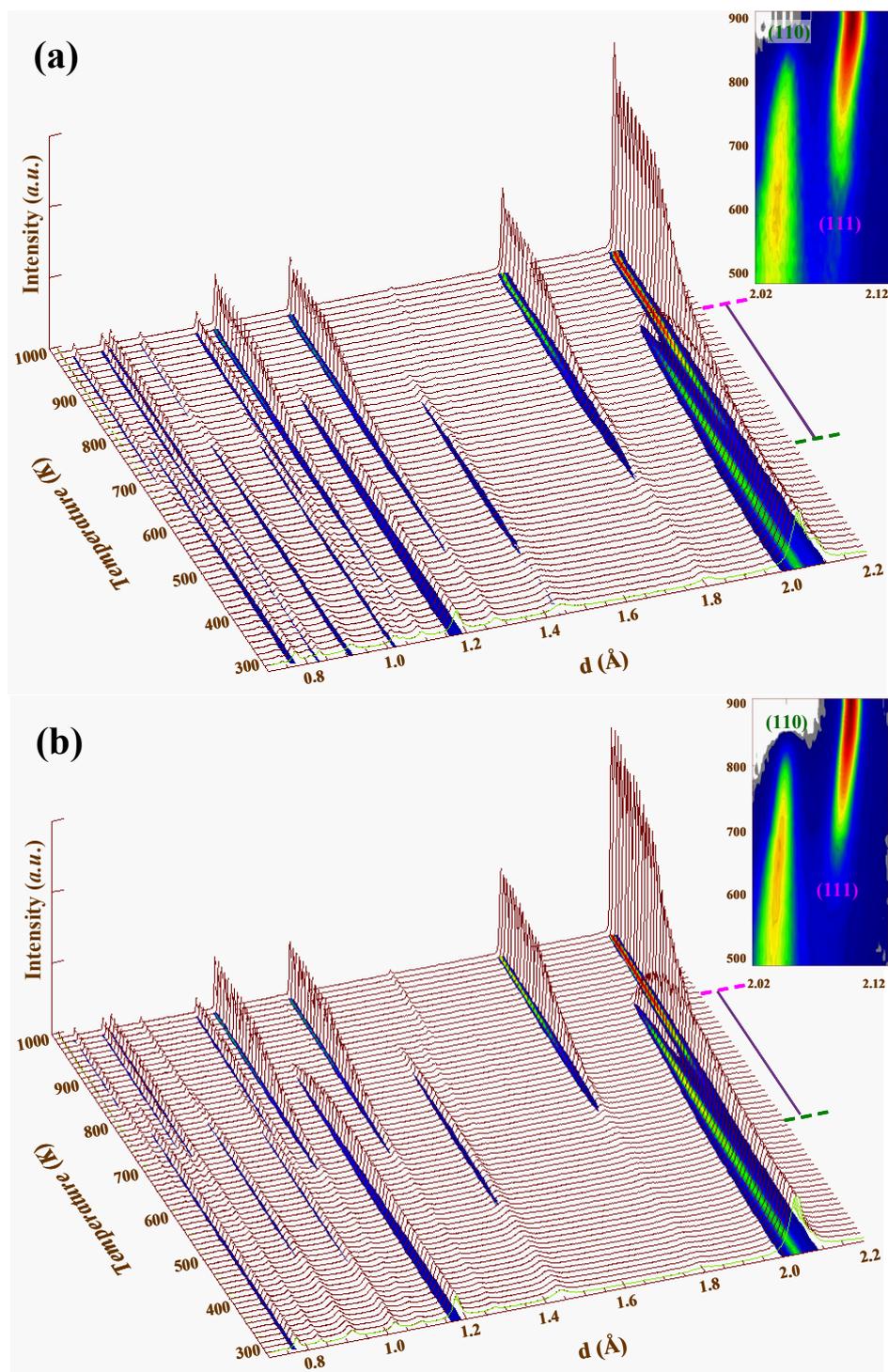
Figure 1. 3D-plot showing the neutron thermo-diffractograms for the $Fe_{70}Ni_{30}$ **(a)** and $Fe_{75}Ni_{25}$ **(b)** samples collected from RT to 1000 K. The right-top insets show the contour plots of the temperature dependence of the interplanar distance for the Bragg reflections (110) and (111) characteristic for the BCC and FCC crystal structures, respectively, in the temperature range marked with dashed lines in the figure.

