

## Mechanically induced disorder and crystallization process in Ni-Mn-In ball-milled alloys

V. Sánchez-Alarcos<sup>1,2</sup>, V. Recarte<sup>1,2</sup>, J. I. Pérez-Landazábal<sup>1,2</sup>, S. Larumbe<sup>1,2</sup>, R. Caballero-Flores<sup>1,2</sup>, I. Unzueta<sup>3,4</sup>, J.A. García<sup>4,5</sup>, F. Plazaola<sup>3</sup> and J. A. Rodríguez-Velamazán<sup>6,7</sup>

<sup>1</sup>Departamento Física. Universidad Pública de Navarra, Campus de Arrosadia, 31006 Pamplona, Spain

<sup>2</sup>Institute for Advanced Materials (INAMAT), Universidad Pública de Navarra, Campus de Arrosadia, 31006 Pamplona, Spain

<sup>3</sup>Elektritate eta Elektronika Saila, Euskal Herriko Unibersitatea UPV/EHU, p.k. 644, 48080 Bilbao, Spain

<sup>4</sup>BC Materials (Basque Centre for Materials, Applications and Nanostructures), 48080 Leioa, Spain

<sup>5</sup>Fisika Aplikatua II Saila, Euskal Herriko Unibersitatea UPV/EHU, p.k. 644, 48080 Bilbao, Spain

<sup>6</sup> Instituto de Ciencia de Materiales de Aragón, Departamento de Física de la Materia condensada, CSIC–Universidad de Zaragoza, E-50009 Zaragoza, Spain

<sup>7</sup> Institut Laue Langevin, 71, Avenue des Martyrs, 38042 Grenoble Cedex, France

\*Corresponding author: *Tel.*: +34 948 169582; *Fax.*: +34 948 169565  
*E-mail address*: vicente.sanchez@unavarra.es

### Abstract.

High mechanical deformation has been induced in a Ni-Mn-In metamagnetic shape memory alloy by means of ball milling. The evolution of both the martensitic transformation and the magnetic properties associated to the microstructural variations has been characterized. The as-milled nanometric particles display an amorphous structure with a frustrated magnetic state compatible with a canonical spin-glass. On heating, an abrupt crystallization process occurs around 500K leading to a cubic B2 structure, which, in turn, does not show martensitic transformation. Modified Arrott plots point to competing long- and short-range magnetic couplings in the B2 structure. On further heating, a relaxation process takes place above 700 K concurrently with a B2-L<sub>21</sub> atomic ordering, giving rise to an anomalous two-step thermal expansion. The combined effect of both processes makes possible the subsequent occurrence of a martensitic transformation, which takes place at the same temperature than in the bulk. The large relative-cooling-power linked to the magnetocaloric effect at the martensitic transformation in the annealed powder makes it interesting for practical applications of magnetic refrigeration at nanoscale.

**Keywords:** Ni-Mn-In, ball-milling, crystallization, atomic order, nanoparticles

## 1. INTRODUCTION

Ni–Mn-based Heusler alloys exhibiting both long-range magnetic ordering and thermoelastic martensitic transformation (MT) are being intensively investigated over recent years, from both fundamental and applied points of view, due to the unique properties they show linked to the occurrence of a first-order structural transformation between magnetically ordered phases [1-3]. The magnetism in these alloys mainly arises from the coupling between the Mn atoms, in which the magnetic moment is chiefly confined, so the magnetic exchange interactions (which can be treated in the framework of a Ruderman-Kittel-Kasuya-Yoshida model) strongly depend on the Mn–Mn distance [4, 5]. Therefore, different sequences of magnetostructural transformations can be observed depending on both the third alloying element and the change in interatomic distances caused by the MT. In particular, in Ni-Mn-Z (Z=In, Sn, and Sb) alloys, the so-called metamagnetic shape memory alloys, the MT takes place between a ferromagnetic austenite and weak magnetic martensitic phase, in such a way that the large magnetization drop occurring at the MT allows the induction of the MT by an applied magnetic field [6]. This phenomena gives rise to multifunctional properties, namely magnetic shape memory, giant magnetoresistance and large inverse magnetocaloric effect (MCE), of great technical interest for practical applications in sensing and magnetic refrigeration [7-14].

One of the main drawbacks of the metamagnetic shape memory alloys, in turn, is the poor mechanical properties they show. All these alloys are very brittle and difficult to handle, and cracks form very easily when the crystal is being thermally cycled through the phase transformation [15, 16]. Alloys in form of films, ribbons, wires or foams [17-20] have been studied as an alternative to overcome the mechanical limitations of the bulk material. In particular, the integration of powder alloys into a polymer to form composites has been found to be especially interesting for the development of magnetically-controlled dampers and actuators. Such composites may show low cost, large mechanical energy absorption and good mechanical properties [21, 22]. In this case, a previous complete characterization of the powder alloy is needed in order to properly tune the response of the composites.

The magnetostructural properties of metamagnetic shape memory alloys have been deeply studied in polycrystalline bulk alloys. Nevertheless, up to now, much less work has been devoted to the analysis of the MT and the magnetic properties at reducing sizes tending to nanoscale. Even though the grain size and the state of internal tensions are known to be two parameters highly influencing the characteristics of the MT through the variation of the elastic energy term [23]. In this sense, it has been recently proposed that below a critical size, shape memory alloy nanoparticles show non hysteretic behavior [24]. Taking into account that the transformation hysteresis linked to a first order transition is an important drawback for magnetocaloric applications, nanoparticle alloys seem to be a promising alternative procedure to improve simultaneously the mechanical behavior and the MCE required for refrigeration systems.

