Effect of cobalt doping on martensitic transformations and magnetic properties of $Ni_{50-x}Co_xMn_{37}Sn_{13}$ (x = 1, 2, 3) Heusler ribbons

Abstract

The effect of cobalt doping on martensitic transformations and magnetic properties of the $Ni_{50-x}Co_x Mn_{37}Sn_{13}$ (x = 1, 2, 3) magnetic shape memory alloys obtained by melt spinning in form of ribbons is studied. The crystallographic structure of all ribbons at room temperature is austenite cubic $L2_1$. SEM micrographs indicate the formation of textured ribbons with columnar grains growing up perpendicular to the ribbons plane. For all ribbons, DSC cyclic scans reveal the martensitic transformation on cooling and the reverse austenitic transformation on heating below room temperature. In addition, they indicate that martensitic transformation temperatures decrease with increasing cobalt content.

Thermomagnetic curves reveal the coexistence of AFM and FM exchange interactions at low temperatures. Likewise, the magnetization change (ΔM) between martensite and austenite phase, as well as the austenite Curie temperature (T_C^A), increase with greater cobalt amount in ribbons. Structural transformations are also sensitive to the external applied magnetic field. This fact suggests that the structural transformations temperatures of the ribbons could be tuned to the desired functional temperature by controlling the cobalt amount replacing Ni. as well as changing the applied magnetic field which could lead to the enhancement of the magnetic properties.

Keywords: Heusler alloys; martensitic transformation; magnetic properties; cobalt doping.

1. Introduction

Ni-Mn-X (X = Ga, In, Sn, Sb) ferromagnetic shape memory alloys are attracting considerable attention due to their promising multifunctional properties such as magnetocaloric effect, magnetic shape memory effect and giant magnetoresistance change, which make them potential candidate for applications in magnetic refrigeration, magnetic

shape memory devices and magnetic actuators [1-5]. These properties are associated to the first order reversible magnetostructural transition. On cooling, the high temperature ferromagnetic cubic austenite phase ($L2_1$) transforms to the weak-magnetic tetragonal, orthorhombic, or monoclinic martensite phase. The magnetostructural transformation induces a huge magnetization change (ΔM) between the austenite and martensite structure [6] accompanied by a considerable magnetic entropy change (ΔS_M) that, in turn, induces either conventional or inverse magnetocaloric effect.

The structural transformations temperatures, as well as magnetic properties of Heusler Ni-Mn-X (X = Ga, In, Sn, Sb) alloys, are very sensitive to the alloy composition [7-9]. Therefore, it is possible to enhance the magnetic properties and to tune the transformation temperatures of theses alloys by varying the composition or by substituting one element for another one. In fact, it was reported that the substitution of Ni atoms by Co atoms could affect the properties of Ni-Mn-Sn Heusler alloys [7,10,11]. In particular, Wang et al. [10] observed an increase of martensitic transition temperature by 25 K and an important enhancement of the magnetization change (ΔM) between the martensite and austenite phases in $(Ni_{49}Mn_{39}Sn_{12})_{98}Co_2$ alloys obtained by arc melting in contrast to the $Ni_{49}Mn_{39}Sn_{12}$. Moreover, Liu et al. [11] reported that ΔM increases dramatically from 0.03 emu/g to 50 emu/g in $Ni_{45}Co_5Mn_{37}In_{13}$ alloys in comparison with $Ni_{49}Co_1Mn_{37}In_{13}$. It was also reported a decrease of martensitic transition temperatures and an increase of Curie temperatures of martensite (T_C^M) and austenite (T_C^A) with the cobalt addition in $Ni_{44-x}Co_xMn_{45}Sn_{11}$ (x = 0, 1, 2) alloys obtained by arc melting [12].

Recently, it was reported the possibility of synthesis of the Ni-Mn-X (X = In, Sn) Heusler alloys in form of ribbons by the melt spinning technique [13, 14]. The obtained ribbons have shown the specific properties reported in bulk Heusler alloys but in more suitable and advantageous shape for technological applications. As an example, the ribbons can improve

the technical characteristics of a refrigeration system by optimizing the heat transfer between the heat exchanger and the working unit [15]. In this paper, we investigate the effect of cobalt doping on structural and magnetic properties of $Ni_{50-x}Co_xMn_{37}Sn_{13}$ (x = 1, 2, 3) alloys ribbons obtained by melt spinning. The effect of applied magnetic field on structural and magnetic properties of the ribbons is also reported.

