Journal of Alloys and Compounds 495 (2010) 495–498

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Neutron powder thermo-diffraction in mechanically alloyed $Fe_{64}Ni_{36}$ invar alloy

Pedro Gorria[a,*], David Martínez-Blanco[b], Jesús A. Blanco[a], Ronald I. Smith[c]

[a] Departamento de Física, Universidad de Oviedo, Avda. Calvo Sotelo s/n, Oviedo 33007, Asturias, Spain
[b] Unidad de Magnetometría, SCT's, Universidad de Oviedo, Julián Clavería 8, 33006 Oviedo, Spain
[c] ISIS Facility, RAL, Chilton, Didcot, Oxon OX11 0QX, United Kingdom

ARTICLE INFO

Article history:
Received 6 August 2008
Received in revised form 14 October 2009
Accepted 15 October 2009
Available online 24 October 2009

Keywords:
Nanostructured materials
Mechanical alloying
Neutron diffraction
Invar alloys

ABSTRACT

Nanostructured $Fe_{64}Ni_{36}$ alloy has been obtained using high-energy ball milling for 35 h of milling time, $Fe_{64}Ni_{36}$ MA-35 h. The initial as-milled $Fe_{64}Ni_{36}$ MA-35 h powders are inhomogeneous, showing a majority phase with a face-centred cubic (fcc) crystal structure [88(2)%] and a minority phase with body-centred cubic (bcc) crystal structure [7(2)%]. The evolution of the microstructure with temperature between 300 K and 1100 K has been followed by means of *in situ* neutron powder thermo-diffraction experiments. The room temperature values for the mean crystalline size and the mechanical-induced microstrain of the fcc phase in the as-milled sample are ~10 nm and ~0.7%, respectively. Moreover, after heating the $Fe_{64}Ni_{36}$ MA-35 h powders up to 1100 K, an increase of around 65 K in the Curie temperature respect to that of the commercial coarse-grained alloy of the same composition is observed. The latter together with the observed temperature dependence of the lattice parameter suggests that the $Fe_{64}Ni_{36}$ MA-35 h sample subjected to the heating process exhibits invar behaviour. On heating up to 1100 K thermal relaxation of the microstructure occurs giving rise to grain growth above 100 nm, nearly vanishing values for the maximum strain, and the transformation of the bcc phase into the fcc one above 800 K, being the latter stable in subsequent heating–cooling processes.

More than a century ago, Guillaume observed that FeNi alloys with face-centred cubic (fcc) crystal structure and composition around $Fe_{65}Ni_{35}$ exhibit vanishing thermal expansion coefficients below the ferro-to-paramagnetic transition. A number of practical applications have taken benefit from this useful property, especially in the design and development of high precision mechanical instruments and standards. However, this effect, commonly known as Invar, is associated with other magneto-volume anomalies, such as the pressure dependences of both the bulk modulus and the Curie temperature, T_C, which have been observed in a number of Fe-based alloys, being intimately related with the Fe–Fe interatomic distances [1,2]. Nevertheless, the ultimate explanation of the invar effect at the microscopic level is not completely understood yet. For this reason, experimental [3–5] as well as theoretical research work in FeNi invar alloys is, still today, intensely undertaken [6,7].

On the other hand, mechanical alloying or ball milling technique offers the possibility of obtaining a huge number of metallic alloys with different compositions and singular microstructural characteristics, such as amorphous [8] or nanostructured materials [9], most of them out from the thermodynamical equilibrium [10]. This fact allows studying the influence of microstructure in the physical–chemical properties compared with those of the parent bulk or coarse-grained alloys. Up to know, it has not been paid much attention to the effects produced by milling on the magneto-volume anomalies in mechanically alloyed Fe-TM (TM = transition metal) binary compounds, and only few works devoted to FeNi [11–13] and FeCu [14–16] alloys have been published.