Ball milling technique is one of the simplest and cheapest methods to produce nanostructured materials. The use of ball milling as a reduction method to nanoscale size has been studied in multiple systems, and interesting physical and chemical phenomena have been found to appear. A considerable modification of the magnetic behavior and the synthesis of new phases have been reported [25-27]. For instance, the reduction in the size of particles by ball milling may optimize the MCE in different magnetic systems, either by increasing the temperature range [28] or by reducing the hysteretic losses linked to a magnetostructural first order transformation [29]. On the other hand, together with grain size reduction, ball milling produces a huge amount of defects (vacancies, dislocations, chemical disorder, strains,...) in the material. A proper analysis of the milled powder may therefore provide valuable information concerning the influence of those defects on both the MT and the magnetic properties. The effect of ball milling on the magnetostructural properties has been studied in Ni-Mn-Ga, where the effect of thermal treatments has been widely characterized and different sequences of structural transition (different from those in the corresponding bulk) have been found in the achieved nanoparticles [30-33]. Likewise, nanoparticles of Ni-Mn-Sn have been recently obtained by ball milling [34, 35]. As in Ni-Mn-Ga, atomic disorder and lattice strain inhibit the MT in the as-milled alloys, while post-mill annealing treatments are needed to restore the MT. A significant influence of annealing on

the ferromagnetic exchange interaction, exchange bias and MCE, has been also reported in these alloys. On the contrary, the use of ball milling in the quest for functional nanoparticles has been scarcely studied in the Ni-Mn-In alloys [36, 37]. In fact, a complete study on the correlation between microstructure and magnetostructural properties in Ni-Mn-In nanoparticles is still absent.

This work is devoted to the study of the evolution of both the martensitic transformation and the magnetic properties with microstructure in ball-milled Ni-Mn-In nanometric particles. It is found that the as-milled sample display an amorphous structure with a frustrated magnetic state compatible with a canonical spin-glass. The crystallization process taking place on heating the milled alloy and the magnetic properties of the resulting B2 structure have been characterized. A relaxation process occurs on annealing above 700 K, concurrently with a B2-L2<sub>1</sub> atomic ordering, giving rise to an anomalous two-step thermal expansion. The combined effect of both processes makes possible the subsequent occurrence of a martensitic transformation, which takes place at the same temperature than in the bulk. The large relative cooling power linked to the magnetocaloric effect at the martensitic transformation in the annealed particles makes them interesting for practical applications of magnetic refrigeration at nanoscale.

## **2. EXPERIMENTAL**

A Ni<sub>50</sub>Mn<sub>34</sub>In<sub>16</sub> alloy was prepared from high purity elements by arc melting under protective Ar atmosphere. The as-cast ingot was homogenized at 1073 K during 15h and then quenched into iced water. The composition of the elaborated alloy was analyzed by EDS in a Jeol JSM-5610LV Scanning Electron Microscope (SEM). The alloy was subjected to a ball milling process in an argon atmosphere during an effective milling time of 40h at room temperature. In order to prevent overheating of the sample and grinding jars, the samples were milled during 5 minutes (effective milling time) and then stopped for 10 minutes, and so on. Ball milling was performed at 300 rpm using a Retsch PM4 with a ball:powder ratio of 7:1 and 7 balls of 5 mm diameter. Both jars and balls were of tungsten carbide. The structural transformations and the possible recovery processes

taking place on annealing the as-milled powder samples were characterized by differential scanning calorimetry (Q-100 DSC, TA Instruments). The magnetic characterization (magnetization and susceptibility measurements) was performed by SQUID magnetometry (QD MPMS XL-7). Particles size and shape were observed by conventional transmission electron microscopy (Hitachi H600 100 kV TEM). The evolution of crystal structure, long-range atomic order, crystallite size and microstrains were determined from in-situ powder neutron diffraction measurements performed on the high-flux D1B two-axis diffractometer, at the Institute Laue-Langevin (Grenoble, France). The diffraction patterns were measured on heating from room temperature (RT) up to 1173K at 1K/min using a neutron wavelength of 1.28 Å. The structures were refined by the Rietveld method using the FullProf package programs [38].

### 3. RESULTS AND DISCUSSION

Figure 1a shows the DSC thermogram performed on cooling/heating the reference bulk alloy between 350K and 165 K. The occurrence of a first-order MT is evidenced by the presence of the exothermic and endothermic peaks corresponding to the forward and reverse MT, respectively. The transformation temperatures, taken as the temperature of the peak maximum, are  $T_M^{forward} = 226$  K and  $T_M^{Reverse} = 241$  K, which means a thermal hysteresis of  $\Delta T = 15$  K for the MT. A second-order magnetic transition taking place in the austenitic phase can also be inferred from the baseline inflection observed above the MT, around 300 K. The complete sequence of magnetostructural transitions have been determined from the low-field (100 Oe) magnetization versus temperature curve,  $M(T)$ , shown in Figure 1b. The magnetization increases on cooling below 300 K, due to the ferromagnetic ordering of the austenitic phase at the Curie temperature,  $T_C^{aust}$ , and then it suddenly decreases on further cooling to the almost paramagnetic martensite. The subsequent increase of magnetization is linked to the magnetic ordering of the low-temperature phase at  $T_C^{mart}$ . As shown in the inset, the magnetization drop associated to the martensitic transformation occurs at lower temperatures on increasing the applied magnetic field,  $H$ , according to the Clausius-Clapeyron equation

$$\frac{dT_M}{dH} = -\mu_0 \frac{\Delta M}{\Delta S} \quad (1)$$

where  $T_M$  is the MT temperature, and  $\Delta M$  and  $\Delta S$  the magnetization and entropy change at  $T_M$ , respectively. Since the different exchange interactions in each structural phase promote a discontinuity in the magnetic entropy at the MT temperature, the application of a magnetic field at temperatures close to  $T_M$  may result in the induction of the transformation, and therefore in a magnetically induced entropy change (that is, in a MCE). The entropy change in isothermal conditions can be calculated by numerical integration of the derivative of the magnetization with respect to temperature following the expression

$$\Delta S_{iso} = S(T, H) - S(T, 0) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH \quad (2)$$

The obtained MCE values are shown in Figure 1c as a function of both temperature and applied magnetic field. A positive peak (inverse MCE) is observed linked to the MT, which increases with the increasing magnetic field up to a maximum value of 12 J/kgK at 6 T, a value similar to that found in the literature for this compound [12].

