Ni-Mn-Sn Heusler: milling and annealing effect on structural and magnetic properties

Florin Popa¹, Traian Florin Marinca¹, Horea Florin Chicinaș¹, Olivier Isnard², Ionel Chicinaș¹

¹Department of Materials Science and Engineering, Technical University of Cluj-Napoca, 103-105 Muncii Avenue, 400641 Cluj-Napoca, Romania

²Institut Néel, CNRS/ University J. Fourier, BP166, 38042 Grenoble, Cédex 9, France

florin.popa@stm.utcluj.ro

Abstract. Nanocrystalline Ni₅₁Mn₁₉Sn₃₀ Heusler alloy was prepared in the form of powder by solid state reaction in a planetary ball mill under argon atmosphere. After 10 h of milling the samples exhibit a mixture of two phases: disordered Heusler structure and half-Heusler structure. The stability of the phases was studied and a transformation of the disordered Heusler phase into the ordered Heusler and Ni₃Sn₂ phase was observed after heat treatment. Magnetic properties strongly depend on the phases promoted during milling and annealing. The phase change after annealing leads to the increase of the sample’s magnetisation.

1. Introduction

Heusler alloys are materials having the X₂YZ formula with a complex crystalline structure (L₂₁) composed of four face centred cubic sub lattices [1]. Generally, Heusler alloys are prepared by high temperature arc melting, with a careful composition control [2, 3]. Among Heusler alloys, Ni-Mn-Sn represents an interesting case, presenting inverse magnetocaloric effect [4]. For the stoichiometric composition, Ni₂MnSn alloy has no martensitic transition, however, non-stoichiometric alloys with higher Mn content exhibit the austenite-martensitic transition and the magnetic order can be antiferromagnetic [5]. A method for obtaining nanocrystalline alloys is mechanical alloying, consisting in elemental powder mixture processing in high-energy ball mills, in order to obtain a solid state reaction. By this method, nanocrystalline alloys, amorphous phases, metastable alloys, out of equilibrium structures/microstructures, extended solid solution, quasicrystals can be obtained [6]. In the Ni-Mn-Sn system, several studies were performed on samples obtained by milling [7] or by melt spinning [8], showing the influence of the nanocrystalline state and of annealing on the structure and transition temperature of the martensitic transformation. The present study is focused on the phase formation of the Ni₅₁Mn₁₉Sn₃₀ non-stoichiometric alloy by mechanical alloying and the evolution of its magnetic and thermomagnetic properties during milling and annealing of the samples.

2. Experimental

Ni₅₁Mn₁₉Sn₃₀ (at. %) alloy was prepared in a planetary ball mill, Fritch-Pulverisette 6, starting from a mixture of elemental nickel, manganese and tin powder, weighed in the proper ratio. The mixture was first homogenized for 15 min in a Turbula type apparatus, and then milled for up to 10 hours in argon.
atmosphere. The ball/powder mass ratio was 9.2:1 at a filling factor of 40%. Several samples were annealed in a Setaram Labsys differential scanning calorimetry furnace at 400 °C with a heating rate of 10 °C/min and maintaining at 400 °C for 60s. The alloy formation was investigated by X-ray diffraction with an INEL 3000 Equinox diffractometer, operating with Co - Kα radiation. The magnetization curves were recorded at room temperature by extraction method technique in a continuous field of up to 2 T. The Curie temperatures have been determined by thermomagnetic measurements with a Faraday balance in small fields (less than 0.1 T).

3. Results and discussion
Ni51Mn19Sn30 alloy formation was studied by X-ray diffraction indicating the phase evolution during milling, as presented in figure 1.

![Figure 1. X-ray diffraction patterns for the as-milled samples.](image)

From Figure 1, the formation of the alloy can be described by the disappearance of the elemental peaks of Ni, Mn and Sn (recorded for the starting sample) and the emergence of a new set of peaks (Heusler structure) for prolonged milling. The Bragg peaks of the Sn and Mn, are no longer observed for samples milled for more than 4 h. In opposition, the Ni peaks are clearly visible up to 6 h of milling. In the sample milled for 8 h the presence of Ni is related to the broad peak asymmetry at its position compared with the starting sample. The Ni-Mn-Sn phase is the majority phase for the samples milled for 10 h, having nanocrystalline structure, with mean crystallite size of 15 ± 2 nm. A closer analysis of the Ni-Mn-Sn phase is presented in Figure 2. Probably due to the non-stoichiometry of the sample and to the high amounts of the stresses induced by milling, the obtained phase is the disordered Ni52MnSn.

The disordered Heusler phase is accompanied by a second phase, identified as being the half-Heusler compounds (NiMnSn). By heating at low temperature (400 °C), the disordered Heusler phase exhibits a decomposition process (Figure 2). Under the influence of temperature, the powder’s initial phase transforms into three components: a Ni2MnSn ordered Heusler phase, a half-Heusler phase (NiMnSn) and Ni3Sn2 phase. This phase transformation has important consequences on the magnetic properties, as presented in Figure 3.

The magnetisation of the milled samples (Figure 3) decreases as the milling is prolonged, from 21.5 Am²/kg (0 h MA) down to 2 Am²/kg (10 h MA). The low magnetization value is connected to the decrease of the Ni content, the Heusler phase being antiferromagnetic having low magnetization [9]. However, the annealing of the sample leads to an important magnetization increase, associated with the ordering of the Heusler phase [9] and probably with the apparition of the Ni3Sn2 phase (with Curie temperature below room temperature). By analysing the 4 h milled sample, when the solid state reaction is initiated (the powders are mechanically activated), it can be observed that a subsequent annealing leads to the same phases - ordered Heusler phase and Ni3Sn2 phase - as in the case of the sample milled for 10 h, which leads to the complete formation of the alloy by milling. Both 4 h and 10 h milled and annealed samples possess almost the same magnetization (15.9 Am²/kg).
Figure 3. Room temperature magnetization curves recorded for the as-milled samples. For comparison annealed sample are also presented.

The higher magnetization values observed after annealing can be better understood by performing thermomagnetic measurements (figure 4), where heating curves show that the magnetization remains almost constant up to 600 °C. After compound ordering, the cooling curves show a sudden increase of magnetization recorded at 65 °C, which is expected for the Curie temperature of the Ni$_2$MnSn ordered compound.

4. Conclusions
Milling up to 10 h of the elemental powders in the Ni$_{51}$Mn$_{19}$Sn$_{30}$ ratio, leads to the formation of the Ni$_2$MnSn disordered Heusler phase accompanied by a minor Half-Heusler phase. By annealing the samples at 400 - 600 °C, the powder’s phase modifies to an ordered Heusler phase (Ni$_2$MnSn), a Ni$_3$Sn$_2$ compound and a Half-Heusler phase (NiMnSn). The magnetization decreases as the disordered Ni-Mn-Sn phase forms, but strongly increases when the phase becomes ordered. The Curie temperature of the ordered phase is 65 °C. The formation of the Ni$_{51}$Mn$_{19}$Sn$_{30}$ alloy by solid state reaction is found to be complex and further studies are in progress.

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