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Magnetic and Structural Characterization of Nickel and Iron Based Heusler Ribbons Ni_2FeZ (Z = In, Sn, Sb)

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Comparison of structural, chemical, and magnetic properties of Ni_2FeZ (Z = In, Sn, Sb) Heusler ribbons produced by melt-spinning method is presented. The aim of work was to prepare the Heusler alloys with the appropriate chemical composition in a single step without additional thermal treatment. Scanning electron microscopy analysis revealed polycrystalline structure of all samples. It is shown that correct $L2_1$ structure of Ni_2FeSb can be obtained in a single production step. On the other hand, no Heusler $L2_1$ phase (nor its variants) occur in Ni_2FeSn alloy. Additionally, magnetic characterization revealed high Curie temperatures of the Heusler phases (above 600 K for Ni_2FeSb and 800 K for Ni_2FeIn).

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1. Introduction

The history of Heusler alloys dates back to 1903, when German scientist Friedrich Heusler discovered the alloy with the composition of Cu_2MnAl. The alloy is ferromagnetic even if its components are not [1, 2]. Since that time, a lot of the Heusler alloys with different compositions have been prepared. The Heusler alloys are promising materials for use in various technical fields including thermoelectrics, spintronics, magnetocaloric and shape memory effects, etc.

The Heusler alloys are ternary alloys having basic formula X_2YZ (with a 2:1:1 stoichiometry) and they crystallize in structure $L2_1$ (space group no. 225, *Fm-3m*). For this structure, four interpenetrating fcc sublattices are typical. This arrangement can be described by ZnS and NaCl sublattices as for the half-Heusler alloys [2].

The most common method of the Heusler alloys preparation is arc-melting. However, long-term annealing at high temperatures is necessary to obtain highly ordered crystalline structure that is crucial for excellent physical properties. This step disqualifies the Heusler alloys from immediate applications. On the other hand, rapid quenching methods are capable to produce large amount of properly ordered Heusler alloy in a single step [3, 4].

There exist simple rules how to produce Heusler alloys giving necessary NaCl crystalline structure from Y and Z elements, in which the X element occupies tetrahedral holes. Therefore, high difference in electronegativity and in atomic diameter of Y and Z helps in production of Heusler alloys [2].

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We have studied production and characterization of Ni_2FeZ (Z = In, Sn, Sb) Heusler alloys. Given elements share their common period (however they differ in electronegativity and atomic diameter), which led us to comparison of the properties of prepared compounds in context of Z element. Apart from simple rules [5–7], the correct structure can be obtained in the alloys where no other phases with higher density exist.

2. Experimental

High-purity metals (Ni = 99.95%, Fe = 99.98%, Sb = 99.2–99.3%, Sn = 99.99%, In = 99.9%) have been used for the preparation of samples. Subsequently, melt spinning method has been employed to produce ribbons.

Microstructure has been studied by scanning electron microscope (SEM) — system TESCAN VEGA 3 XMU equipped with the energy-dispersive X-ray spectroscopy (EDX) to determine chemical composition. X-ray powder diffraction was used to resolve the crystal structure using Cu K_α radiation at room temperature. Magnetization has been measured by vibrating sample magnetometer (VSM) technique. Hysteresis loops have been measured at room temperature in the range of magnetic field of $\pm$400 kA/m in parallel and perpendicular direction with respect to the ribbon plane. The temperature dependence of magnetization has been measured in the field of 300 kA/m in the temperature range from room temperature up to the 1073 K.

3. Result and discussion

The EDX analysis of Ni_2FeZ Heusler alloys was performed on at least 3 points at the surface and average compositions are shown in Table I. Chemical compositions of produced ribbons correspond well to the theoretical ones. In all cases the measuring error was less than $\pm$2%.

TABLE I

Chemical composition of prepared Heusler alloys.

	Ni_2FeIn	Ni_2FeSn	Ni_2FeSb
Ni	49.3%	52.3%	50.7%
Fe	23.1%	21.5%	25.2%
In	27.6%	26.2%	24.1%

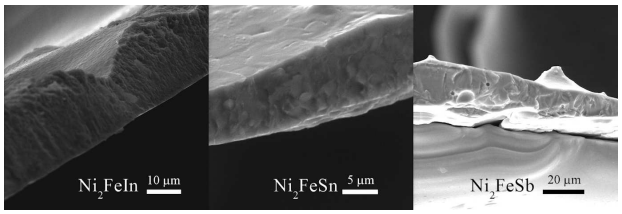

Fig. 1. SEM micrograph of Ni_2FeIn, Ni_2FeSn and Ni_2FeSb.

Microstructural analysis revealed polycrystalline character of all samples. Columnar crystal structure appears when Z = In and Sb, that grows across the ribbon section perpendicularly to the ribbon surface (see Fig. 1). In contrary, polycrystalline structure of Ni_2FeSn has rounded crystals distributed randomly.