Once characterized, the reference bulk alloy was subjected to high energy ball-milling in order to produce nanoparticles. No martensitic transformation was detected from the DSC thermograms performed on the as-milled sample, suggesting a critical impact of the ball-milling on the crystallographic structure of the alloy. Figure 2a shows the room temperature neutron diffraction pattern of the as-milled samples. The absence of well-defined Bragg reflections seems to confirm the achievement of an almost amorphous phase, as a result of the structural distortion and the associated introduction of structural defects caused by milling. In fact, the presence of some small and broad peaks would indicate some marginal degree of crystallinity in the alloy. As shown in the TEM image in the inset, the milled powder mainly consists on spheroidal nanometric particles (tens of nm) together with some bigger clusters. In this respect, the slight peaks on the diffractogram could be also thought to be due to crystalline order inside nanoparticles, that is, to size effects on crystalline powder. As we will see, the clear occurrence of a crystallization process discards this latter hypothesis. The magnetic properties of the as-

milled alloy have been analyzed from the temperature dependence of magnetization and AC susceptibility measurements. Figure 2b shows the zero-field cooled/ field cooling/ field heating (ZFC/FC/FH) curves obtained on the as-milled sample under 100 Oe. The splitting between the ZFC and FC curves at low temperature (sharp jump in ZFC), typical of frustrated magnetic systems, suggests a spin-glass state, as recently proposed in similar alloys [36]. As shown in the upper inset, the low magnetization values at 6 T and the high magnetic anisotropy (the system does not saturate) are indeed in agreement with a spin-glass behavior. Furthermore, a frequency-dependent maximum linked to the freezing temperature (temperature of the maximum in the ZFC curve,  $T_f$ ), appears in the measurements of the real part of susceptibility. The corresponding frequency dependence of the freezing temperature,  $T_f(f)$ , perfectly fits to the Vogel-Fulcher law [39], again in agreement with a spin-glass state. Further measurements delving into the low temperature magnetic properties of the milled alloys point to a canonical spin-glass state [40].

The microstructural evolution and the recovery processes taking place on heating the amorphous sample have been studied by means of ‘in-situ’ powder neutron diffraction experiments. Figure 3a shows the thermodiffractograms obtained on heating from RT up to 1220 K at a 1 K/min constant rate. It can be seen that the amorphous structure remains stable up to 500 K. At this temperature crystallization occurs, as evidenced by the sudden appearance of Bragg reflections. The occurrence of this process does indeed confirm the amorphous-like state of the as-milled alloy. Specifically, the sample crystallizes to a disordered B2 cubic structure with nearest-neighbors long-range atomic order. On heating around 700 K, the appearance of L2<sub>1</sub> superstructure reflections (those in which the h, k, l indices are all odd, according to the corresponding unit cell structure factor) indicates the occurrence of an ordering process from B2 to a L2<sub>1</sub> cubic structure with next-nearest-neighbors long-range atomic order. A similar B2-L2<sub>1</sub> ordering process is observed on heating bulk Ni-Mn-In alloys previously quenched from high temperatures. In that case, in turn, the ordering temperature (which indeed depends on the degree of disorder retained by quenching) typically lies between 500 K and 600 K [41, 42]. On further heating above 900 K, the intensity of the L2<sub>1</sub> reflections gradually decreases until it completely

vanishes as a consequence of the L2<sub>1</sub>-B2 order-disorder transition, which takes place at 1050 K, a temperature again almost 100 K higher than in bulk alloys [41, 42]. The temperature dependence of the integrated intensity of the (111) reflection shown in Figure 3b illustrates the evolution of long-range atomic order of the nanometric particles with temperature. The two consecutive ordering processes are clearly identifiable from the appearance and subsequent disappearance of the superstructure reflection.

The microstructural relaxation can be also explored from the analysis of the width of the Bragg peaks of the diffraction patterns. In this respect, the integral breadth method has been used to determine the microstructural effects from the analysis of the diffraction peaks' shape. This method allows us to obtain separately the crystallite size and microstrain contributions to the full-width at half maximum (FWHM) of the diffraction peaks from its fitting to a Thompson-Cox-Hasting pseudo-Voigt profile function. The profile instrumental resolution function used for the analysis of the diffraction patterns has been obtained from the RT diffractogram performed on a Na<sub>2</sub>Ca<sub>3</sub>Al<sub>2</sub>F<sub>14</sub> sample (typical calibration compound). As an example, Figure 4 shows the diffractograms obtained for the B2 structure at three different temperatures, together with the respective fits by Rietveld method. It can be seen that the broadening of the reflections significantly decreases (and simultaneously the integrated intensity increases) on heating up to 1173 K, pointing out a relaxation of the microstructure. It is also worth noting the presence of small additional peaks, especially one at around  $2\theta = 29^\circ$ , probably ascribed to the appearance of a small amount of manganese oxide. In any case, just a very small mass fraction of the alleged oxide is inferred from the relative intensity of the peaks, so no significant effect are expected neither on the magnetic properties nor on the alloy composition. The evolution of both microstrain and crystallite size with temperature is shown in Figure 5a. The main microstructural relaxation takes place between 700 K and 800 K, where the microstrain abruptly decreases from 0.35% to 0.1%. This is precisely the temperature range in which the B2-L2<sub>1</sub> ordering process occurs (see Figure 3b). Taking into account that atomic ordering implies atomic diffusion, as long as it is mediated by vacancies, it points to vacancy elimination and/or vacancy-assisted