The aim of this work is twofold: (i) to investigate the microstructural changes taking place during continuous heating from room temperature to 1100 K in the as-milled $Fe_{64}Ni_{36}$ MA-35 h alloy by means of *in situ* neutron powder thermo-diffraction (NPTD) experiments [17], and (ii) to ascertain if the mechanically alloyed sample already exhibits invar behaviour, comparing the temperature dependences of both the magnetization and the lattice parameter of the mechanically alloyed sample with those of a coarse-grained commercial alloy with the same composition (Goodfellow $Fe_{64}Ni_{36}$ Invar®).

The as-milled alloy has been obtained from starting pure Fe (99.98%) and Ni (99.995%) powders (Goodfellow) using a high-energy Retsch PM/400 planetary ball mill for 35 h and under Ar atmosphere. NPTD experiments were carried out on the POLARIS diffractometer (ISIS facility, UK). The data were collected over the time-of-flight range 2000–19,600 s in the backscattering detector bank, $\langle 2\theta \rangle = 145^\circ$. The wide d-spacing range allowed us to determine lattice parameters of both samples with accuracy better than 0.001 Å. The sample mass used for the experiment was approximately 4 g and it was continuously heated from 300 K to 1100 K at a rate of 1 K/min meanwhile a diffraction pattern was collected

---

[*] Corresponding author. Tel.: +34 985102899; fax: +34 985103324.
E-mail address: pgorria@uniovi.es (P. Gorria).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.10.112

each 5 min, enough to achieve good statistics. The Fullprof package based in the Rietveld method was employed for the analysis of the diffraction patterns [18], and from the peak profile fitting the average crystalline grain size, $\langle\tau\rangle$, and the maximum strain, ε, were determined (for more details about the calculation and definition of $\langle\tau\rangle$ and ε see Eqs. A.8, A.9 and A.14 in the appendix of Ref. [17]). It is worth noting that due to the large *d*-space range covered by the POLARIS diffractometer (0.2–4 Å), more than 35 Bragg reflections can be discriminated, thus allowing a precise determination of microstructural parameters.

The room temperature neutron powder diffraction (NPD) pattern corresponding to the $Fe_{64}Ni_{36}$ standard powders (see Fig. 1a) shows very intense and narrow Bragg peaks belonging to a unique fcc-FeNi crystalline structure with a value for the lattice parameter, $a = 3.591(1)$ Å. However, the room temperature NPD pattern of the as-milled $Fe_{64}Ni_{36}$ MA-35 h sample (see Fig. 1b) is characterized by the appearance of broad Bragg peaks indicating the small crystalline size of the nanograins and the existence of large internal microstrain [17,19] caused by the milling process. Together with the reflections associated with the majority fcc-FeNi phase [88(2)%] with a lattice parameter, $a = 3.596(1)$ Å, there exist small peaks that can be ascribed to a body-centred cubic (bcc) Fe(Ni) phase [7(2)%] with $a = 2.866(1)$ Å [20], and to an impurity Fe oxide phase [magnetite or maghemite (<5%)].