2. Experimental procedures

Non-stoichiometric $Ni_{50-x}Mn_{37}Sn_{13}Co_x$ (x = 1, 2, 3) Heusler alloys were prepared by arc melting from the high pure elements (> 99.9 at.%) under argon atmosphere. Constituent elements were melted four times to achieve a good homogeneity. The obtained ingots were induction-melted in a quartz tube in a melt spinning system. They were ejected in argon environment onto the polished surface of a copper wheel rotating at linear speed of 48 m/s. The microstructure morphology and the chemical composition of the melt-spun ribbon were examined by scanning electronic microscope (SEM) equipped with an X-ray energy dispersive spectroscopy (EDS) microanalysis system. The melt spinning technique has advantages such as compositional homogeneity and texture polycrystalline with small grain size in ribbons samples produced by this method, which can favor martensitic phase nucleation [16]. Furthermore, the structure and properties depends on several factors as the velocity of the rotating wheel or the ejection conditions [17]. In this work, all samples were obtained with the same melt-spinning conditions. The crystallographic structure of the ribbons at room temperature was characterized by X-ray diffraction (XRD) using the Cu Kα radiation (λ = 0.154060 nm) with a step size of 2θ = 0.02 ° and a counting time of 15s. The XRD patterns were analyzed using MAUD program [18] that is based on the Rietveld method [19]. The austenite-martensite structural transformations were studied by differential scanning calorimetry (DSC). Cyclic experiments, with cooling and heating rate of 10 K/min, were

performed under liquid nitrogen atmosphere to determine the different thermal characteristics of the ribbons. Thermomagnetic measurements were carried out using a vibrating sample magnetometer (VSM-VersaLab, QD). Zero-field-cooling (ZFC), field-cooling (FC) and field-heating (FH) protocols, in the temperature range from 50 K up to 400 K and applied magnetic field up to 30 kOe, were used.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the obtained ribbons at room temperature. XRD patterns indicate that all the ribbons have the same crystalline structure which consists of high symmetrical cubic $L2_1$ austenite phase. It is worth noting that the Co substitution of Ni does not affect the crystalline structure of the ribbons at room temperature. XRD patterns were analyzed by the Rietveld method. The Rietveld refinement was realized by generating a theoretical diffraction pattern of cubic $L2_1$ phase. The structural parameters of the ribbons obtained from the refinement of XRD patterns are listed in table 1. We note here that the lattice parameter, a, of the ribbons decreases slowly and the crystallite size increases with the increase of cobalt concentration. Such slight decrease of lattice parameter has been observed in $Mn_{50}Ni_{40-x}Co_xSn_{10}$ (x = 0, 6) alloys obtained by arc melting [20]. The values of lattice parameter are comparable to those reported by other authors [14]. The apparent non-linear behavior (Vegard's law) of the dependence between lattice parameter and Co content is probably related to a less stable crystalline structure than the perfect substitution between Co and Ni. This effect has been previously reported in the Ni-Mn-Sn-Co system [21].

Table 1. Structural parameters of $Ni_{50-x}Co_xMn_{37}Sn_{13}$ (x = 0, 1, 2, 3) Heusler alloys ribbons deduced from the Rietveld refinement of XRD patterns.

Fig. 2 shows the fracture cross-section morphology of the obtained ribbons. The ribbons thickness is around 8 µm. All of them have a similar morphology consisting of a columnar

structure with grains growing-up through the ribbon thickness perpendicular to the ribbon plane. The wheel side of the ribbons shows a thin layer of small equiaxed grains. The chemical composition of the obtained ribbons was checked by EDS microanalysis. The results are listed in table 2. All ribbons have a chemical composition close to the respective nominal one for each of them.

Table 2. Composition of the $Ni_{50-x}Co_xMn_{37}Sn_{13}$ (x = 1, 2, 3) alloys ribbons determined by EDS microanalysis and the corresponding outer electron concentration per atom *e/a*.

Fig. 3 shows the DSC cooling and heating scans of the ribbons. The DSC scans of the three ribbons show an exothermal peak on cooling. This corresponds to the structural transformation of alloys from the high temperature austenite phase to the low temperature martensitic phase. On heating, an endothermic peak is revealed by the scans of all ribbons. This corresponds to the reverse structural transformation from martensitic to austenitic phase.