dislocation annihilation as the main recovery processes. On the other hand, the crystallite size increases exponentially with the increasing temperature, from 20 nm at RT (in agreement with TEM observations) to 150 nm at 1100 K, approximately. As expected, the higher growth rate is reached above 800 K, just after the recovery process (microstrain drop). Likewise, it is interesting to note that the temperature dependence of the lattice parameters (Figure 5b) shows a marked change in slope between 700 K and 800 K, concurrently with both the B2-L2<sub>1</sub> ordering and the relaxation processes, thus giving rise to an anomalous two-step thermal expansion.

The crystallization process observed from thermodiffraction has been also analyzed from DSC measurements. Figure 6 shows the thermogram obtained on heating the amorphous powders up to 700 K at a 1 K/min rate (same heating rate than in neutron diffraction experiment). A narrow exothermic peak (P1) overlapped to a much broader peak (P2) is observed between 500 K and 600 K. The temperature range of appearance and the width of the P1 peak are in agreement with the sharp crystallization process revealed by diffraction measurements. In turn, no significant structural variation is detected linked to the P2 peak. Nevertheless, the enthalpy of the whole double-peak ( $\Delta H \approx 70\text{J/g}$ ) is similar to that obtained for the crystallization process in similar alloys, so the same origin could be attributable to both peaks. The kinetics of the associated processes has been analyzed using the well-known Kissinger's method, from which the activation energy of a thermally activated process can be obtained from the variation of the DSC peak temperature ( $T_p$ ) as a function of the heating rate ( $\phi$ ), through the expression

$$\ln \frac{\phi}{T_p^2} = -\frac{E_a}{k_B T_p} + B \quad (3)$$

where  $k_B$  is the Boltzmann constant,  $E_a$  is the activation energy and  $B$  is a constant. The activation energies, determined from the linear fit of  $\ln(\phi/T_p^2)$  vs  $1/T_p$  shown in the inset of Figure 6, are  $E_a = 1.7$  eV and  $E_a = 1.8$  eV for the P1 and P2 peaks, respectively. The similarity between both values, which are also in agreement with those obtained for the crystallization process in ball-milled amorphous Fe<sub>2</sub>MnGe alloys [43], reinforces the idea of a similar origin for the processes linked to both exothermic peaks.

Figure 7 shows the temperature dependence of magnetization at low applied fields (100 Oe) for milled samples heated up to 538 K and 630 K, that is, just above the P1 and P2 exothermic peaks shown in the thermogram. First, it is interesting to highlight that no martensitic transformation is detected in any case, neither from the  $M(T)$  curves nor from respective DSC measurement performed between 170 K and 673 K (not shown here). It means that crystallization to a B2 structure is not a sufficient condition for the MT to occur. On the other hand, the evolution of magnetization with temperature) is almost the same after both heating treatments: the samples are paramagnetic at high temperatures and becomes magnetically ordered on cooling below 250 K. This transition temperature is quite lower than the Curie temperature of the bulk sample (see Figure 1), in agreement with the higher atomic disorder in the B2 structure and the corresponding higher contribution of the antiferromagnetic coupling between Mn atoms [41]. The global behavior of  $M(T)$  under 60 kOe is also similar (see inset), albeit the low temperature magnetization values are quite higher after heating above the P2 peak. Nevertheless, as mentioned above, no structural variation is observed linked to that peak. In fact, just a slight increase in the B2 order parameter (associated to a slight decrease of the occupancy the  $1a$  Ni-sites by Mn atoms) is detected from the Rietveld analysis of the corresponding diffractograms (shown in Figure 4).

In order to analyze the evolution of magnetic properties through the crystallization process, isofield magnetization measurements at different temperatures around the magnetic transition have been also performed on both samples. Figure 8 shows the magnetic-field dependence of magnetization between 175 K and 275 K for applied fields up to 60 kOe. For the sample heated up to 630 K (Figure 8b) the evolution of the  $M(H)$  curves corresponds to a typical para-ferromagnetic transition; at high temperatures (above  $T_C$ ) magnetization increases linearly with magnetic field whereas below  $T_C$  magnetization shows a sharp increase at low fields and a further slow increase at high fields, almost reaching saturation. In the sample heated up to 538 K (Figure 8a), in turn, magnetization does not reach saturation in the ferromagnetic region, which could be indicative of magnetic disorder, magnetic inhomogeneity or antiferromagnetic clusters. The

presence of short-range correlations and the characteristics of the magnetic transition have been studied through the analysis of the critical exponents, which have been determined from the magnetization data according to the modified Arrott plots method. This method is based on the Arrott-Noakes equation of state  $(H/M)^{1/\gamma} = a\varepsilon + bM^{1/\beta}$ , where  $\varepsilon = (T-T_C)/T_C$  is the reduced temperature,  $a$  and  $b$  are constants, and  $\gamma$  and  $\beta$  are the critical exponents that characterize the second-order magnetic transition near  $T_C$  [44].  $\gamma$  and  $\beta$  are associated to the spontaneous magnetization ( $M_S$ ) and the initial magnetic susceptibility ( $\chi_0$ ), respectively, through the expressions [45]:

$$M_S(T) = M_0(-\varepsilon)^\beta, \quad \varepsilon < 0 \quad (4)$$

$$\chi_0^{-1}(T) = \left(\frac{H_0}{M_0}\right) \varepsilon^\gamma, \quad \varepsilon > 0 \quad (5)$$