The effect of sample heating on the kinetics of the microstructural thermal relaxation is shown in Fig. 2a, where the temperature evolution of both the mean crystalline size, $\langle\tau\rangle$, and the maximum strain, ε, of the fcc-FeNi majority phase in the as-milled $Fe_{64}Ni_{36}$ MA-35 h sample during the heating process is displayed. The values of $\langle\tau\rangle$ and ε remain unchanged from room temperature up to 450 K, suggesting that the microstructure of the powders does not vary substantially in this temperature range. However, at around 450 K the thermal relaxation process begins, giving rise to a linear decrease of the value of ε, with an approximate rate of 0.12% each 100 K, reaching vanishing values at around 1000 K. In addition, the grain growth is not significant for temperatures below 600 K, whereas further heating provokes an exponential-like increase of $\langle\tau\rangle$ with crystalline sizes larger than 80 nm above 900 K. The NPD patterns have not enough resolution to consider values of neither $\langle\tau\rangle$ nor ε for temperatures above 1000 K. The pattern collected at 300 K after cooling down from 1100 K (see Fig. 1c) shows intense Bragg peaks similar to those present in that corresponding to the $Fe_{64}Ni_{36}$ standard alloy (see Fig. 1a). Furthermore, it is worth mentioning that the Bragg peaks belonging to the low-content bcc-Fe(Ni) phase and present in the NPD pattern of the $Fe_{64}Ni_{36}$ MA-35 h as-milled powders (see Fig. 1b), have disappeared in the room temperature NPD pattern after the heating process (see Fig. 1c). This fact suggests that the microstructure of the predominant fcc-FeNi phase changes during heating up, and that the bcc-Fe(Ni) phase transforms into the fcc one. Fig. 2b shows the variation with temperature of the phase percentages (obtained from the Rietveld refinement of the diffraction patterns) during heating. It is observed that the relative amount of both fcc- and bcc-FeNi phases remains unchanged up to around 580 K. At higher temperatures the transformation from bcc to fcc starts, just around the same temperatures at which the grain growth of the nanocrystallites begins. The correlation between these two phenomena is easy to understand if we take into account that a bcc-to-fcc transformation does not imply atomic diffusion, it is governed only by slight plane displacements.

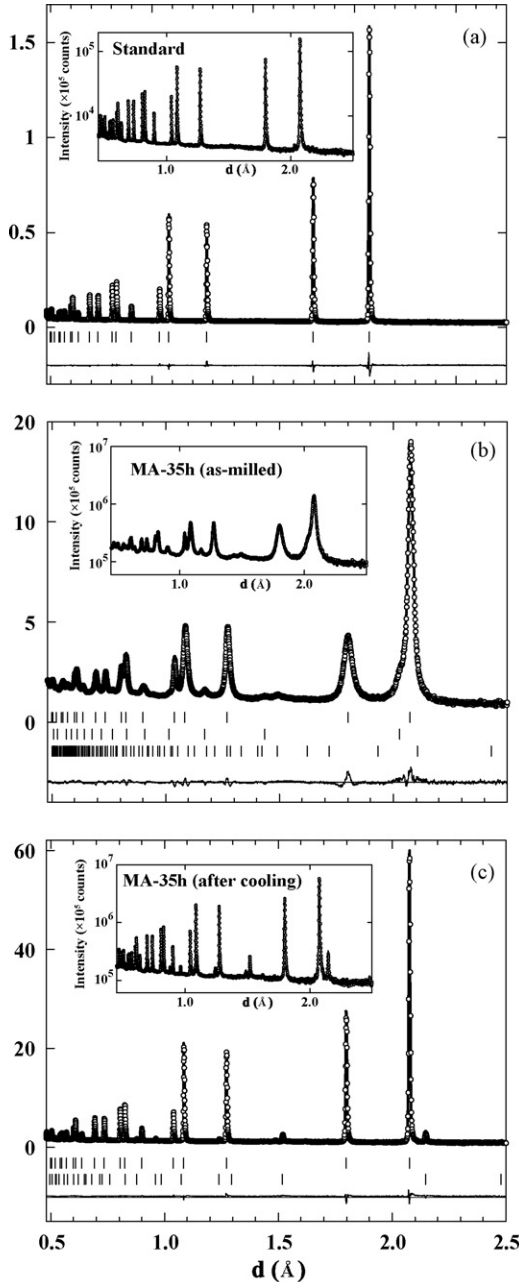

Fig. 1. Observed (dots) and calculated (solid line) room temperature neutron powder diffraction patterns of $Fe_{64}Ni_{36}$ standard (a) and $Fe_{64}Ni_{36}$ MA-35 h mechanically alloyed powders, (b) as-milled, (c) after heating up to 1000 K (see text for details). Positions of the Bragg reflections are represented by vertical bars [first vertical row corresponds to the fcc-FeNi phase; second row in (b) is associated with the minority bcc-Fe(Ni) phase, while third row in (b) and second row in (c) correspond to an iron oxide impurity]. The observed-calculated difference is depicted at the bottom of the patterns. The insets show the diffraction patterns using the same *d* range and a logarithmic scale for the intensity.

