Magnetic and Structural Characterization of NiXSb (X = Mn, Cr) Heusler Ribbon

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Half-Heusler alloys with composition NiMnSb and NiCrSb have been prepared by rapid-quenching method. NiMnSb half-Heusler alloy is characterized by single phase \( C\textsubscript{1b} \) with polycrystalline structure while crystalline structure of NiCrSb shows multiphase system. Magnetic measurements indicated high anisotropy and easy magnetization direction in the parallel direction with respect to ribbon axis for NiMnSb alloy while paramagnetic behavior appears for NiCrSb alloy down to 50 K.

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1. Introduction

The Heusler alloys are promising materials for applications in various areas such as magnetic cooling, shape memory devices, or spintronics [1, 2]. Generally, the Heusler alloys are divided into two groups: (1) half-Heusler alloys with stoichiometric formula XYZ (\( C\textsubscript{1b} \) structure) and (2) full-Heusler alloys with stoichiometric composition \( X\textsubscript{2}YZ \) (\( L\textsubscript{2}1 \) structure) (where X and Y are atoms of transition metals, Z are atoms of semiconductor or non-magnetic metals) [1–3].

Particularly, four parameters are necessary for successful spintronic material: (a) high spin polarization, (b) high magnetic moment per atom, (c) high Curie temperature \( T\textsubscript{c} \), and (d) low Gilbert damping. Some Heusler alloys based on Co or Ni fulfil all of the above mentioned conditions [2].

Typical example of half-Heusler alloy with interesting spin-polarization properties are alloys with composition of NiMnSb [3–5]. NiMnSb Heusler alloys crystallizes in non-centrosymmetric cubic structure \( C\textsubscript{1b} \) [1].

NiMnSb alloy is usually prepared by arc melting method, which is followed by long-term, high-temperature annealing. However, preparation alloy with manganese is complicated because of small amount of manganese is evaporated. This problem can be solved by substitution Mn with Cr. The NiCrSb composition has wider energy gap with the Fermi level at a top of the valence band [3]. On the other hand, it has been shown that rapid quenching allows a single step production of large amount of samples without necessity of further thermal treatment.

In the given contribution, we deal with single-step production and basic magnetic, chemical and structural characterization of rapidly quenched NiMnSb and NiCrSb half-Heusler alloys.

2. Experimental

The master alloys of \( \text{Ni}_{33.3}\text{Mn}_{33.3}\text{Sb}_{33.4} \) (10 g) and \( \text{Ni}_{33.3}\text{Cr}_{33.3}\text{Sb}_{33.4} \) (10 g) were prepared by arc-melting method from pure elements (Ni = 99.95%, Mn = 99.9%, Cr = 99.99% and Sb = 99.9%) in argon atmosphere. The ingots were re-melted 3 times to ensure homogenization of samples. NiMnSb and NiCrSb ribbons were prepared from master alloys by melt spinning on copper cylinder (rapid quenched method) with linear speed of 20 m/s at helium atmosphere.

Chemical composition and microstructure were determined by scanning electron microscope (SEM) — system TESCAN VEGA 3 XMU equipped with the energy-dispersive X-ray spectroscopy (EDX) to estimate chemical composition. The final chemical composition was obtained by averaging the analysis at 3 different points.

Structure of alloys was determined by Panalytical X’Pert with Cu K\( \alpha \) (\( \lambda = 1.54178 \) Å) emitter.

Temperature dependence of magnetization and hysteresis loops (in parallel and perpendicular direction with respect to ribbon axis) were measured by vibrating sample magnetometer (VSM) VERSALAB at the University of Presov. Hysteresis loops were measured at 50 K and temperature dependence of saturation magnetization was measured in the temperature range 50–400 K under applied magnetic field of 10 kOe.
3. Results and discussion

SEM analysis of NiMnSb ribbon (Fig. 1) shows polycrystalline structure with preferred perpendicular orientation of columnar grains (size 1–2 µm). On the other side, NiCrSb ribbon shows polycrystalline structure with spherical grains. Chemical composition of NiMnSb ribbon obtained by EDX analysis is slightly out of the stoichiometric formula (Ni = 27.7 at.%, Mn = 38.8 at.%, Sb = 33.5 at.%). EDX analysis of NiCrSb ribbon reveals average chemical composition is also slightly out of the stoichiometric one (Ni = 29.2 at.%, Cr = 37.7 at.%, Sb = 33.1 at.%).