where  $M_0$  and  $H_0/M_0$  are the critical amplitudes. From the Arrott-Noakes equation, the plot of  $M^{1/\beta}$  versus  $(H/M)^{1/\gamma}$  at different temperatures around  $T_C$  are straight lines that lie parallel to each other for high fields, being the line crossing the coordinate origin that corresponding to  $T_C$ . Starting from initial trial values of  $\beta=0.5$  and  $\gamma=1.0$ ,  $M_S(T)$  and  $\chi_0^{-1}(T)$  data are obtained from the intersection of the linear extrapolation of the straight lines with the  $M^{1/\beta}$  and  $(H/M)^{1/\gamma}$  axis, respectively. These data are fitted to equations (4) and (5), respectively, and the obtained parameters are then used for the next  $M^{1/\beta}$  versus  $(H/M)^{1/\gamma}$  plot, repeating the process iteratively until  $\beta$  and  $\gamma$  values converge.  $M_S(T)$  and  $\chi_0^{-1}(T)$  data fitted to equations (4) and (5), respectively, and the critical exponents obtained from the last iterative step are shown in Figure 9. The obtained values are  $\beta=0.50$ ,  $\gamma=1.26$  and  $T_C = 219$  K after heating above P1 and  $\beta=0.47$ ,  $\gamma=1.27$  and  $T_C = 233$  K after heating above P2 peak. Likewise, the critical exponents have been also determined by the Kouvel-Fisher method [46], from the linear relations

$$M_S(T) \left[ dM_S(T) / dT \right]^{-1} = (T - T_C) / \beta \quad (6)$$

$$\chi_0^{-1}(T) \left[ d\chi_0^{-1}(T) / dT \right]^{-1} = (T - T_C) / \gamma \quad (7)$$

Figure 10 shows the plot of both  $M_S(T)[dM_S(T)/dT]^{-1}$  and  $\chi_0^{-1}(T) [d\chi_0^{-1}(T) /dT]^{-1}$  (again after the last step of an iterative process) as a function of temperature. The critical exponents obtained from the linear fits are  $\beta=0.46$ ,  $\gamma=1.21$  and  $T_C = 219$  K after heating above P1 and  $\beta=0.47$ ,  $\gamma=1.21$  and  $T_C = 233$  K after heating above P2 peak, almost the same than those achieved from modified Arrot plots. The Curie temperature increases 14 K after heating above the second peak, in agreement with the higher magnetization at high field and consistently with the above mentioned slight increase of the B2 order parameter. In both cases, the obtained  $\beta$  values are close to that predicted by the mean-field theory ( $\beta=0.5$ ) whereas  $\gamma$  values agree with that proposed by 3D Ising model ( $\gamma = 1.24$ ) [46], pointing out to competing long- and short-range magnetic couplings in the B2 structure (as expected, indeed). Nevertheless, the corresponding critical exponents show no difference at all after both annealing treatments, and therefore the same nature can be attributed to the magnetic transition in both cases. The difference between the high field magnetization values in Figure 7 could be then due to the above mentioned B2 atomic order variations and, mainly, to the fact that the crystallization process is not concluded at 538 K (the P1 peak is truncated as a consequence of the overlapping with P2 peak) and some amorphous fraction still persists. In any case, no significant structural or magnetic variation is observed linked to the P2 peak, so an instrumental origin (a low thermal conduction in the powder, favored by the presence of small amount of oxide) could be the most likely explanation.

The occurrence of MT in the milled sample is just observed once heated above 900 K, that is, once the B2-L2<sub>1</sub> atomic ordering and the microstructural relaxation process have been fulfilled. As an example, Figure 11a shows the temperature dependence of magnetization for the milled powder heated up to 1173 K. The global behavior of magnetization is practically the same than in the bulk (see Figure 1b), with a sudden increase corresponding to the para-ferromagnetic transition and a hysteretic drop linked to the MT observed around 300 K and 220 K, respectively. Moreover, the MT temperature lies close to that in the bulk, which (taking into account the dependence of MT on composition) agrees with the very small amount of oxide inferred from Figure 4. Nevertheless, the MT on the annealed powder spreads over a quite higher temperature range, due to the higher storage of the strain energy linked to the reduced particle size. The

magnetocaloric effect associated to the MT in the annealed particles has been estimated from the magnetization curves at different applied fields (see inset in Figure 11a), through equation (2). Figure 11b shows the magnetically-induced isothermal entropy change as a function of both temperature and applied magnetic field. An inverse MCE is observed associated to the MT, together with a direct MCE linked to second-order magnetic transition. The maximum positive entropy change, achieved for the higher applied field (6 T), is  $\Delta S = 2\text{J/kgK}$ . Even though this value is considerably lower than in the bulk, the broad temperature range covered by the MT in the milled sample results in a broad associated entropy peak ( $\Delta T = 75\text{ K}$ ), thus giving rise to a quite large relative cooling power ( $\text{RCP} = \Delta S \cdot \Delta T$ ) (which is the main performance metric to rank magnetocaloric materials, as long as it quantifies the magnitude of heat extracted in a thermodynamic cycle [47]). In particular, a RCP value of 150 J/kg is obtained in the milled particles, which is comparable to those values found in similar bulk alloys [48]. This means that, by means of ball milling and adequate thermal treatments, functional Ni-Mn-In metamagnetic shape memory alloys interesting for practical applications of magnetic refrigeration at nanoscale (around 150 nm after annealing) are achieved.

