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To cite this article: T Bachagha *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **504** 012009

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Martensitic transformation and magnetic behavior in Mn-rich Heusler MnNiIn shape memory alloys

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Abstract. The present work is devoted to study the microstructure and magnetic behavior of Mn-rich Heusler MnNiIn alloys. The Mn-substituted alloys with $\text{Mn}_{50}\text{Ni}_{50-x}\text{In}_x$ (at.%) ($x=7.5$ and 10) were prepared by melt-spinning technique. Experimental results show that the alloys crystallized into a monoclinic martensite structure 14M type, for the $\text{Mn}_{50}\text{Ni}_{42.5}\text{In}_{7.5}$ alloy and $L2_1$ type cubic austenite structure for the $\text{Mn}_{50}\text{Ni}_{40}\text{In}_{10}$ alloy. The characteristic temperatures decreased with the increase of In content under different magnetic fields: 50 Oe, 500 Oe, 5 kOe and 30 kOe. For the $\text{Mn}_{50}\text{Ni}_{42.5}\text{In}_{7.5}$ alloy, the presence of a paramagnetic-ferromagnetic transition is noted. This transition in the austenitic phase occurs before the martensitic transformation during cooling. On the other side, for the $\text{Mn}_{50}\text{Ni}_{40}\text{In}_{10}$ alloy, there is the presence of a martensitic transformation followed by a ferromagnetic transition. This transformation is carried out between a paramagnetic cubic austenite type and a ferromagnetic monoclinic martensite. This allows us to conclude that Indium addition plays a role to change the structure and magnetic behavior in MnNiIn alloys.

1. Introduction

Heusler-based Mn-Ni shape memory alloys exhibit both ferromagnetic and shape memory effects. The ferromagnetic shape memory effect can be controlled by temperature and magnetic field. These alloys exhibit a martensitic transformation. This transition goes from a cubic austenitic $L2_1$ or B2 phase at high temperature to a martensitic phase whose structure can be $L1_0$, 10M and 14M at low temperature [1-4]. Their properties make them particularly interested for the development of new magnetic actuators, magnetic sensors and refrigerants for attractive refrigeration [5].

Mn-Ni-In system has prospective significance as a shape memory alloy. The studies on these Heusler materials based on Mn are limited until recently. Llamazares et al. [6] have reported that a martensitic transformation into $L2_1$ to 14M occurred in $\text{Mn}_{50}\text{Ni}_{40}\text{In}_{10}$ alloy, and that the two phases had a ferromagnetic order. In $\text{Mn}_{50}\text{Ni}_{50-x}\text{In}_x$ ($x=9.75-11$) alloys, the transformation occurred between ferromagnetic austenite type $L2_1$ and low magnetic martensite 14M is noticed by Xuan et al. [7]. Similar result reported that a martensite tetragonal in $\text{Mn}_{50}\text{Ni}_{40-x}\text{In}_{10}\text{Co}_x$ was observed by Wu et al. [8].

In this paper, we investigate the impact of Indium addition on structure transition and magnetic behavior in $\text{Mn}_{50}\text{Ni}_{50-x}\text{In}_x$ (at.%) ($x=7.5$ and 10) ribbons. To better understand the dependence between the composition responsible for the martensitic transformation and the magnetic behavior in these alloys.