Fig. 1. SEM micrographs of NiMnSb and NiCrSb ribbon.

Fig. 2. X-ray diffraction patterns of NiMnSb and NiCrSb ribbon measured at 298 K.

Fig. 3. Temperature dependence of magnetization of NiMnSb and NiCrSb ribbon.

Fig. 4. Hysteresis loops of NiMnSb and NiCrSb ribbon at 50 K. Black lines (1) correspond to parallel orientation of magnetic field. Red line (2) corresponds to perpendicular orientation of magnetic field. Green line (3) corresponds to perpendicular orientation of magnetic field without demagnetizing effect.

XRD (see Fig. 2) of NiMnSb ribbon confirms single crystalline phase that was identified as crystalline C1_b structure with space group F-43m and lattice constant a = 5.982 Å. In contrary, XRD diffraction pattern of NiCrSb ribbon show multiphase structure (see Fig. 2). At least four of them were recognized as NiCrSb, Cr, NiSb, and Ni. Measurements of temperature dependence of saturation magnetization of NiMnSb (see Fig. 3) confirm single phase behavior characteristic for ferromagnetic materials. The Curie temperature of NiMnSb alloys is well above 400 K, which is out of our measuring
range (the Curie temperature of NiMnSb alloy should be as high as 900–1112 K [2]). Calculated magnetic moment (estimated from the measurement at 50 K) is 4.05 \( \mu_B \) /f.u., which fit to the previously measured value 4.02 \( \mu_B \) /f.u. [6].

Temperature dependence of magnetization for NiCrSb ribbon (Fig. 3) measured in parallel direction with respect to the ribbon axis shows paramagnetic behavior down to 50 K. Value of magnetic moment obtained from measurement at 50 K at magnetic field 10 kOe is 0.823 \( \mu_B \) /f.u., which is similar to that for paramagnetic NiMn-based Heusler alloys [7].

The hysteresis loops of NiMnSb ribbons measured at 50 K in the perpendicular and parallel direction with respect of ribbon axis are shown in Fig. 4. Hysteresis loops of NiMnSb ribbon point to the ferromagnetic behavior with coercive field around 5.5 Oe for the parallel direction and 10.5 Oe for perpendicular one. The remanent magnetization is 1.3 emu/g for parallel direction and 0.36 emu/g for perpendicular one. Saturation field for parallel direction is 3.6 kOe while in perpendicular direction the sample is not saturated even at 10 kOe. This points to the strong anisotropy with the easy magnetization axis parallel to the ribbon axis. First contribution to anisotropy arises from the shape of the sample (ribbon). However, reducing the demagnetizing effect (Fig. 4, green line 3) does not reduce anisotropy completely. The second contribution to the anisotropy is magnetocrystalline one, which arises from the directional ordering of the crystal growth that is perpendicular to the ribbon plane (see Fig. 1a).

On the other hand, substitution of manganese with chromium results in multiphase system where hysteresis loop confirm paramagnetic behavior without saturation in the field of 10 kOe (Fig. 4) as it was already shown for paramagnetic Heusler alloys [7].

4. Conclusions

We have studied possibility of production of NiMnSb and NiCrSb half-Heusler alloy by rapid quenching method without additional thermal treatment. Structural analysis shows homogeneous highly ordered single phase \( C1_b \) for NiMnSb half-Heusler alloy, having the chemical composition slightly out of the stoichiometric one. On the other hand, NiCrSb composition is characterized by non-homogeneous structure that reveals multiphase system (containing NiCrSb, Cr, NiSb, and Ni phases).

Magnetic measurements of hysteresis loops of NiMnSb ribbon measured at 50 K confirms well defined anisotropy with the easy axis parallel to the axis of the ribbon. Temperature dependence of magnetization shows the Curie temperature well above the 400 K and magnetic moment 4.05 \( \mu_B \) /f.u. It points to the fact that rapid quenching is suitable production process to obtain large amount of materials with well-defined structure and magnetic properties in a single production step.

On the other hand, magnetic measurements of NiCrSb ribbon reveal paramagnetic behavior down to the 50 K.

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References