#### 4. SUMMARY AND CONCLUSIONS

High mechanical deformation has been induced in a Ni-Mn-In metamagnetic shape memory alloy by means of ball-milling. The evolution of both microstructure (which includes crystallography, atomic order, defects, internal stresses and microstrains) and the magnetic properties has been analyzed as a function of the temperature. The as-milled nanometric particles display an amorphous structure with a frustrated magnetic state compatible with a canonical spin-glass. On heating, an abrupt crystallization process occurs around 500K leading to a cubic B2 structure, which, in turn, does not show martensitic transformation. On further heating, a relaxation process takes place above 700 K concurrently with a B2-L21 atomic ordering, giving rise to an anomalous two-step thermal expansion. The combined effect of both processes makes possible the

subsequent occurrence of a martensitic transformation, which takes place at the same temperature than in the bulk. The large relative cooling power linked to the magnetocaloric effect at the martensitic transformation in the annealed particles makes them interesting for practical applications of magnetic refrigeration at nanoscale.

## ACKNOWLEDGEMENTS

This work has been carried out with the financial support of the Spanish "Ministerio de Economía y Competitividad" (Projects number MAT2012-37923-C02 and MAT2015-65165-C2-R). We also acknowledge ILL and SpINS for beam time allocation (experiment CRG-2158). RCF acknowledges a Postdoctoral fellowship from the Univeridad Pública de Navarra. JARV acknowledges CSIC for a JAEdoc contract. J. Pons is acknowledged for TEM observations.

## References

- [1] R.C. O'Handley, S.M. Allen, Shape-memory alloys, Magnetically activated ferromagnetic shape-memory materials, in: M. Schwartz (Ed.), *Encycl. Smart Mater*, 2002.
- [2] R. Kainuma, W. Ito, R.Y. Umetsu, V.V. Khovaylo, T. Kanomata, Metamagnetic shape memory effect and magnetic properties of Ni-Mn based Heusler alloys, *Mater. Sci. Forum* 684 (2011) 139-150.
- [3] M. Acet, Ll. Mañosa, A. Planes, Magnetic-field-induced effects in martensitic Heusler-based magnetic shape memory alloys, in: K.H.J. Buschow (Ed), *Handbook of magnetic materials Vol.19*, Elsevier, Amsterdam, 2011, pp. 231-289.
- [4] E. Sasioglu, L.M. Sandratskii, P. Bruno, First-principles calculation of the intersublattice exchange interactions and Curie temperatures of the full Heusler alloys  $Ni_2MnX$  ( $X=Ga, In, Sn, Sb$ ), *Phys. Rev. B* 70 (2004) 024427.
- [5] E. Sasioglu, L.M. Sandratskii, P. Bruno, Role of conduction electrons in mediating exchange interactions in Mn-based Heusler alloys, *Phys. Rev. B* 77 (2008) 064417.
- [6] Y. Sutou, Y. Imano, N. Koeda, T. Omori, R. Kainuma, K. Ishida, K. Oikawa, Magnetic and martensitic transformations of  $NiMnX$  ( $X=In, Sn, Sb$ ) ferromagnetic shape memory alloys, *Appl. Phys. Lett.* 85 (2004) 4358.
- [7] S.Y.Yu, Z.H. Liu, G.D. Liu, J.L. Chen, Z.X. Cao, G.H. Gu, B. Zhang, X.X. Zhang, Large magnetoresistance in single-crystalline  $Ni_{50}Mn_{50-x}In_x$  alloys ( $x=14-16$ ) upon martensitic transformation, *Appl. Phys. Lett.* 89 (2006) 162503.
- [8] V.K. Sharma, M.K. Chattopadhyay, K.H.B. Shaeb, A. Chouhan, S.B. Roy, Large magnetoresistance in  $Ni_{50}Mn_{34}In_{16}$  alloy, *Appl. Phys. Lett.* 89 (2006) 222509.

