

Structural behavior of Ni-Mn-(In, Sn) Heusler melt spun ribbons

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Abstract. In present contribution we discuss the structural properties of the austenite and martensite phases that form in as-spun ribbons of some selected compositions of the ternary system $Ni_{50}Mn_{50-x}(In,Sn)_x$, their characteristic crystallographic texture and the effect of vacuum annealing. X-Ray diffraction analysis showed that in all the cases austenite crystallized in an ordered cubic $L2_1$ -type structure. For thermally annealed samples diffraction lines becomes narrower in comparison with those of as-quenched samples, cell parameters tend reduce and crystallographic texture is preserved and improved. Furthermore, the structure and the martensitic temperature transformation can significantly differ from that of bulk alloys. Thus, materials with different structure, magnetoelastic behavior and transformation temperatures can be produced by melt spinning controlling starting composition and quenching conditions. In textured ribbons, the columnar, almost 1-dimensional, shape of the grains makes structural changes more difficult than in bulk materials (3-dimensional shape), thus explaining the differences observed in their structure and temperature magnitudes involved.

1. Introduction

Ferromagnetic Ni-Mn-X (X= In, Sn) shape memory alloys are of considerable interest because of their exceptional magnetoelastic properties. These Ga-free alloys has been recently attempted to overcome the high cost of gallium and the usually low martensitic transformation temperature of Ni-Mn-Ga alloys [1]. Recently, we produce Ni-Mn-(In,Sn) Heusler alloys by rapid solidification using melt spinning technique [2-4]. The procedure allows both the fabrication of these shape memory alloys as single phase homogeneous polycrystalline materials avoiding sometimes the homogenization annealing step required in case of bulk alloys and the production of textured samples.

2. Experimental procedure

Ferromagnetic as-cast pellets of the Ni-Mn-In and Ni-Mn-Sn Heusler alloys systems were prepared by arc melting from 99.98% pure Ni, 99.98% % pure Mn, 99.999 % pure Sn and 99.999 % pure In, using Bühler MAM-1 compact arc melter. Ingots were melted four times to ensure a good starting homogeneity. The samples were melt-spun in argon environment. Several samples were vacuum-annealed after melt-spinning process.

X-ray diffraction (XRD) experiments were performed in a Siemens D 500 (S2) diffractometer coupled with a TTK temperature chamber. The ribbons flakes (about 1 cm large) were put parallel to the plane defined by the incident and diffracted beams using a special device for low temperature patterns. Scanning was carried out in the interval $20^\circ \leq 2\theta \leq 80^\circ$ with a step increment of 0.05° .

3. Results and discussion

The X-Ray diffraction patterns at room temperature for alloys $Ni_{50}Mn_{36}In_{14}$ and $Ni_{50}Mn_{34.5}In_{15.5}$ are given in figures 1 and 2, respectively. In both alloys, the crystalline phase is the cubic austenite $L2_1$. The superstructure 111, 311 and 331 reflections confirm this. Texture effects are a minority. As expected, the main peak corresponds to the 220 reflection and only a small change in the 400-to-422 intensity ratio is found. The lattice parameter increases when raising the In content, following a linear trend (versus at.% of indium) as it has previously been found by Krenke et al [5].

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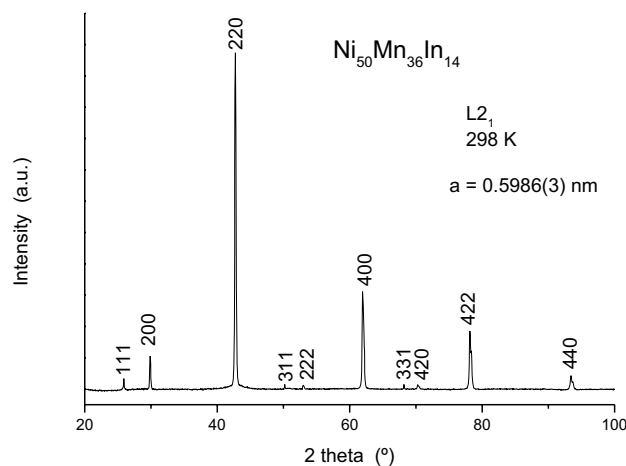


Fig. 1. X-Ray diffraction pattern at 298 K of $\text{Ni}_{50}\text{Mn}_{36}\text{In}_{14}$ Heusler alloy.