Table 3 collects the structural transformations temperatures of the alloys (M_s, M_f, A_s, A_f), the thermal hysteresis ΔT and the martensitic transformation temperature T_M defined as $(M_s+A_f)/2$. The enthalpy (ΔH) and the entropy (ΔS) changes associated to the structural transformations are also included in table 3.

Table 3. Characteristic transformations temperatures in $Ni_{50-x}Co_xMn_{37}Sn_{13}$ (x = 1, 2, 3) alloys ribbons derived from DSC scans.

It can be seen that, with increasing the cobalt content, the martensitic starting temperature, M_s, decreases; M_s values are 254, 251 and 228 K for the alloys with x = 1, 2 and 3 at. % of Co, respectively. The other characteristic transformations temperatures, M_f, A_s, A_f and T_M, are also shifted toward low temperatures. The change in transformations temperatures is significant for $Ni_{47}Mn_{37}Sn_{13}Co_3$ (x = 3) alloy. This implies that the Co strengths the stability of the cubic austenite parent phase. Such decrease in the transformations temperatures of the ribbons with

the increase of cobalt amount has been reported in Ni-Mn-Sn ferromagnetic alloys [20, 22-23]. This decrease can be explained, in base, to the electron valence concentration (*e/a)*. It is known that there is a linear correlation between *e/a* and the martensite starting temperature M_s [23]. M_s decreases with decreasing *e/a*. Cobalt atom has less electrons in its outer shell (9 ($3d^7 4s^2$)) than nickel atom (10 ($3d^8 4s^2$)). Then, the substitution of Ni atoms by Co ones could lead to a decrease of *e/a*. Fig. 4 shows a clear decrease of the martensitic starting temperature *Ms* of the ribbons with the decrease of *e/a* calculated from EDX microanalysis. *e/a* deceases as the amount of cobalt increases in the ribbons composition (table 2). Furthermore, in Ni-Co-Mn-Sn alloys, the martensitic transformation can be also affected by other factors as Ni/Mn ratio and grain size of the austenitic phase [21] that should be taken in account.

The thermal hysteresis (ΔT), defined as the difference between the temperatures corresponding to the austentite and martensite peaks in DSC scans, increases with increasing the cobalt content in the ribbons. ΔT values are 15, 17 and 21K for the alloys with x = 1, 2 and 3 at. % of Co, respectively. The increment of ΔT may result from the atomic disorder induced by the Co addition that rise the energy required for phase boundary motion which might result in a decrease of the thermal elasticity in martensitic transformation. A similar effect was reported in Fe-doped Ni-Mn-Ga alloy [24] and in Fe-doped Ni-Mn-In alloys [25]. Enthalpy and entropy values are very similar on cooling (c) or on heating (h). It is also found a maximum in the enthalpy and entropy of the transformation for the alloy with x = 2 at. % of Co. Thus, there is no trend as a function of Co content (or *e/a* parameter). The same effect has been previously detected in melt-spun alloys of the Ni-Mn-Sn-Co system [26]. Likewise, by following procedure given in ref. [27], it is possible from DSC analysis to obtain the percentage of the elastic energy (E_{el}) and the dissipation work (W_d) of the reversible martensitic cyclic transformation. For the alloys with x = 1, 2 and 3 at. % of Co, the elastic

energy percentage is 2.1, 2.2 and 2.8 % and the dissipation work percentage is 5.7, 6.4 and 8.6 % respectively.

Fig. 5 displays the magnetization temperature dependence $M(T)$ of the as-quenched $Ni_{50-x}Co_xMn_{37}Sn_{13}$ (x = 1, 2 and 3) ribbons under an applied magnetic field of 300 Oe. The ZFC, FC and FC *M* vs. *T* curves show clearly the magneto-structural transformation of the studied alloys on heating and on cooling. On heating, the magnetization $M(T)$ increases rapidly indicating the inverse magneto-structural transformation from low magnetization martensitic phase to ferromagnetic austenite phase. A bifurcation in the transformation shape is observed for the alloy with x = 1 at. % of Co around 180 K in FC and FH curves. This effect allows us to state that the alloy is magnetically inhomogeneous. In previous works, this behavior has been attributed to the coexistence of ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions [20, 28]. This can be explained by the excess of Mn atoms that occupy a fraction of the other elements sites in the crystal structure and couple antiferromagnetically with the Mn atoms at regular Mn sites [29]. This thermomagnetic response suggests that the alloy could undergo an intermartensitic phase transition. It was also found that this effect disappears at higher magnetic field [30]. Around 200 K, the three alloys samples display a splitting between ZFC and FC (as well as between ZFC and FH) curves that pronounces at lower temperature. This behavior also reveals the coexistence of AFM and FM exchange interactions at low temperatures [20]. Moreover, the low magnetization values in ZFC *M(T)* curves could reflect a magnetic state in which the FM moments are pinned by AFM ones. However, after FC process, FM strength increases giving rise to a large magnetization [20].