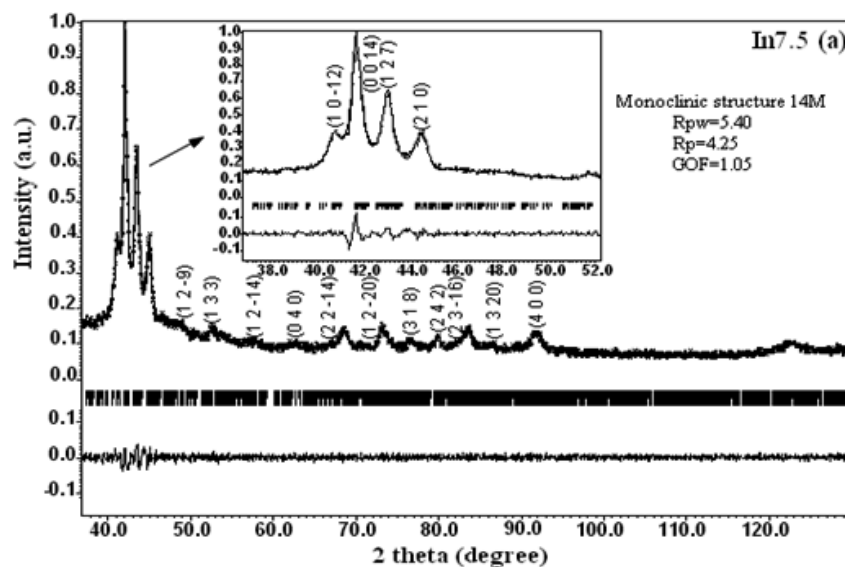


2. Experimental procedure

Polycrystalline $\text{Mn}_{50}\text{Ni}_{50-x}\text{In}_x$ (at.%) ($x = 7.5$ and 10) bulk alloys were elaborated using the arc melting technique from 99.99% Ni, 99.98% Mn and 99.998% In, under argon atmosphere. To obtain a good homogeneity, the alloys were melted four times. Then, they are ejected on a copper wheel rotating at a linear speed of 48 m.s^{-1} . The prepared samples are named as follows: In7.5 and In10, respectively. Several techniques are used to study the structural changes and magnetic behavior. X-ray diffraction (XRD) analyses were performed using Cu-K_α radiation ($\lambda = 1.5418 \text{ \AA}$) in a Phillips X'pert PRO (XP-2) powder diffractometer. The structure was refined by using Jana software [9]. The measures of magnetic characterization are carried out in the laboratories of the General Research Service (SGIker) of the University of the Basque Country. To measure the magnetic properties of the tapes, the physical property measurement system (PPMS-9T) is used with the 6000 Platform model of the Quantum Design Co commercial house with a magnetic sample vibration module. The technique used to determine different magnetic properties per the temperature is that of vibrant sample magnetometry (VSM).

3. Results and discussion

The XRD patterns of the Heusler $\text{Mn}_{50}\text{Ni}_{50-x}\text{In}_x$ (at.%) ($x = 7.5$ and 10) alloys are shown in Fig. 1. For In7.5 alloy, it's clear that all Bragg peaks are sharps and were indexed as a modulated monoclinic (14M) martensite with space group $P2_1/m$ and the following lattice parameters; $a=0.42824$ (3) nm, $b=0.57874$ (3) nm, $c=2.98962$ (4) nm, and $\beta=93.86^\circ$ (see Fig. 1a). By substituting 10.at% In with Ni, the diffraction peaks change radically, which is indexed in $L2_1$ -type cubic austenite with space group $\text{Fm}\bar{3}m$ and a lattice parameter $a=0.59895$ nm (see Fig. 1b). The existence of peaks associated with reflections indexed as (3 1 1) and (3 3 1) confirms this structure. The Miller indexes were distributed with the guide of order programs such as Treor and Dicvol.



(a) $\text{Mn}_{50}\text{Ni}_{42.5}\text{In}_{7.5}$

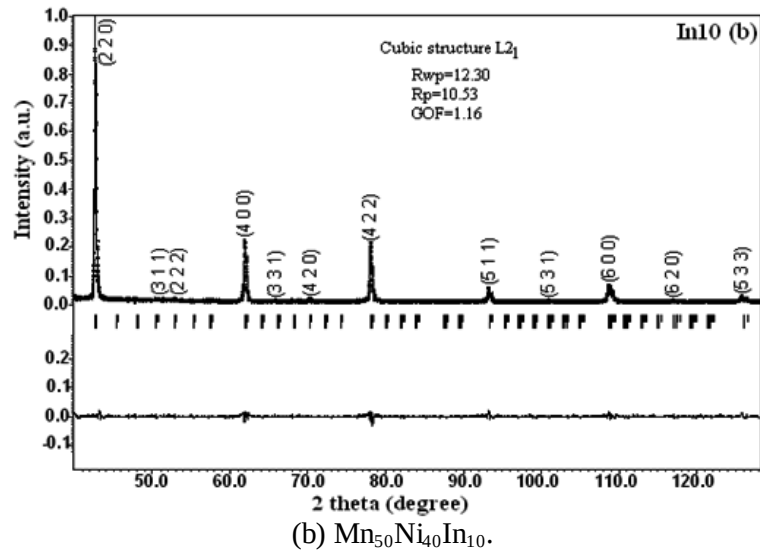


Figure 1. XRD patterns of the Mn-Ni-In melt-spun ribbons at room temperature.