- [9] R. Kainuma, Y. Imano, W. Ito, Y. Sutou, H. Morito, S. Okamoto, K. Kitakami, A. Oikawa, O. Fujita, T. Kanomata, K. Ishida, Magnetic-field-induced shape recovery by reverse phase transformation, *Nature* 439 (2006) 957-960.
- [10] J. Du, Q. Zheng, W.J. Ren, W.J. Feng, X.G. Liu, Z.D. Zhang, Magnetocaloric effect and magnetic-field-induced shape recovery effect at room temperature in ferromagnetic Heusler alloy Ni–Mn–Sb, *J. Phys. D: Appl. Phys.* 40 (2007) 5523.
- [11] T. Krenke, E. Duman, M. Acet, E.F. Wassermann, X. Moya, Ll. Mañosa, A. Planes, Inverse magnetocaloric effect in ferromagnetic Ni–Mn–Sn alloys, *Nat. Mat.* 4 (2005) 450-454.
- [12] T. Krenke, E. Duman, M. Acet, E.F. Wassermann, X. Moya, Ll. Mañosa, A. Planes, E. Suard, B. Ouladdiaf, Magnetic superelasticity and inverse magnetocaloric effect in ferromagnetic Ni–Mn–In, *Phys. Rev. B* 75 (2007) 104414..
- [13] A. Planes, Ll. Mañosa, M. Acet, Magnetocaloric effect and its relation to shape-memory properties in ferromagnetic Heusler alloys, *J. Phys.: Condens. Matter.* 21 (2009) 233201.
- [14] X. Moya, S. Kar-Narayan, N.D. Mathur, Caloric materials near ferroic phase transitions, *Nature Mater.* 13 (2014) 439-450.
- [15] G.B. Rao, J.Q. Wang, E.H. Han, W. Ke, Study of residual stress accumulation in TiNi shape memory alloy during fatigue using EBSD technique, *Mater. Lett.* 60 (2006) 779-782.
- [16] H. Scherngell, A.C. Kneissl, Generation, development and degradation of the intrinsic two-way shape memory effect in different alloy, *Acta Mater* 50 (2002) 327-341.
- [17] R. Niemann, O. Heczko, L. Schultz, S. Fähler, Metamagnetic transitions and magnetocaloric effect in epitaxial Ni–Co–Mn–In films, *Appl. Phys. Lett.* 97 (2010) 222507.
- [18] R. Caballero-Flores, T. Sánchez, W.O. Rosa, J. García, L. González-Legarreta, D. Serantes, V.M. Prida, Ll. Escoda, J.J. Suñol, B. Hernando, On tuning the magnetocaloric effect in Ni-Mn-In Heusler alloy ribbons with thermal treatment, *J. Alloys and Comp.* 545 (2012) 216-221.
- [19] C. Gómez-Polo, J.I. Pérez-Landazábal, V. Recarte, V. Sánchez-Alarcos, G. Badini-Confalonieri, M. Vázquez, Ni-Mn-Ga ferromagnetic shape memory wires, *J. Appl. Phys.* 107 (2010) 123908.
- [20] M. Acet, Magnetic shape memory: Magnetoelastic sponges, *Nature Mater.* 8 (2009) 854-855.
- [21] J. Feuchtwanger, M.L. Richard, Y.J. Tang, A.E. Berkowitz, R.C. O’Handley, S.M. Allen, Large energy absorption in Ni–Mn–Ga/polymer composites, *J. Appl. Phys.* 97 (2005) 10M319. (2005).
- [22] J. Liu, N. Scheerbaum, S. Kauffmann-Weiss, O. Gutfleisch, NiMn-based alloys and composites for magnetically controlled dampers and actuators, *Adv. Eng. Mater.* 14 (2012) 653-667.
- [23] J. Ortín, A. Planes, Thermodynamic analysis of thermal measurements in thermoelastic martensitic transformations, *Acta Metall.* 36 (1988) 1873-1889.
- [24] Z. Zhang, X. Ding, J. Sun, T. Suzuki, T. Lookman, K. Otsuka, X. Ren X, Nonhysteretic superelasticity of shape memory alloys at the nanoscale, *Phys. Rev. Lett.* 111 (2013) 145701.
- [25] C. Suryanarayana, Mechanical alloying and milling, *Progress Mater. Sci.* 46 (2001) 1-184.
- [26] M.E. McHenry, D.E. Laughlin, Nano-scale materials development for future magnetic applications, *Acta Mater.* 48 (2000) 223.
- [27] A. Calka, D. Wexler, Mechanical milling assisted by electrical discharge, *Nature* 419 (2002) 147.

- [28] P. Gorria, P. Alvarez, J. Sánchez-Marcos, J.L. Sánchez-Llamazares, M.J. Pérez J.A. Blanco, Crystal structure, magnetocaloric effect and magnetovolume anomalies in nanostructured Pr<sub>2</sub>Fe<sub>17</sub>, *Acta Mater.* 57 (2009) 1724.
- [29] W. Dagula, O. Tegus, X.W. Li, L. Song L, E. Bruck, D.T. Cam Thanh DT, F.R. de Boer, K.H.J. Buschow, Magnetic properties and magnetic-entropy change of MnFeP<sub>0.5</sub>As<sub>0.5-x</sub>Si<sub>x</sub>(x=0–0.3) compounds, *J. Appl. Phys.* 99 (2006) 08Q105.
- [30] Y.D. Wang, Y. Ren, Z.H. Nie, D.M. Liu, P.K. Liaw, J.Q. Yan, R. McQueeney, J.W. Richardson, A. Huq, Structural transition of ferromagnetic Ni<sub>2</sub>MnGa nanoparticles, *J. Appl. Phys.* 101 (2007) 63530.
- [31] B. Tian, F. Chen, Y. Liu, Y.F. Zheng, Structural transition and atomic ordering of Ni<sub>49.8</sub>Mn<sub>28.5</sub>Ga<sub>21.7</sub> ferromagnetic shape memory alloy powders prepared by ball milling, *Mater. Lett.* 62 (2008) 2851-2854.
- [32] Y.V.B. de Santanna, M.A.C. de Melo, I.A. Santos, A.A. Coelho, S. Gama, L.F. Cótica, Structural, microstructural and magnetocaloric investigations in high-energy ball milled NiMnGa powders, *Sol. State Comm.* 148 (2008) 289-292.
- [33] K. Vallalperuman, R. Chokkalingam, M. Mahendran, Annealing effect on phase transformation in nano structured Ni–Mn–Ga ferromagnetic shape memory alloy, *Phase Transitions* 83 (2010) 509-517.
- [34] A.L. Alves, E.C. Passamani, V.P. Nascimento, A.Y. Takeuchi, C.J. Larica, Influence of grain refinement and induced crystal defects on the magnetic properties of Ni<sub>50</sub>Mn<sub>36</sub>Sn<sub>14</sub> Heusler alloys, *J. Phys. D: Appl. Phys.* 43 (2010) 345001.
- [35] A. Ghotbi Varzaneh, P. Kameli, V.R. Zahedi, F. Karimzadeh, H. Salamati, Effect of heat treatment on martensitic transformation of Ni<sub>47</sub>Mn<sub>40</sub>Sn<sub>13</sub> ferromagnetic shape memory alloy prepared by mechanical alloying, *Met. Mater. Int.* 4 (2015) 758-764.
- [36] D.M. Liu, Z.H. Nie, Y. Ren, Y.D. Wang, J. Pearson, P.K. Liaw, D.E. Brown, Structural transitions and magnetic properties of Ni<sub>50</sub>Mn<sub>36.7</sub>In<sub>13.3</sub> particles with amorphous-like phase, *Metall. Mat. Trans. A* 42 (2011) 3062-3070.
- [37] X. Fei, W. Li, J. Liu, F. Xu, G. Tang, W. Tan, S. Li, Phase transition of ball-milled Ni<sub>50-x</sub>Mn<sub>37</sub>In<sub>13</sub>Co<sub>x</sub> (x=0.5) alloy powders, *Mater. Sci. Forum* 809 (2015) 377-383.
- [38] J. Rodríguez-Carvajal, Recent Advances in Magnetic Structure Determination by Neutron Powder Diffraction, *J. Physica B* 192 (1993) 55-69.
- [39] S. Shtrikman, E.P. Wohlfarth, The theory of the Vogel-Fulcher law of spin glasses, *Phys. Lett. A* 19 (1981) 467-470.
- [40] S. Larumbe, I. Unzueta, V. Sánchez-Alarcos, J.I. Pérez-Landazábal, V. Recarte, J.A. García, F. Plazaola, Low temperature magnetic properties of a Ni<sub>50</sub>Mn<sub>34</sub>In<sub>16</sub> ball-milled metamagnetic shape memory alloy, *J. Non-Cryst. Solids* 44 (2016) 16-20.
- [41] V. Recarte, J.I. Pérez-Landazábal, V. Sánchez-Alarcos, J.A. Rodríguez-Velamazán, Dependence of the martensitic transformation and magnetic transition on the atomic order in Ni–Mn–In metamagnetic shape memory alloys, *Acta Mater.* 60 (2012) 1937-1945.
- [42] V. Sánchez-Alarcos, V. Recarte, J.I. Pérez-Landazábal, C. Gómez-Polo, J.A. Rodríguez-Velamazán, Role of magnetism on the martensitic transformation in Ni–Mn-based magnetic shape memory alloys, *Acta Mater.* 60 (2012) 459-468.



