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Influence of mechanical alloying and heat treatment processing on the Ni_2MnSn Heusler alloy structure

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ABSTRACT

Formation of the Ni_2MnSn Heusler alloy by solid state reaction from elemental powders was investigated. The solid state reaction was conducted in a planetary ball mill under argon atmosphere up to 28 h of milling. During the milling, after selected intervals samples were collected and studied by X-ray diffraction to record phase changes. After 16 h of milling a two phase mixture (Ni_2MnSn with B_2 structure and NiMnSn with C_{1b} structure) was found. Further, the thermal stability of the samples was investigated, and phase precipitation was found. The formed phases are ordered Full Heusler (L_{21}) and Ni_3Sn_2. The formation temperature and their amount evolution versus temperature and milling time is discussed. An inversion of the formation temperature was found for the L_{21} and Ni_3Sn_2 phase, during the DSC study, in relation with the milling time. For the B_2 compound a stability range on temperature was identified (from 25 to 300 °C), as well as for the L_{21} and Ni_3Sn_2 phases (from 400 to 600 °C) in the case of 28 h milled sample. The milled and annealed sample exhibit nanocrystalline state, formation mechanism under temperature was concluded to be by precipitation.

1. Introduction

The impact of technology on the environment has conducted to development of clean technologies, and one field is magnetic refrigeration. Promising candidates for magnetic refrigeration materials are the Heusler alloys, and particularly the Ni-Mn-Ga or Ni-Mn-Sn systems. These systems possess ferromagnetic shape memory effect and theirs transformation temperatures depend on both composition and structure [1,2].

The properties of the Heusler alloys with X_2YZ formula are tightly connected with their crystal structure, most commonly L_{21} type, described as four face centred cubic sub lattices [3]. However, disorder can be present in the sample, generated by site occupation modification. If the atoms possess similar atomic number, the Y and Z atomic positions can be occupied randomly and the symmetry of the structure decreases. The resulting structure is described by the B_2 (CsCl) structure [4]. The structure changes are important in the Heusler alloys due to the fact that they control the martensitic transformation by the means of composition variation and by internal stresses [5]. Aspects concerning the structure and phase diagrams of several Heusler alloys are presented in Ref. [6].

Among the Heusler alloys, Ni-Mn-Sn represents an interesting case, presenting inverse magnetocaloric effect [7]. For the stoichiometric alloy no structural change was recorded in a large temperature range, but it was found that modifying the chemical vicinity of the Mn atoms the magnetic properties can be adjusted [8].

The adjustment of the magnetic properties can be achieved by disorder in two ways: by chemical substitution or by milling. There are different aspects implying the disorder: in the chemical disorder case, the atoms are replaced by different atomic species at certain sites and in milling case, the core remains unchained and the disorder is located at the grain boundary [8]. The milling can induce anti-site defects, generating higher atomic disorder [9].

Studies concerning the disordering of the Heusler structure in the Ni_2MnSn compound were performed and a L_{21}-B_2 transformation was observed by changing Mn and Sn position by milling. Further the heat treatment was found to restore the mechanically induced disorder if the temperature is higher than 300 °C [10]. Other studies evidenced a tendency for B_2 structure formation and showed that the disorder promoted by quenching and milling are different [11]. In the case of Ni-Mn-Sn alloys the annealing temperature is important, since depending on annealing temperature decomposition undergoes [12].

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The opportunity of tailoring the properties by milling offer a new route for obtaining these alloys directly with structural disorder: mechanosynthesis route. Mechanosynthesis was employed with success for obtaining several compositions in the Ni-Mn-Sn ternary system [13]. The mechanosynthesis route consists in processing an elemental powder mixture 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 microstructures, extended solid solution and quasicrystals can be obtained [14].

Former studies on samples obtained by milling [13] or by melt spinning [15,16], have highlighted the influence of the nanocrystalline state and of the annealing on the structure and transition temperature of the martensitic transformation. It was pointed out that by performing melt quenching, the required annealing duration on the ribbons is reduced. Also, the annealing process modifies the short-range interactions, affecting the exchange interaction and properties [5]. Another aspect regarding the ribbons obtained by rapid solidification, is that they possess at room temperature a martensitic (monoclinic) structure and the austenitic transition is induced by applied field [17]. In some cases, for the ribbons obtained by melt-spinning, additional phases (Ni_3Sn_2 and $Mn_{1.77}Sn$) were observed [18]. From the thermodynamic studies, it was pointed out that the Heusler structure (L_{21}) is most energetic favourable to form [19], but is somehow difficult to obtain a single phase and up to 5% of Ni_3Sn_2 can appear [19,20].

This paper presents a study devoted to the synthesis of the Ni_2MnSn Heusler alloy by solid-state reaction induced by mechanical alloying and to investigate the phase evolution after the subsequent annealing. The phase evolution is studied in relation to their structural changes occurred during processing.