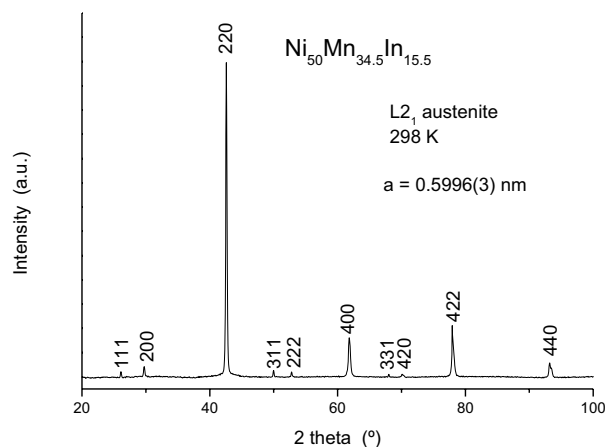


Fig.2. X-Ray diffraction pattern at 298 K of $\text{Ni}_{50}\text{Mn}_{34.5}\text{In}_{15.5}$ Heusler alloy.

In alloys with similar composition obtained directly by arc melting, the XRD patterns at room temperature correspond to modulated martensite structures [5]. The monoclinic structure was 10M (alloys with 15.5 and 15 at.% In) or 14M (alloy with 10 at.% In). The cubic austenite was found in alloys in the range between 16 and 25 at.% In. Furthermore, mixed modulated and textured structures were found at room temperature in spun $\text{Ni}_{50}\text{Mn}_{36}\text{In}_{14}$ [6]. The modification of either the production conditions or small changes in composition favours the thermal stability of different structures and, in consequence, different magneto-elastic behaviour. In this work, the alloys were obtained in a columnar, almost 1-dimensional, shape perpendicular to the ribbon surfaces. The small and constrained grains in the ribbons might have made difficult the transition to the martensite phase and shift it to lower temperatures. Thus, a large under-cooling is necessary for the martensitic transformation. Usually, this effect is complemented with a decreased Curie temperature of the ribbon, probably associated with the increased degree of quenched-in short-range disorder around defects, as proposed by Chernenko et al. [7]. Obviously, slight shift in the valence electron concentrations also increases the structural complexity. Furthermore, unpublished own results in the Ni-Mn-In system allow us to state that it is possible to develop a B2 cubic structure at room temperature after spun, and that a subsequent vacuum annealing stabilize a more ordered L₂₁ structure. Annealing homogenizes the composition and increases the chemical order in the sample. Likewise, when the L₂₁ phase is obtained (in as-spun ribbons) the posterior vacuum annealing only produce minor structural modifications. Diffraction lines become narrower, cell parameters tend to be reduced and crystallographic texture is preserved and sometimes even slightly improved.

An additional X-ray diffraction measurement was performed at 150 K. In the In_{14} alloy, the monoclinic 10M structure was found, textured in the 125 reflection (as shown in figure 3). In this case, the shift of the austenite-martensite transition to lower temperature when spinning is confirmed. Nevertheless, in the $\text{In}_{15.5}$ alloy the

transformation was not found and the remaining phase was the highly-ordered $L2_1$ (as shown in figure 4). The differences correspond to a decrease in the lattice parameter and to a small change in the different reflection peaks intensities, such as in the 400 and 422 peaks. In bulk alloys, the compositions near 16 at.% of indium are close to the limit of martensite transformation [5].

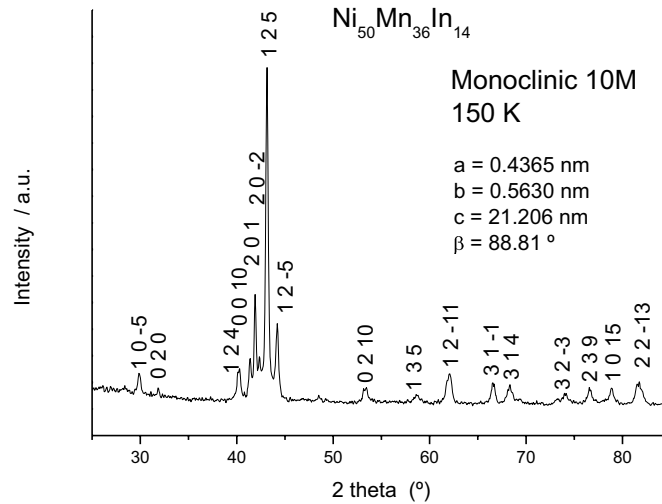


Fig. 3. X-Ray diffraction pattern at 150 K of $Ni_{50}Mn_{36}In_{14}$ Heusler alloy.