In our case, the high values of the maximum strain reached on these materials provokes a decrease of at least 100 K in the A_i respect to that observed on coarse-grained conventional alloys. Furthermore, the degree of anisotropy of the microstrain and the existence of structural defects located at the grain boundaries lead to a temperature-expanded martensite-austenite transformation due to the step-by-step individual transformation of remaining isolated particles with lower values for the microstrain. On the other hand, as the density of structural defects and the size of the grain boundaries are being progressively reduced during the temperature-induced relaxation, the mean crystalline size of the BCC domains grows following an exponential trend. The latter is produced by a coalescence of neighbor BCC nanograins.
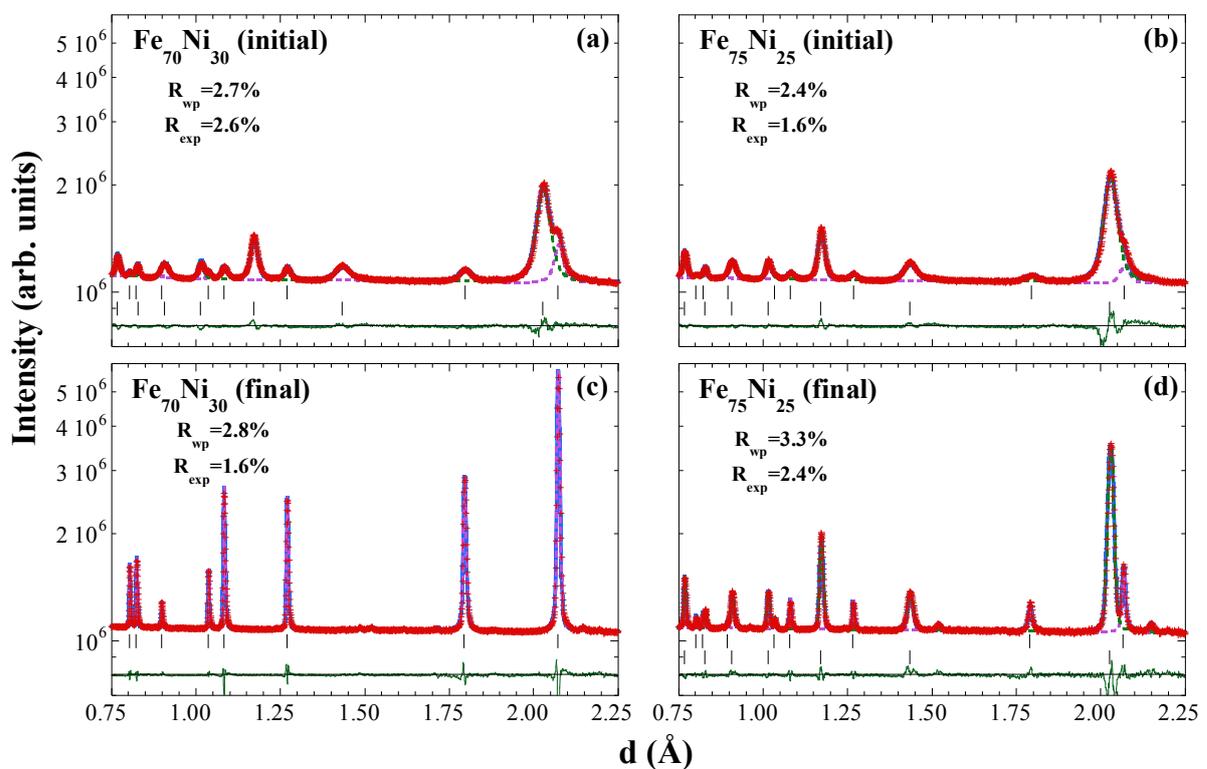

Figure 2. Observed (red crosses) and calculated (blue solid line) room temperature neutron powder diffraction patterns for the $Fe_{70}Ni_{30}$ (a-c) and $Fe_{75}Ni_{25}$ (b-d) of the samples in the as-milled state (initial) and after heating process (final). Positions of the Bragg reflections belonging to FCC and BCC crystal structures are represented by vertical bars (first and second series, respectively). The difference (observed-calculated pattern) is depicted at the bottom of each figure.