X-ray diffraction revealed existence of two phases Ni_2FeIn alloy (Fig. 2). One phase has been characterized to be *Fm-3m* phase with the lattice parameter $a = 6.17(1)$ Å. The absence of (111) peak points to the most probable $B2$ disorder [2]. The second phase was recognized to be $Fe_{75}Ni_{25}$ phase (space group *Fm-3m*) with lattice parameter $a = 3.59(0)$ Å. More detailed analysis shows presence of NiFe phase up to 27%. X-ray analysis of Ni_2FeSn alloy also shows two phases. First one is the hexagonal phase $P6_3/mmc$ with the lattice parameters $a = b = 4.13(5)$ Å, $c = 5.15(5)$ Å. The second phase was identified to be $Fe_{75}Ni_{25}$ phase with the lattice parameter $a = 3.59(4)$ Å (as in the case of Ni_2FeIn) that occupies up to 46 vol.% in the alloy. In contrary, Ni_2FeSb alloy is characterized by *Fm-3m* space group with $L2_1$ structure, typical for highly ordered full Heusler alloys with the lattice parameter $a = 5.81(9)$ Å. Small traces of secondary phases (5.8 vol.% of hexagonal phase $P6_3/mmc$ with the lattice parameters $a = b = 4.00(4)$ Å, $c = 5.16(8)$ Å and $\alpha = \beta = 90°$, $\gamma = 120°$ and 15.2 vol.% of cubic phase $Fe_{75}Ni_{25}$ with the lattice parameter $a = 3.60(5)$ Å) can also be detected from X-ray.

If we compare the X-ray analysis with Ref. [2], it turns out that Ni_2FeIn does not fit requirement of correct electronegativity difference between X, Y, and Z elements in the Heusler structure. Moreover, Fe and In are immiscible [8].

Hence, even though the Heusler phase appears in this case, $B2$ disorder appears (mutual displacements of Y and Z elements [2]). On the other hand, Ni_2FeSn is in good agreement with Ref. [2] regarding the atomic radius and difference in electronegativity of the elements. However, the Heusler structure was not observed in Ni_2FeSn alloy. It could be connected to the fact that atomic density of hexagonal phase is higher than that highly ordered hypothetical Ni_2FeSn Heusler alloy. Therefore, hexagonal phase is preferable. Ni_2FeSb Heusler alloy agrees perfectly with Ref. [2] regarding the atomic difference and electronegativity difference of all elements. Hence, highly ordered $L2_1$ structure can be easily produced repeatedly (in fact, alloy of such composition has been produced repeatedly and we have obtained the same results from structural analysis). Small traces of hexagonal structure could appear due to similar atomic density of highly ordered $L2_1$ Heusler structure.

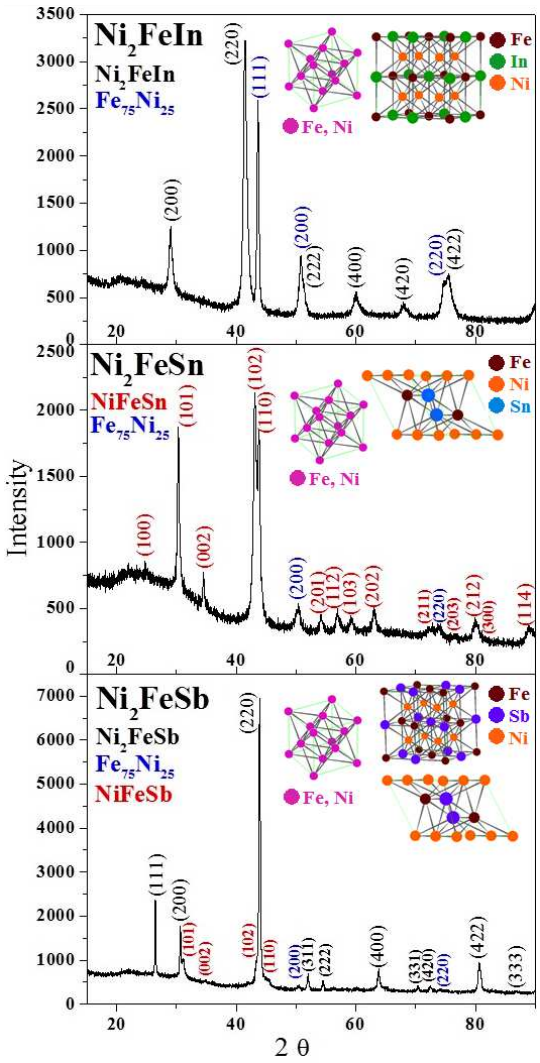

Fig. 2. X-ray diffraction patterns of Ni_2FeIn, Ni_2FeSn and Ni_2FeSb.