In order to study the magneto-structural transition behavior, Fig. 2 shows the curves of magnetization $M(T)$ measured in various magnetic fields ranging from 50 to 30 kOe, for the two elaborated ribbons. It is clearly observed that similar thermomagnetic behaviors for both alloys. Also, the presence of hysteresis between the ZFC and FC curves around the martensitic transition implied the transition is the first-order. The characteristic transition temperatures; A_s , A_f , M_s and M_f are determined from these magnetization curves. It is noted that during an increase in Indium content, these temperatures decrease.

Fig. 2a shows the $M(T)$ of the Heusler $\text{Mn}_{50}\text{Ni}_{42.5}\text{In}_{7.5}$ alloy. It is observed that the temperatures of the martensitic transition are almost independent of the external magnetic field applied. The characteristic phase transition temperatures and thermal hysteresis for both ribbons determined from the $M(T)$ curve are listed in Table 1. Instead of it, we note that the magnetization value increases when a larger magnetic field is applied. Hysteresis is greater when larger magnetic fields are applied. This is consistent with the experiences of other authors [10].

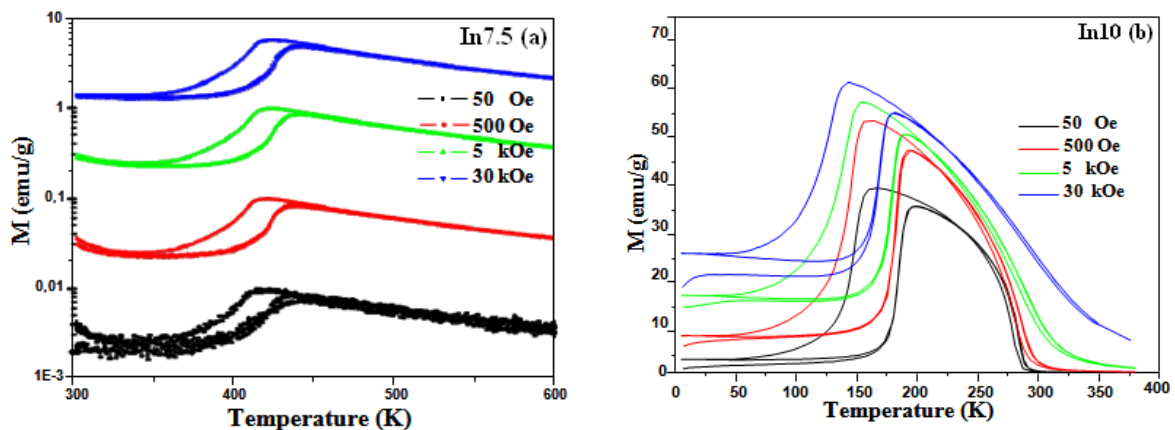


Figure 2. Thermomagnetic curves $M(T)$ for the both ribbons: (a) $\text{Mn}_{50}\text{Ni}_{42.5}\text{In}_{7.5}$ and (b) $\text{Mn}_{50}\text{Ni}_{40}\text{In}_{10}$, were measured in different magnetic fields from 50 Oe to 30 kOe.

Table 1. Values of martensitic transformation temperatures of the In7.5 alloy a different magnetic field: 50 Oe, 500 Oe, 5 kOe and 30 kOe.