On the other hand, the lattice parameter of the fcc-FeNi phase at $T = 300$ K in the $Fe_{64}Ni_{36}$ MA-35 h milled sample, after being heated up to 1100 K, has a value $a = 3.597(1)$ Å. This fact means that, even though the heating produces the thermal relaxation of the microstructure, the lattice parameter is ca. 0.2% larger than that of the standard alloy [3.591(1) Å, as mentioned above]. It must be pointed out that changes in the composition are discarded, because chemical analysis gives the same relative percentages of Fe and Ni (64:36) with an uncertainty lower than 1%. Moreover, if a second heating is performed on the sample, the temperature variation of the lattice parameter exhibits two different regimes (see Fig. 3a): (i) a very slow increase in the value of the lattice parameter, $a(T)$, below 560 K (which allows us to estimate a very low value for the thermal expansion coefficient, $\alpha_T = -(1/V)(\partial V/\partial T) \approx 2 \times 10^{-6}\ K^{-1}$), and (ii) a change in the slope of the $a(T)$ curve for temperatures

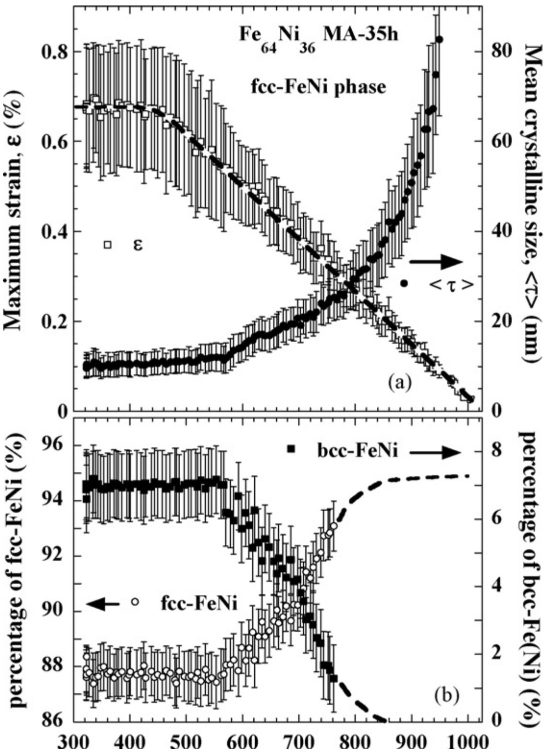

Fig. 2. (a) Temperature dependence of the microstructure (maximum strain, ε, and mean crystalline size, $\langle\tau\rangle$) for the fcc phase in the $Fe_{64}Ni_{36}$ MA-35 h sample and (b) of the relative percentages of fcc and bcc phases, for the $Fe_{64}Ni_{36}$ MA-35 h as-milled sample, being derived from profile fitting of neutron diffraction pattern collected during the first heating process. The lines are guide for the eyes. The vertical bars appearing in the mean size and the maximum strain correspond to a measure of the degree of anisotropy, not to the estimated error.