- [43] L. Zhang, E. Brück, O. Tegus, K.J.H. Buschow, F.R. de Boer, The crystallization of amorphous Fe<sub>2</sub>MnGe powder prepared by ball milling, *J. Alloys and Compd.* 352 (2003) 99-102.
- [44] A. Arrott, J.E. Noakes, Approximate equation of state for nickel near its critical temperature, *Phys. Rev. Lett.* 19 (1967) 786.
- [45] H.E. Stanley, *Introduction to phase transitions and critical phenomena*, London Oxford University Press, London, 1971.
- [46] J. S. Kouvel, M.E. Fisher, Detailed magnetic behavior of Nickel near its Curie point, *Phys. Rev.* 136 (1964) A1626.
- [47] K.A. Gschneidner Jr, V.K. Pecharsky, Magnetocaloric materials. *Annu. Rev. Mater. Sci.* 30 (2000) 387–429.
- [48] N.M. Bruno, C. Yegin, I. Karaman, J.-H Chen, J.H. Ross Jr., J. Liu, J. Li, The effect of heat treatments on Ni<sub>43</sub>Mn<sub>42</sub>Co<sub>4</sub>Sn<sub>11</sub> meta-magnetic shape memory alloys for magnetic refrigeration, *Acta Mater.* 74 (2014) 66-84.

### **Figure captions**

FIG. 1: (a) DSC thermogram performed on cooling/heating the reference bulk at 10 K/min. (b) Temperature dependence of magnetization for the bulk alloy at 100 Oe (inset:  $M(T)$  for different applied fields ranging from 100 Oe up to 60 kOe). (c) Magnetically-induced entropy change in the bulk alloys as a function of temperature and applied magnetic field.

FIG. 2: (a) Room temperature neutron diffraction pattern of the as-milled samples (inset: TEM micrograph). (b) ZFC/FC/FH curves obtained on the as-milled sample under 100 Oe (Upper inset: field dependence of magnetization. Lower inset: linear fitting to the Vogel-Fulcher law).

FIG. 3: (a) In-situ neutron powder thermodiffractograms on heating between 330 K and 1220 K at 1 K/min. (b) Integrated intensity of the (111) reflection as a function of temperature.

FIG. 4: Measured neutron diffraction pattern (dots), calculated profile (full line) and difference between the measured and calculated profiles (dashed line) for the milled alloy at 538 K, 630 K and 1170 K.

FIG. 5: (a) Microstrain and crystalline size as a function of temperature. (b) Evolution of lattice parameters (in terms of the B2 cell) with temperature.

FIG. 6: DSC thermogram on heating the milled sample at 1 K/min. Inset: plot of  $\ln(\phi/T_p^2)$  vs  $1/T_p$  for the P1 and P2 peak temperatures.

FIG. 7: Temperature dependence of the magnetization (cooling curves) at 100 Oe for milled samples heated up to 538 K and 630 K (just above P1 and P2 peaks, respectively). Inset: corresponding  $M(T)$  curves under 60 kOe applied field.

FIG. 8: Magnetic-field dependence of magnetization between 175 K and 275 K for applied fields up to 60 kOe for (a) sample heated up to 538 K and (b) sample heated up to 630 K.

FIG. 9: Temperature dependence of spontaneous magnetization ( $M_S$ ) and inversely initial susceptibility ( $\chi_0^{-1}$ ) together with their fitting to equations (4) and (5), respectively. (a) Sample heated up to 538 K, (b) sample heated up to 630 K.

FIG. 10: Kouvel-Fisher plots for the  $M_S(T)$  and  $\chi_0^{-1}(T)$  data. (a) Sample heated up to 538 K, (b) sample heated up to 630 K.

FIG. 11: (a) Temperature dependence of magnetization at 100 Oe for the nanometric particles heated up to 1170 K (inset:  $M(T)$  for different applied fields ranging from 100 Oe up to 60 kOe). (b) Magnetically-induced entropy change in the milled alloy heated up to 1170 K alloys, as a function of temperature and applied magnetic field.