With increasing temperature, the first order martensite to austenite transformation appears. At higher temperature, the magnetization decreases rapidly for the three alloys. This decrease corresponds to the magnetic second order transition from ferromagnetic to paramagnetic state

of the austenite phase. On cooling, the martensitic transformation is disclosed through the existence of thermal hysteresis arising from its first-order nature.

A dip peak (x = 1) and a step (x = 2) appear near 280 K in the *M(T)* curves under the field of 300 Oe. This effect detected below Curie temperature (T_C^A) is due to the so-called Hopkinson effect [31]. This latter is associated to an increase on magnetic susceptibility below T_C due to a magnetic anisotropy decreasing. Likewise, this effect disappears as increasing the applied magnetic field because a lower thermal energy density is opposed to rotate magnetization towards the direction of external field [32]. It also disappears in the alloy with x = 3 at. % of Co because Co atoms works as a ferromagnetic activator.

The transformations temperatures, the austenite Curie temperature (T_C^A) and the magnetization change (ΔM) between the martensite and austenite structure of the three alloys deduced from $M(T)$ at 300 Oe curves are reported in table 4. As was observed in DSC scans, the martensitic transformations temperatures shift to lower temperature with the increase of the cobalt amount in the alloys. The martensite starting temperatures (M_s) are 250 K, 249 K and 230 K for alloys with x = 1, 2 and 3. % of Co, respectively.

Table 4. Characteristic transformations temperatures and magnetization change in $Ni_{50-x}Co_xMn_{37}Sn_{13}$ (x = 1, 2, 3) Heusler alloys ribbons deduced from thermomagnetic curves.

We underline here that the transformations temperatures deduced from $M(T)$ curves are a little bit smaller than those deduced from DSC scans analysis. This could be ascribed to the effect of the applied magnetic field. We observe also an increase of austenite Curie temperature (T_C^A) with the increase of cobalt amount in the alloys. T_C^A values are 319 K, 321 K and 330 K for the alloys with x = 1, 2 and 3 at. % of Co, respectively, indicating that Co stabilizes the parent phase. The increase of T_C^A is attributed to the enhanced exchange

interaction due to the substitution of Co by Ni [7, 12] that it is attributed to that exchange interaction of Co-Mn is several times larger that of Ni-Mn [33]. The change in the austenite Curie temperature is significant for the alloy $Ni_{47}Co_3Mn_{37}Sn_{13}$ (x = 3). A characteristic temperature interval is defined as (T_C^A-M_f) [34]. This difference is 77, 86 and 127 K for alloys with x = 1, 2 and 3 at. % of Co, respectively. A high increase of this difference is associated to a reduction in the entropy change, as detected (DSC analysis) in alloy with 3 at. % of Co. Likewise, the obtained T_C^A values are above that of $Ni_{50}Mn_{37}Sn_{13}$ ribbons obtained by melt spinning [14] which is about 302 K. An enhancement of the magnetization jump between the martensite and austenite phase is also observed, which could improve the magnetocaloric effect of these alloys. The increase of austenite Curie temperature and magnetization jump, can be explained by the Co excess that enhances the ferromagnetic correlations with Mn magnetic moments. First-principle calculations in $Ni_{50-x}Co_x Mn_{25+y}Sn_{25-y}$ shape memory alloys revealed that the substitution of Co for Ni turns the Mn-Mn interaction from antiferromagnetic to ferromagnetic one [35]. This fact is important because T_C^A limits the operational range of Ni-Mn-Sn based alloys. Furthermore, this behavior is coherent with the no detection of Hopkinson effect and nor the anomaly near 180 K for the alloy with x = 3 at. % of Co.