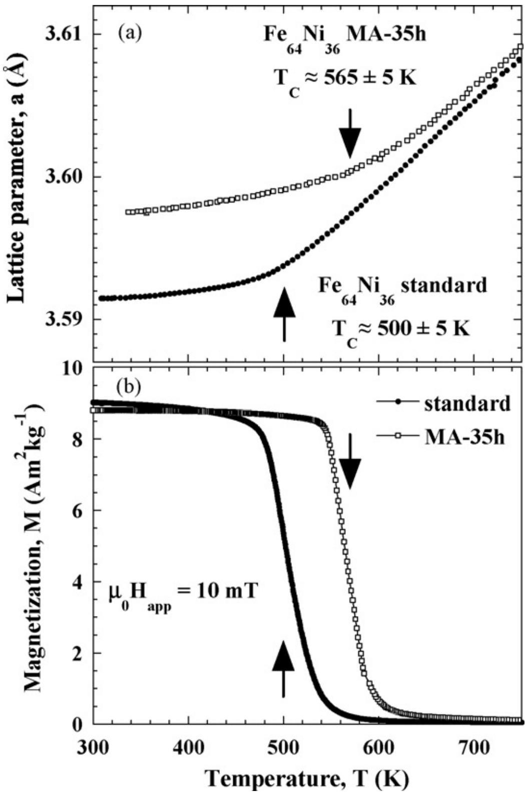

Fig. 3. Temperature dependences of the lattice parameter (a) and the magnetization (b) of the $Fe_{64}Ni_{36}$ standard and mechanically alloyed and heated $Fe_{64}Ni_{36}$ MA-35 h powders. The Curie temperatures are indicated with an arrow.

above 560 K. Subsequent heating–cooling cycles display the same $a(T)$ behaviour. In Fig. 3a the $a(T)$ curve obtained from the an NPTD experiment performed in the standard invar-$Fe_{64}Ni_{36}$ powders is also shown for comparison. These findings suggest that the invar character of the $Fe_{64}Ni_{36}$ MA-35 h milled powders is maintained after the heating process, but the temperature range in which the thermal expansion coefficient remains small is enlarged at least in 60 K.

In order to check whether the temperature dependence of the magnetization is also affected after the milling and heating procedures, a PPMS-14 T (Quantum Design) magnetometer equipped with a VSM option and a furnace up to 1000 K was used to measure the magnetization vs. temperature, $M(T)$, curves. In Fig. 3b the $M(T)$ curves observed under an applied magnetic field, $\mu_0H = 10$ mT, for both the standard and the milled and further heated $Fe_{64}Ni_{36}$ samples are shown. In this figure it can be clearly seen that the $M(T)$ goes to vanishing values at higher temperatures in the milled and heated sample than in the standard powders. The values of the Curie temperature, T_C, have been estimated from the minimum of the dM/dT vs. T curves (not shown). A shift of the T_C value from 500 K to around 565 K in the milled and heated $Fe_{64}Ni_{36}$ MA-35 h sample respect to the $Fe_{64}Ni_{36}$ standard invar alloy is observed. Hence, both $M(T)$ and $a(T)$ behaviours seem to be intimately correlated. Taking into account that the milling and subsequent heating up to 1100 K produces a slight increase of the lattice parameter, and therefore of the cell volume, the Fe–Fe interatomic distances increase, thus giving rise to a reinforcement of the ferromagnetic coupling. This fact can be the responsible for the observed enhancement of T_C and, as a result of this, for the extension of the temperature range for invar behaviour in the milled and heated $Fe_{64}Ni_{36}$ MA-35 h sample. However, further experiments, concerning magnetic and elastic measurements under extreme conditions (high pressure and/or temperature), are under progress in order to attain more conclusive clues.

In summary, *in situ* neutron powder thermo-diffraction experiments in $Fe_{64}Ni_{36}$ solid solutions allow following in detail the microstructural transformations of these compound at high temperatures. The initial as-milled $Fe_{64}Ni_{36}$ MA-35 h powders have a mixture of fcc- (~88%) and bcc- (~7%) FeNi crystalline phases, with average crystalline grain size and maximum strain of 10 nm and 0.7%, respectively, for the majority fcc phase. Heating above 450 K gives rise to a linear decrease of the maximum strain (~0.12% each 100 K) due to thermal relaxation, while at higher temperatures, $T > 560$ K, a progressive and exponential-like grain growth takes place. The latter, coincides with the start of the structural phase transformation of the minority bcc phase into fcc. No supplementary transformations occur after finishing this structural phase transformation (around 850 K), neither during further heating nor during cooling down to room temperature. Finally, it is worth noting that the $Fe_{64}Ni_{36}$ MA-35 h milled sample, after being heated up to 1100 K, exhibits a moderate shift of T_C (65 K), towards higher temperatures and what is more, this sample already displays invar behaviour with a value for the thermal expansion coefficient, $\alpha_T \approx 2 \times 10^{-6}\ K^{-1}$ for $T < T_C$.