2. Experimental

Ni_2MnSn Heusler alloy was prepared by mechanosynthesis using as raw materials commercial nickel 123 carbonyl, manganese (Alpha Aesar) and tin powder (Alpha Aesar). The starting sample consists in a mixture of the three powders in the proper atomic ratio - Ni_2MnSn which was homogenized 15 min prior to milling. The milling experiments were performed in sealed vials filled with argon, on a Fritch Pulverisette 6 planetary ball mill, using steel balls. The main disk speed was 350 rpm, the filling factor was 25% and the ball to powder ratio (BPR) was 7.2:1. The milling was conducted up to 28 h and for alloy formation study during milling, samples were taken at selected intervals. The formation and the structure of the milled sampled was analysed by X-ray diffraction (XRD) using INEL 3000 Equinox diffractometer, operating with CoKα radiation (1.79026 Å) in the 2 theta range of 20–80°. From the XRD patterns, the mean crystallite size was computed using the Scherrer formula, using as reference sample tin powder [21]. The phase analysis was conducted by means of Rietveld fitting procedure, implemented in the Fullprof software [22]. The phase formation and their thermal stability was studied by differential scanning calorimetry (DSC), using a Setaram Labsys apparatus. All of the experiments were performed in argon atmosphere to avoid oxidation of the samples, and the heating rate was 10 °C/min. The morphology and chemical homogeneity of the samples was studied with a JEOL JSM-5600LV scanning electron microscope (SEM), equipped with an Oxford Instruments EDX (Energy dispersive X-ray spectrometry) detector (INCA 200 software).

The powders composition was verified by EDX analysis on compacted powders and it was found that after 28 h of milling the as-milled sample has the following composition: Ni50·4Mn23·6Sn23·5Fe2.5. The annealed sample at 600 °C by DSC has the following composition: Ni49·7Mn25·3Sn22·9Fe2.1. The error was less than 1%.

3. Results and discussion

The morphology of the powder samples has been investigated by scanning electron microscopy. The SEM images corresponding to the samples milled for 0, 4, 8 and 28 h are presented in Fig. 1. In the SEM micrograph corresponding to the starting mixture, one can notice the presence of three type of particles corresponding to the three elements present in the starting mixture. The nickel particles have a sponge-like aspect, the tin particles have a spherical aspect while the manganese particles have an irregular polyhedral shape. Upon milling, the powders morphology changes from the initial aspect corresponding to the elemental powder consisting in an unmilled mixture to finer grain powder, exhibiting similar shapes and colour, suggesting chemical homogeneity. In the image study both the fragmentation of the Mn particles and the spreading of the Sn particles embedded by the Ni particles can be observed. The visual analysis is sustained by the chemical distribution maps, recorded by EDX analysis and presented in Fig. 2.

The chemical elemental map analysis, reveals for the un-milled sample, different composition areas, where only one type of element is present, due to the elemental powders presence in the initial powers mixture. The milling changes the distribution of these elements, and after 4 h of milling, the tin and nickel elements are evenly distributed, in agreement with the XRD analysis that indicates the formation of several Ni-Sn phases. Manganese particles are fragmented and they have not been completely incorporated in the Ni-Sn matrix. The situation is preserved up to 8 h of milling. In this milling duration range, the only important effect of milling duration on the manganese particles is the significant size reduction. Concerning Sn and Ni phases, they are homogeneously distributed and form a matrix surrounding the larger Mn particles. Finally, at 28 h milling durations, all the elements are uniformly distributed in the samples. The elemental uniform distribution is a good indication for alloy formation, as confirmed by XRD.

The evolution of the phases during the milling up to 28 h is presented in Fig. 3. As a reference the X-ray diffraction pattern of the un-milled sample (initial mixture of the elemental powders) is given and noted with 0 h MA.

In the XRD pattern of the starting sample can be observed the peaks corresponding to the starting elements in the mixture: Ni, Mn and Sn (JCPDS files no. 04-0850, 32-0637 and 04-0673 respectively). The diffraction patterns of the short milling times (2 h) presents only a peaks broadening. Upon increasing milling duration, the peak broadening becomes more pronounced, suggesting a higher decrease of the crystallite size and cumulative second order internal stresses introduction [23]. Alongside to peak broadening, some of the characteristic peaks of the elemental powders are starting to fade. First for durations larger than 6 h, the peaks corresponding to Sn are no longer visible, suggesting its reaction with the other constituents upon milling. Next, increasing milling durations up to 8 h leads to the dissolution of Ni. The elemental Mn characteristic peaks can be noticed for milling durations up to 16 h. The elemental diffraction peak disappearance is accompanied by the formation of new phases – Ni_2MnSn indexed as B_2 structure and NiMnSn indexed as C_{1b} structure. The formation of these new phases is suggested by the occurrence of some new Bragg reflections (at 35.6, 41.2, 47.7 and 50.9°). The solid state reaction of the constituents occurs by realising a more intimate contact between the elemental particles for prolonged milling. Supplementary, the microcracks and large specific surface generated by repeated cold welding and fracture modify the internal energy of elemental powder mixture, promoting atomic diffusion and phase formation [24,25].