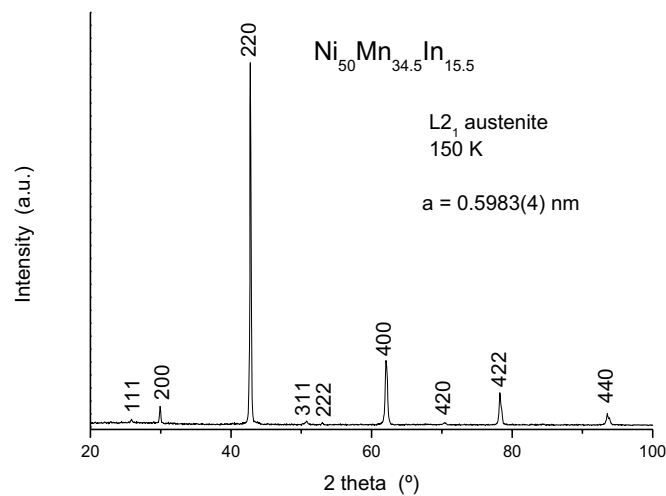


Fig.4. X-Ray diffraction pattern at 150 K of $Ni_{50}Mn_{34.5}In_{15.5}$ Heusler alloy.

Furthermore, structural analysis was also performed in alloys with Sn. For the $Ni_{50.3}Mn_{35.3}Sn_{14.4}$ sample, the crystalline structure at room temperature is a single austenite phase with cubic bcc $L2_1$ and lattice parameter $a = 0.5977$ nm, whereas the phase obtained at 150 K was indexed on the basis of a modulated 7M orthorhombic martensite, showing lattice parameters $a = 0,6162$ nm, $b = 0,6048$ nm, and $c = 0,5633$ nm. Traces of secondary or spurious phases were not detected. Structures of both phases coincide with those found in as-spun ribbons [2], but differ from the martensite found in bulk arc-melted materials that was identified as orthorhombic with a 10M modulation [8]. Likewise, in as-spun alloy with 12 at.% Sn, the structure at room temperature is the monoclinic martensite 10M. A similar phase was found in bulk alloys, but with different main reflections, indicating that samples with different texture can be produced.

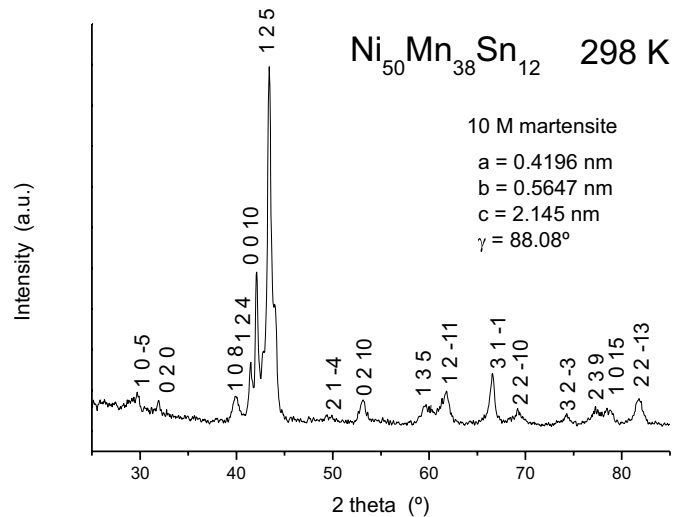


Fig.5. X-Ray diffraction pattern at 298 K of $\text{Ni}_{50}\text{Mn}_{38}\text{Sn}_{12}$ Heusler alloy.

Complementary studies on more compositions, and also modifying and controlling the processing parameters, are needed in order to achieve a better understanding of the structure behaviour of this Ga-free Heusler alloys.

4. Conclusions

Structural analysis confirms the development of alloys with different structures depending on the processing conditions. In the Ni-Mn-In system, a linear behaviour between $L2_1$ lattice parameter and In at.% has been detected. An extension of the stability, at room temperature, of the $L2_1$ phase in front of the austenite-martensite transition has also been found. Likewise, in the melt spun alloys of the Ni-Mn-Sn system, the structures can be the same of those of bulk alloys but with different texture. Nevertheless, sometimes even the martensite structure differs.

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