Acknowledgements

The authors thank Spanish MICINN for financial support under project MAT2008-06542-C04-03. We also thank ISIS facility for the allocation of neutron beam time.

References

[1] E.F. Wassermann, in: K.H.J. Buschow, E.P. Wohlfarth (Eds.), Ferromagnetic Materials, vol. 5, North-Holland, Amsterdam, 1990, p. 237.
[2] W. Pepperhoff, M. Acet, Constitution and Magnetism of Iron and Its Alloys, Springer, Berlin, 2001.

[3] F. Decremps, L. Nataf, Phys. Rev. Lett. 92 (2004) 157204.
[4] M. Matsushita, T. Inoue, I. Yoshimi, T. Kawamura, Y. Kono, T. Irifune, T. Kikegawa, F. Ono, Phys. Rev. B 77 (2008) 064429.
[5] P. Gorria, et al., Phys. Rev. B 80 (2009) 064421.
[6] M. van Schilfgaarde, I.A. Abrikosov, B. Johansson, Nature (London) 400 (1999) 46.
[7] A.V. Ruban, M.I. Katsnelson, W. Olovsson, S.I. Simak, I.A. Abrikosov, Phys. Rev. B 71 (2005) 054402.
[8] P. Gorria, J.S. Garitaonandia, M.J. Pérez, J.A. Blanco, J. Campo, Phys. Status Solidi (RRL) 3 (2009) 28.
[9] P. Gorria, P. Álvarez, J. Sánchez Marcos, J.L. Sánchez Llamazares, M.J. Pérez, J. Blanco, Acta Mater. 57 (2009) 1724.
[10] C. Suryanarayana, Prog. Mater. Sci. 46 (2001) 1.
[11] S. Wei, R. Duraj, R. Zach, M. Matsushita, A. Takahashi, H. Inoue, F. Ono, H. Maeta, A. Iwase, S. Endo, J. Phys.: Condens. Matter 14 (2002) 11081.
[12] P. Gorria, D. Martínez-Blanco, M.J. Pérez, J.A. Blanco, R.I. Smith, J. Magn. Magn. Mater. 294 (2005) 159.
[13] P. Gorria, et al., Phys. Status Solidi (RRL) 3 (2009) 115.
[14] P. Gorria, D. Martínez-Blanco, J.A. Blanco, A. Hernando, J.S. Garitaonandia, L. Fernández Barquín, J. Campo, R.I. Smith, Phys. Rev. B 69 (2004) 214421.
[15] P. Gorria, D. Martínez-Blanco, J.A. Blanco, M.J. Pérez, A. Hernando, L. Fernández Barquín, R.I. Smith, Phys. Rev. B 72 (2005) 014401.
[16] E. Ma, Prog. Mater. Sci. 50 (2005) 413–509.
[17] D. Martínez-Blanco, P. Gorria, J.A. Blanco, M.J. Pérez, J. Campo, J. Phys.: Condens. Matter 20 (2008) 335213.
[18] J. Rodríguez Carvajal, Physica B 192 (1993) 55.
[19] D. Martínez-Blanco, P. Gorria, M.J. Pérez, J.A. Blanco, R.I. Smith, J. Magn. Magn. Mater. 316 (2007) 328.
[20] J.F. Valderruten, G.A. Pérez Alcázar, J.M. Grenèche, J. Phys.: Condens. Matter 20 (2008) 485204.