H(Oe) In7.5	M_s(K)	M_f(K)	A_s(K)	A_f(K)	ΔT(K)
50 Oe	407	378	402	436	21
500 Oe	413	375	402	431	21
5 kOe	412	381	404	435	19
30 kOe	417	383	405	431	19

For the Mn₅₀Ni₄₀In₁₀ alloy, as appeared in Fig. 2b, the application of an external magnetic field causes a slight decrease in martensitic transformation temperatures. These temperatures and their corresponding $dM/dT(T)$ conditions are exhibited in Table 2. These allow us to visualize the temperature range in which the structural transitions occur. These transitions occur in a temperature range with a thermal hysteresis of the order of $\Delta T = 38$ K. This allows us to deduce the first order of the transformation martensitic.

Table 2. Values of martensitic transformation temperatures of the In10 alloy a different magnetic field: 50 Oe, 500 Oe, 5 kOe and 30 kOe.

H(Oe) In10	M_s(K)	M_f(K)	A_s(K)	A_f(K)	ΔT(K)
50 Oe	154	123	176	198	38
500 Oe	152	118	174	196	38
5 kOe	136	102	162	188	36
30 kOe	132	98	158	176	36

By moving the transformation temperatures as a function of the magnetic field, we note that the maximum of the magnetization is not always given at the same isothermal temperature. The effect of the temperature sinks in the direct transformation which took place, more precisely, for M_f which showed a shift about of -25 K. The magnetic behavior is also reflected in the asymmetric decay of the 50 kOe in magnetization curves. This is consistent with the results found by Llamazares et al. [10]. On the contrary, the variation of the magnetization does not depend on the temperature, for the In7.5 alloy.

The magnetization measurements $M(T)$ indicate that the In addition on MnNiIn decreased the transformation temperatures and increase the magnetization difference between austenite and martensite. Generally, this change can be explained by two main factors: the means of the concentration of valence electrons (e/a) and the difference in atomic radius between the substituted elements [11, 12].

For the primary factor, this concentration is calculated using the following formula:

$$(e/a) = \frac{1}{2} [10xNi + 7xMn + 3xIn]/100. \quad (1)$$

x = atomic percentage of the element. At this level, it is assumed that the valence electrons per atom are 7 for Mn, 10 for Ni and 3 for In. Therefore, the (e/a) values for In7.5 and In10 are: 8.05 and 7.9, respectively. Consequently, the ratio (e/a) plays a crucial role in the adjustment of the change temperatures, if Mn is partially replaced by In. For the second factor, the atomic radii are 0.125 nm for Ni, 0.135 nm for Mn and 0.162 nm for In. This factor makes the austenite unstable: during a contraction of the unit cell, this would favour the martensitic change or the expansion of this cell provokes the suppression of this change [13]. In our examination, we replace a small Mn with a bigger In, it is inescapable that the unit cell at high temperature grows to a specific degree. The two factors would make the austenite unsteady and along these lines prompt change at a higher temperature. Comparative outcomes in agreement are acquired by different authors [14].

Fig. 3 demonstrates the estimations of the difference in the magnetization of the austenite and martensite stages, ΔM , depending on the magnetic field, $M(H)$, various temperatures of isotherm: 350, 400, 425, 450, 475 and 500 K. The maximum value is obtained at 450 K for all external magnetic fields applied made conceivable by not changing the transformation temperatures especially with the external magnetic field.

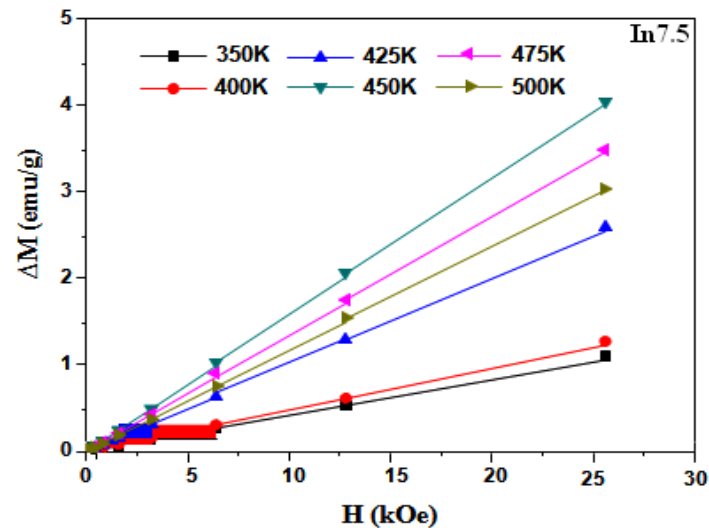


Figure 3. Representation of the estimations of the difference in the magnetization at different temperatures of isotherm for In7.5 alloy.