Temperature dependence of saturation magnetization of Ni_2FeZ (Z = In, Sn, Sb) ribbons (see Fig. 3) corresponds to the X-ray analysis. In all cases, $Fe_{75}Ni_{25}$ cubic phase is present with $T_C \approx 620$ K. This phase is indicated by kinks in the temperature dependence of magnetization (green dots in Fig. 3). The second phase (recognized by X-ray analysis as $B2$ variants of

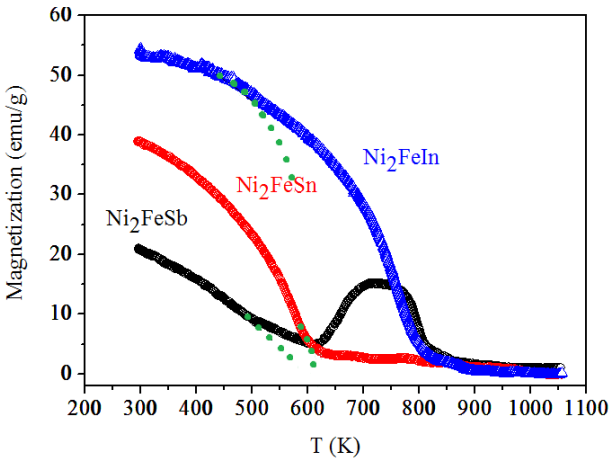

Fig. 3. Temperature dependence of magnetization of Ni_2FeIn, Ni_2FeSn, and Ni_2FeSb.

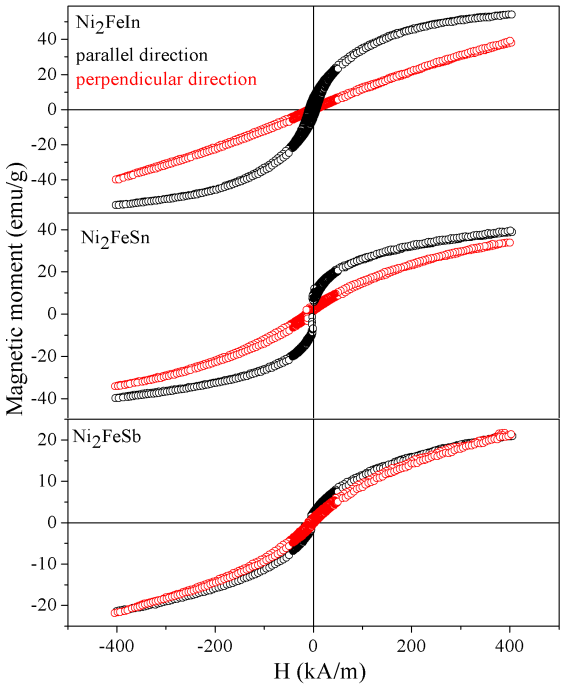

Fig. 4. Hysteresis loops of Ni_2FeIn, Ni_2FeSn and Ni_2FeSb.

Ni_2FeIn Heusler phase) shows the Curie temperature close to 820 K. In the case of Ni_2FeSn alloy, both phases seems to have similar Curie temperature therefore the temperature dependence of magnetization shows smooth decrease to $T_C \approx 620$ K. $Fe_{75}Ni_{25}$ phase is manifested also in Ni_2FeSb alloy by small kink at 500 K that points to its $T_C \approx 620$ K (see green dotted line). The Curie temperature of the Heusler phase Ni_2FeSb should be over 600 K. However, it is not possible to estimate the Curie temperature due to crystallization of new phase. Crystallization of new magnetic phase is expressed by increase of magnetization up to 700 K. In order to distinguish between Heusler and hexagonal phase, three different Ni_2FeSb alloys have been annealed for 1 h at the temperatures 600, 650, and 700 K. The X-ray analysis of annealed alloys showed increment of hexagonal phase NiFeSb ($P6_3/mmc$) at the expense of the Heusler phase Ni_2FeSb (not shown here).

Hysteresis loops for Ni_2FeZ (Z = In, Sn, Sb) ribbons (see Fig. 4) revealed ferromagnetic and anisotropic character of Ni_2FeIn and Ni_2FeSn with the easy magnetization plane parallel to the ribbon surface. As shown in the SEM analysis (Fig. 1), Ni_2FeIn alloy is characterized by the preferential crystal growth (perpendicular to the ribbon surface) that promotes anisotropy evolution. In contrary, SEM analysis of Ni_2FeSb alloy shows large crystals without any preferred orientation. As a result, this alloy shows significant isotropic character as shown in Fig. 4.

4. Conclusions

We have shown that rapid quenching is suitable method to produce high quality Heusler alloys when proper rules are followed. Appearance of other phase with higher atomic density must be avoided. In that case, the most suitable candidate for the Heusler compound, with typical structural composition is the compound with chemical composition Ni_2FeSb. This alloy shows the Curie temperature above 600 K and is highly isotropic. Moreover, Ni_2FeSb Heusler alloy can be repeatedly prepared without alteration of its structural properties.

Acknowledgments

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