Structural and Martensitic Transformation of Heusler Mn-Ni-Sn Alloys

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Abstract. The improved functional stability of shape memory alloys, which undergo a reversible martensitic transition, is essential to their applications and remains a matter of critical research based on advanced shape memory technology. In this paper, the microstructure, phase structure and martensitic transformation of Heusler Mn₅₀Ni₅₀₋ₓSnₓ (x = 5, 7.5 and 10) alloys studied by scanning electron microscopy, X-ray diffraction and differential scanning calorimetry. The results show that the structure of martensite phase is identified to be 14M monoclinic structure, while, the austenite phase is with L₂¹ cubic structure. The martensitic transition temperatures are found to decrease with the increase in Sn content due to the decrease in valence electron concentration ((e/a) ratio).

Introduction

In the last decade, shape memory alloys, such as Ni-Mn-Ga [1], Mn-Ni-X (X= In, Sn, Sb) [2-4] and Mn-Ni-Al [5], have attracted much scientific attention as it concerns the sensors, magnetic cooling systems and actuators industry, as a result of their exceptional properties. These properties originate from the martensitic transition from the high temperature martensite phase to the low temperature austenite phase. In addition, Sn is cheaper than In and Sb, Heusler Mn-Ni-Sn alloys have received much more consideration. Although Heusler materials with a high content of Mn are expected to possess improved physical properties, limited examinations on Heusler materials rich in Mn (50 at.%) were conducted until recently.

In this paper, we report the effect of Sn addition in Heusler Mn₅₀Ni₄₀₋ₓSnₓ (x = 5, 7.5 and 10) alloys, on the changes of martensite structure, martensitic transition temperatures, and the thermal analysis during rapidly solidified process. These materials can be candidates for future applications.

Experimental Procedure

As-cast ingots of Heusler Mn₅₀Ni₅₀₋ₓSnₓ (x = 5, 7.5 and 10) alloys were prepared by arc-melting from highly pure elements of Mn, Ni and Sn (> 99.98%) and re-melted several times to ensure chemical composition homogeneity, using Buhler MAM-1 compact arc melter in an argon atmosphere. Afterwards, the samples were induction melted in a quartz crucible with a circular nozzle of 0.6 mm and then ejected onto a spinning copper wheel with a speed of 48m/s. The melt-spinning process was carried out in an argon atmosphere. The prepared samples are named as follows: Sn5, Sn7.5, and Sn10, respectively. Their microstructures and chemical compositions were determined by scanning electron microscopy (SEM) using a ZEISS DSM-960A microscope operated at 30 kV and linked with an energy dispersive spectrometry (EDX) attachment. The structural of the ribbons was performed using an X-ray diffractometer (Siemens D500), with Cu-Kα radiation (λ=1.5406 Å). These structures were refined using Jana software [6]. The DSC measurements were carried out to examine the characteristic temperatures of martensitic transition. The cyclic experiments (heating-cooling) were recorded at 10 K/min under argon atmosphere. Differential scanning calorimetry scans above room
temperature were performed in the DSC high-temperature DSC modulus of the Setaram Setsys system, and the DSC scan below room temperature was performed in the DSC 30 device of Mettler-Toledo working with a liquid nitrogen cooling system.

Results and Discussion

Figure 1 shows the micrographs corresponding to the free surface, and of the fracture cross section morphology of the ribbons. The SEM images of the free surfaces of Sn5, Sn7.5 and Sn10 ribbons are presented in Fig. 1a1, 1a2, 1a3, respectively. The free surface of the Sn5 and Sn7.5 alloys obviously present the lamellar microstructure of the martensite structure (Fig. 1a1, 1a2). These ribbons are mechanically fragile and brittle, and cleave easily along the perpendicular direction to the ribbon plane. While, the free surface of the Sn10 alloy is characterized by a granular microstructure of the austenite structure (Fig. 1a3).