Fig. 4 shows the magnetization curves in the In10 alloy under various magnetic fields up to 50 kOe, at different isothermal temperatures: 5, 50, 100, 150, 200 and 305 K. On note that the dominant stable phase is the austenitic phase and that the isotherm $M(H)$ does not reflect a change in the chemical composition. At a temperature of 5 K, it is noted that the martensitic phase is predominant due to the coincidence of two curves during heating and cooling. However, at 100 K, the field curve deviates continuously from the saturation behavior and exhibits moderate irreversible hysteresis. This allows us to look for a phenomenon highlighted in the curve $M(H)$ recorded at 150 K, related to the presence of a reverse transition induced by the field. It should be noted that this field-induced transition starts from very low field values. The large positive slope still observed at 30 kOe and the distinction between the magnetization value obtained and that displayed by the austenite at 200 K, suggest that the field value required for a complete transformation is considerably higher. This confirms the results obtained by Li et al. [15].

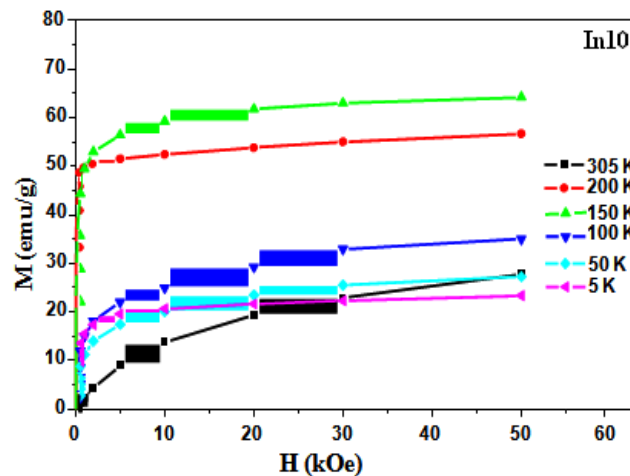


Figure 4. Representation of the magnetization (up to 50 kOe) depending on the magnetic field at different temperatures of isotherm for In10 alloy.

4. Conclusions

In summary, the impact of In addition on magnetic behavior of $\text{Mn}_{50}\text{Ni}_{50-x}\text{In}_x$ (at.%) ($x = 7.5$ and 10) alloys was studied. On the basis of the experimental results obtained, some conclusions can be cited. When increasing the In content, the crystal structure changes. It has transformed into a monoclinic martensite structure 14M type, for the $\text{Mn}_{50}\text{Ni}_{42.5}\text{In}_{7.5}$ alloy to $L2_1$ type cubic austenite structure for the $\text{Mn}_{50}\text{Ni}_{40}\text{In}_{10}$ alloy. The transformation temperatures were decreased with the increase of In content. For the $\text{Mn}_{50}\text{Ni}_{42.5}\text{In}_{7.5}$ alloy, the presence of a paramagnetic-ferromagnetic transition is noted. This transition in the austenitic phase occurs before the martensitic transformation during cooling. On the other side, for the $\text{Mn}_{50}\text{Ni}_{40}\text{In}_{10}$ alloy, there is the presence of a martensitic transformation followed by a ferromagnetic transition. The addition of Indium content plays an important role to change the structure and magnetic behavior in MnNiIn alloys.

Acknowledgement

This work was funded by the “Taishan Scholar” Project of Shandong Province and Key Basic Research Project of Shandong Natural Science Foundation of China (No. ZR2017ZB0422).

Author contributions Bachagha T prepared the manuscript under the direction of Zhang J. Zhang J, Sunol JJ and Khitouni M revised the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

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