Finally, if we compare the room temperature neutron diffraction patterns corresponding to the as-milled and that of the samples after the heating process (see figure 2) the most noticeable features are: (i) a large sharpening of the Bragg peaks have occurred due to the microstructural relaxation and (ii) while in the $Fe_{70}Ni_{30}$ sample only the FCC phase is observed (the reverse BCC-FCC transformation should occur at lower temperatures), the situation in the $Fe_{75}Ni_{25}$ sample is much more complex, because both BCC and FCC coexist at room temperature, indicating that the BCC-FCC transformation has not been fully completed yet.
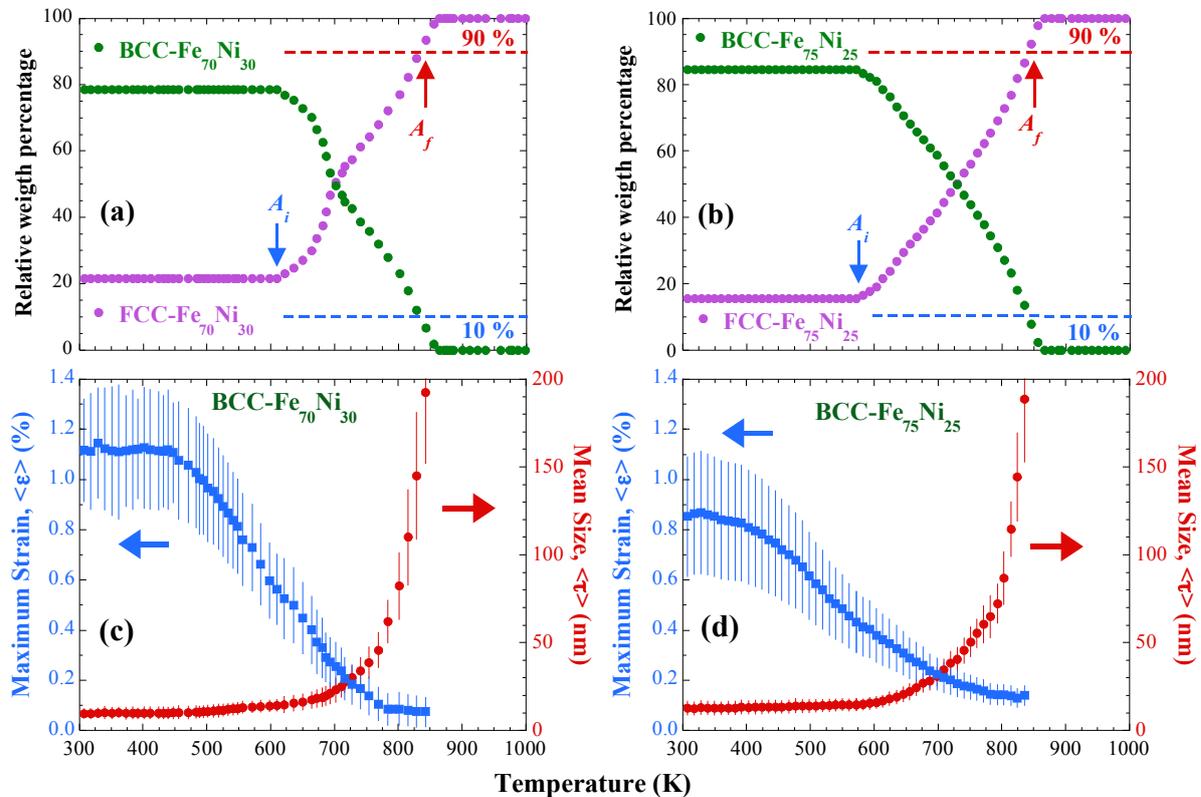
Figure 3. Temperature evolution of the relative phase percentages (top) and microstructure (mean maximum strain, $< \varepsilon >$, and mean crystalline size, $< \tau >$) for the BCC phases of the $Fe_{70}Ni_{30}$ and $Fe_{75}Ni_{25}$ samples. Vertical bars on microstructure plots represent the degree of anisotropy, not the estimated error.

4. Summary and conclusions

High-energy ball milling has been used to synthesize $Fe_{70}Ni_{30}$ and $Fe_{75}Ni_{25}$ metastable solid solutions with a mixture of BCC and FCC crystal structures on the as-milled state. Their metastable nature largely affects the thermodynamical equilibrium phase diagram, in particular the martensitic transformation of the BCC phases. This transformation takes places at lower temperatures (≈ 550 K) and is enlarged over a wider temperature range (250 K) than in conventional cold-rolled FeNi alloys. The latter, as revealed by neutron thermo-diffraction experiments, is clearly correlated with the temperature-induced microstructural relaxation.

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