The effect of the external applied magnetic field on the martensitic transformation and on the magnetization of Co-doped ribbons is also detected. Fig. 6 shows the temperature magnetization dependence $M(T)$ under various applied magnetic fields ranging from 30 Oe to 30 kOe. For all alloys, the martensitic transformations temperatures decrease more slowly for alloys x = 1 and x = 2 than for x = 3 alloy with the increase of the applied magnetic field that stabilizes the ferromagnetic austenite phase. As expected, the magnetization change between martensite and austenite rises with applied magnetic field. Furthermore, the magnetization value of the austenite and martensite phases also rises as increasing up to 3 kOe the applied

magnetic field. It is worthwhile to remarking that the splitting between ZFC and FC (and between ZFC and FH) curves is disappeared at 30 kOe for x = 1 and x = 2 alloys samples while it is absent at a lower field of 3 kOe for the x = 3 alloy.

The variation with the applied magnetic field of the martensitic starting temperature *Ms* and the magnetization change (ΔM) between the martensitic and the austenite phases is shown in Fig. 7. We can observe that (ΔM) is more sensitive to the applied magnetic field between 30 Oe and 3000 Oe. The martensite starting temperature *Ms* decreases slowly with the increase of the applied magnetic field. A similar effect on martensitic transformation temperatures and magnetic properties of Ni-Mn-Sn ribbons has been previously reported [36]. Likewise, it is known that the combination of a large ΔM and a small ΔS benefit the magnetic-field-induced phase transformation (MFPIT) from martensite to austenite at a constant temperature close to A_s [37]. In our study $\Delta M/\Delta S$ values are 1.25, 1.88 and 2.78 K/T for the alloys with x = 1, 2 and 3 at. % of Co, respectively. It can be concluded that the optimal alloy for MFPIT and consequently magnetic shape memory effect is $Ni_{47}Co_3Mn_{37}Sn_{13}$.

4. Conclusions

The effects of cobalt substitution and the applied magnetic field on martensitic transformations and magnetic properties of $Ni_{50-x}Mn_{37}Sn_{13}Co_x$ (x = 1, 2, 3) melt spun ribbons were investigated. The crystallographic structure of the ribbons is cubic $L2_1$ at room temperature. The substitution of nickel atoms by cobalt ones gives rise to an increase of Curie temperature, a decrease in the martensitic transformation temperatures and the enhancement of magnetic properties of the ribbons. The applied magnetic field also decreases the martensitic transformation temperature and increases the magnetization change (ΔM) between the martensitic and the austenite phases. The obtained results suggest that cobalt is an

interesting alternative to tune the transformation temperature of the Ni-Mn-Sn alloys and to improve their magnetic properties. From $\Delta M/\Delta S$ values, the best composition for magnetic shape memory effect is $Ni_{47}Co_3Mn_{37}Sn_{13}$.

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Figure captions

Fig. 1. Room temperature XRD patterns of $Ni_{50-x}Co_xMn_{37}Sn_{13}$ (x = 1, 2, 3) Heusler alloys ribbons.

Fig. 2. SEM micrographs of the fracture cross-section of $Ni_{50-x}Co_xMn_{37}Sn_{13}$ (x = 1, 2, 3) alloys ribbons.

Fig. 3. DSC cyclic scans of $Ni_{50-x}Co_xMn_{37}Sn_{13}$ (x = 1, 2, 3) alloys ribbons.

Fig. 4. Martensitic transformation starting temperature M_s vs. valence electron concentration per atom *e/a* for $Ni_{50-x}Co_xMn_{37}Sn_{13}$ (x=1, 2, 3) ribbons.

Fig. 5. ZFC, FC, and FH thermomagnetic curves $M(T)$ measured at applied magnetic field of 300Oe for $Ni_{50-x}Co_xMn_{37}Sn_{13}$(x=1, 2, 3) ribbons.

Fig. 6. Thermomagnetic curves $M(T)$ under ZFC, FC and FH protocols of the $Ni_{50-x}Mn_{37}Sn_{13}Co_x$ (x=1, 2, 3) ribbons in different applied magnetic fields.

Fig. 7. Magnetic field dependence of **a)** the martensitic transformation start temperature M_s and **b)** the magnetic change (ΔM) between the martensitic and the austenite phases of the $Ni_{50-x}Mn_{37}Sn_{13}Co_x$ (x = 1, 2, 3) alloys ribbons.