For the Sn5 alloy, the grain size is somewhere between 2.60 and 8.86 μm and intake 2.10 and 8.68 μm for the Sn7.5 alloy. However, the microstructure of the Sn10 alloy shows that the grain size varies between 8.73 and 15 μm. A microcrystalline microstructure is visible inside each grain for the presence of various zones where the solidification of the material ends. The fracture cross sections of the Sn5, Sn7.5 and Sn10 alloys can be seen in Fig. 1(b1-b3), respectively. It can be observed that the thickness values vary between 10 and 16 μm. In addition, the cross-section shows the growth of columnar crystals influenced by the temperature parameter between the surface in contact with the cold wheel and the free surface. The large columns develop perpendicular to the contact surface with the wheel. As crystalline growth approaches the free surface, the grain size tends to be homogenized. It is also observed that the large columns of alloys with martensitic structure were more defined than those of austenitic structure. The obtained results of EDX microanalysis of chemical composition examined by scanning electron microscopy (SEM) show conformity with assumption of the chemical composition of the studied as-spun ribbons (Fig. (1c1-c3)). The compositions analysis was found to be in good agreement with the nominal compositions of the as-spun ribbons (51.4 at% Mn-43.0 at% Ni-5.6 at% Sn), (50.7 at% Mn-41.0 at% Ni-8.3 at% Sn) and (48.7 at% Mn-40.4 at% Ni-10.9 at% Sn). To determine the thermal analysis conditions, the knowledge of crystal structure at room temperature
is basic [7]. The XRD patterns at room temperature for alloys Sn5, Sn7.5 and Sn10 are given in Figure 2. The fitting parameter $R_p$ values are 0.0942, 0.0842 and 0.0961 for ribbons Sn5, Sn7.5 and Sn10, respectively. The XRD measurements manifest that the ribbons Sn5 and Sn7.5 exhibit a single martensite phase of 14M monoclinic structure. The lattice parameters are: $a=4.282\pm0.003$ Å, $b=5.658\pm0.006$ Å, $c=29.902\pm0.009$ Å with an angle $\beta=93.24^\circ$ for Sn5 alloy but, for Sn7.5 alloy, $a=4.321\pm0.004$ Å, $b=5.612\pm0.005$ Å, $c=30.019\pm0.008$ Å with an angle $\beta=93.38^\circ$. These parameters are in good relation with those recently detailed for melt-spun ribbons of close chemical composition [8]. Both diffraction patterns were indexed and related to the monoclinic structure using Rietveld analysis via the Jana software.

![Figure 2. Rietveld refinement of the XRD patterns of Sn5, Sn7.5 and Sn10 ribbons at room temperature.](image)

For the Sn10 alloy, the ribbon phase is completely transformed into a cubic L2$_1$ austenite phase with lattice parameters: $a=b=c= 5.998 \pm 0.004$ Å. The superstructure (3 1 1), (3 3 1) and (5 3 1) reflections confirm this [2]. All the results in these alloys are consistent with those Ni-rich Ni-Mn-Sn alloys acquired by other authors [9]. The effect of Sn content on the structural parameters of obtained alloys is illustrated in Figure 3. It can be observed that the transformation from 14M monoclinic structure (for Sn5 and Sn7.5 alloys) to L2$_1$ cubic structure (for Sn10 alloy) is performed by the expansion in the parameter $c$ and the reduction in parameters $a$ and $b$. In addition, more clearly for the main peak position (0 0 14), it should be noted that this peak moves to smaller angular positions by increasing the Sn content. Therefore, the replacement of Ni by Sn (higher atomic radius) causes an increase in the volume of the unit cell. Moreover, the increase of the Sn content facilitates the austenite of the current phase and thus, reduces the temperature range of the structural transformation.

![Figure 3. Representation of the cell parameters and the volume according to the percentage of Sn for the obtained alloys.](image)
Based on the XRD results, it is clear that the DSC scans of the Sn5 and Sn7.5 alloys should be performed by heating from room temperature in order to detect the martensitic transition. Likewise, the DSC scan of the Sn10 alloy could be performed by cooling from room temperature. The corresponding DSC results are given in Figure 4.

Figure 4. DSC cyclic scan for the alloys (Sn5, Sn7.5 and Sn10) at a heating/cooling rate of 10 K.min⁻¹. Arrows indicate heating (down: austenite to martensite) and cooling (up: martensite to austenite).

The characteristic transformation temperatures at which martensite start and finish ($M_s$ and $M_f$) and austenite start and finish ($A_s$ and $A_f$) are collected in Table 1.

**Table 1. Various transition temperatures of Heusler Mn$_{50}$Ni$_{50-x}$Sn$_x$ (x= 5, 7.5 and 10) alloys.**

|          | $M_s$ (K) | $M_f$ (K) | $A_s$ (K) | $A_f$ (K) | $\Delta T$ (K) | ($e/a$) |
|----------|-----------|-----------|-----------|-----------|----------------|---------|
| Sn5      | 567.5     | 551       | 597       | 613       | 45             | 8.122   |
| Sn7.5    | 410       | 389       | 413       | 430       | 17             | 7.981   |
| Sn10     | 160       | 147       | 166       | 180       | 20             | 7.885   |

The martensitic transition temperatures were found to decrease with increasing Sn content due to the decrease in valence electron concentration ($e/a$).

The entropy ($\Delta S$) and enthalpy ($\Delta H$) changes in structural transformations are calculated from calorimetry data [9]. The calculated values are listed in Table 2. It is to be noticed that both the enthalpy and entropy changes decrease with the increase in ($e/a$) ratio, caused by the increase of Sn concentration. Similar results of Ni-Mn-Sn alloys have reported that both $\Delta S$ and $\Delta H$ increased with the increase of ($e/a$) ratio [9]. The enthalpy variation is slightly higher in the heating process than in the reverse process. This is a consequence of the fact that the energy stored by the martensitic phases is greater than the austenitic phases and the relaxation of internal tensions during heating. This stored energy justifies the difference between the values of $\Delta H$ between the direct and the inverse process (the same for the variation of the entropy). There are many factors intervene by favoring a small variation of entropy, for example, a less distortion of the martensitic structure compared to austenitic structure.

**Table 2. The effect of Sn content in the enthalpy and entropy variations during the structural transformation.**

| Samples | $\Delta H$ (J/mol) | $\Delta S$ (J/mol.K) |
|---------|--------------------|----------------------|
|         | Heating(Endo)     | Cooling(Exo)         | Heating(Endo) | Cooling(Exo) |
| Sn5     | 2253.62            | 2216.62              | 3.81          | 3.79         |
| Sn7.5   | 3269.24            | 3187.38              | 7.78          | 7.68         |
| Sn10    | 206.72             | 219.68               | 1.21          | 1.32         |

**Conclusion**

In the present paper, we have reported the impact of Sn addition in Heusler Mn$_{50}$Ni$_{50-x}$Sn$_x$ (x= 5, 7.5 and 10) alloys, on the changes of structure and the martensitic transformation temperatures. The
The crystal structure of martensite is identified to be 14M monoclinic structure, whereas the austenite is identified to be L2₁ cubic structure. The martensitic transformation temperatures decrease with the increase of Sn content due to the decrease in valence electron concentration (e/a). For Sn5 and Sn7.5 ribbons, they have the transformations at high temperature above 400 and 550K, respectively. This fact limits them in their applications such as actuators, sensors and magnetic cooling systems.

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References

[1] Y.C. Dai, L. Hou, Y. Fautrelle, Z.B. Li, C. Esling, Z.M. Ren, X. Li, Martensitic transformation and detwinning in directionally solidified two-phase Ni-Mn-Ga alloys under uniaxial compression. J. Alloys. Compd. 722 (2017) 721-728.

[2] T. Bachaga, R. Daly, L. Escoda, J.J. Sunol, M. Khitouni, Influence of chemical composition on martensitic transformation of MnNiIn shape memory alloys. J. Therm. Anal. Cal. 122 (2015)167-173.

[3] T. Bachaga, R. Daly, M. Khitouni, L. Escoda, J. Saurina, J.J. Sunol, Thermal and Structural Analysis of Mn₄⁹.₃Ni₄₃.₇Sn₇.₀ Heusler Alloy Ribbons. Entropy. 17 (2015) 646.

[4] V.D. Buchelnikov, V.V. Sokolovskiy, Magnetocaloric effect in Heusler Ni-Mn-X alloys (X= Ga, In, Sn, Sb). Phys. met. Matellogr. 112 (2011) 633.

[5] M.V. Lyange, E.S. Barmina, V. Vladimir, V. Khovaylo, Structural and Magnetic Properties of Ni-Mn-Al Heusler Alloys: A Review. Mater. Sci. Found. 81-82 (2015) 232-242.

[6] V. Petricek, V. Eigner, M. Dusek, A. Cejchan, Discontinuous modulation functions and their application for analysis of modulated structures with the computing system JANA2006. Z. Kristallogr. 231(2016) 301-312. DOI 10.1515/zkri-2015-1913.

[7] T. Bachaga, R. Daly, J.J. Sunol, J. Saurina, L. Escoda, L.G. Legarreta, B. Hernando, M. Khitouni, Effects of Co additions on the martensitic transformation and magnetic properties of Ni-Mn-Sn shape memory alloys. J. Supercond. Nov. Magn. 28 (2015) 3087-3092.

[8] T. Krenke, E. Duman, M. Acet, E.F. Wassermann, X. Moya, L. Manosa, A. Planes, Inverse magnetocaloric effect in ferromagnetic Ni-Mn-Sn alloys. Nat. Mater. 4 (2005) 450-454.

[9] T. Krenke, M. Acet, E.F. Wassermann, X. Moya, Ll. Mañosa, A. Planes, Martensitic transitions and the nature of ferromagnetism in the austenitic and martensitic states of Ni-Mn-Sn alloys. Phys. Rev. B. 72 (2005) 014412.