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COMPARISON OF MAGNETIC AND STRUCTURAL PROPERTIES OF RAPIDLY QUENCHED BULK AND RIBBON Ni_2MnGa HEUSLER ALLOYS

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We are dealing with the magnetic and structural properties of Ni_2MnGa Heusler alloys prepared by different rapid quenching methods. They allow a fast production of relatively large amount of alloy by arc melting (bulk, rod) or by melt spinning methods (ribbon).The SEM studies reveal slight variation of chemical composition for rod and ribbons. However, X-ray diffraction confirms the same single B2 crystalline phase at room temperature in both cases. Temperature dependence of magnetization reveals different structural transition temperatures for rods and ribbons. Moreover, different anisotropies have been induced during production reflecting the different temperature gradient during quenching for rod (which shows no preferred easy axis) and ribbon (which shows easy magnetization axis parallel to the ribbon surface).

Keywords: Heusler alloy, magnetocaloric effect, rapid quenching method

1 INTRODUCTION

The Heusler alloys are new perspective materials with interesting properties such as magnetocaloric effect, spin polarization, shape-memory and etc. These alloys are divided into two groups as half - Heusler alloys with stoichiometric formula XYZ and full – Heusler alloy with stoichiometric formula X_2YZ [1-2]. Typical example of full-Heusler alloys is alloy with composition of Ni_2MnGa. This alloy crystallizes in the cubic structure ($L2_1$). Heusler alloy of composition Ni_2MnGa is very interesting material for use in magnetocaloric cooling [2-4]. For the effect of magnetic cooling, large change of entropy in narrow temperature range is very important, together with the value of Curie temperature near that of room temperature. In addition, structural transition helps to increase the entropy variation in Ni_2MnGa Heusler alloy [5].

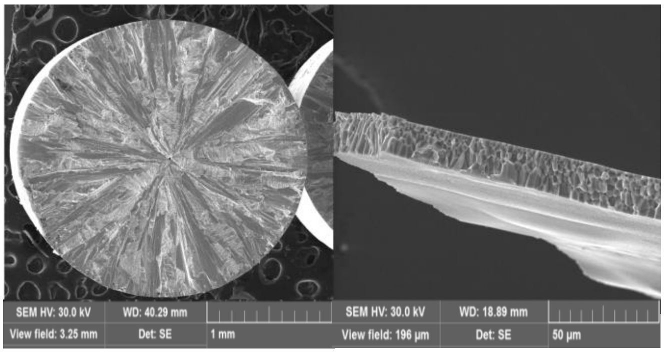

Fig. 1. SEM Imagine of the Ni_2MnGa rod (left) and ribbon (right)

The Heusler alloys are usually prepared by arc-melting method followed by high temperature annealing for a long time (hours, weeks, months) [6]. However, rapid quenching method has been recently applied for a fast production of large amount of alloy without the necessity of long thermal treatment [7, 8].

In this article, we show magnetic and structural properties of Ni_2MnGa (ribbon, rod) full-Heusler alloys prepared by rapid quenching method. Typical Curie temperature of this composition is near to the room temperature (320-350K) [2]. Two shapes have been selected for the studies: a rod – prepared by suction casting and a ribbon – prepared by melt spinning.

2 EXPERIMENTAL

Ni_2MnGa alloys, in the form of the rod, were prepared by arc-melting method followed by the suction casting. The method of preparation allows to prepare the rod with diameter of 3 mm and length of 30 mm. The ribbon with the same composition is prepared from the same bulk master alloy by melt-spinner method.

Chemical composition and crystal growth directions in the rod and the ribbon are characterized by scanning electron microscopy (SEM). The structure and phases were verified by X-ray diffraction.

Temperature dependence of saturation magnetization and hysteresis loop (at 300 K) for the ribbon and the rod were measured on vibrating sample magnetometer (VSM) VERSALAB in Presov. Temperature dependence of saturation magnetization was measured in the temperature range 50 to 400 K at applied magnetic field of 1T.

3 RESULTS AND DISCUSSION

The rapid quenching method introduces preferred orientation of the crystals growth, which is usually in the direction of the stresses introduced by rapid cooling. Hence, SEM analysis of ribbon shows perpendicular orientation

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of grains (see Fig.1 right) with respect of the ribbon axis. Similarly, the rod shows radial orientation of grains (see Fig.1 left) since the stresses introduced by rapid quenching are perpendicular to the rod surface.

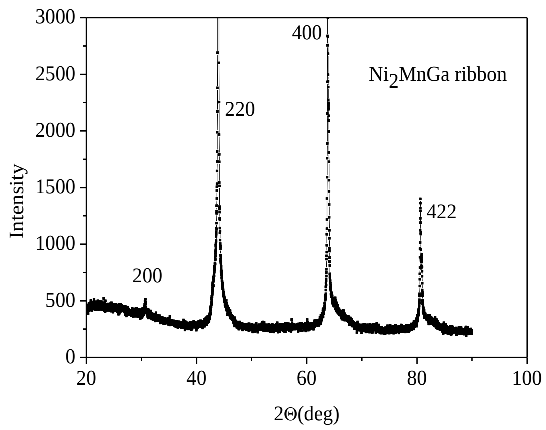

Fig. 2. X-ray diffraction patterns for Ni_2MnGa rapidly quenched ribbon

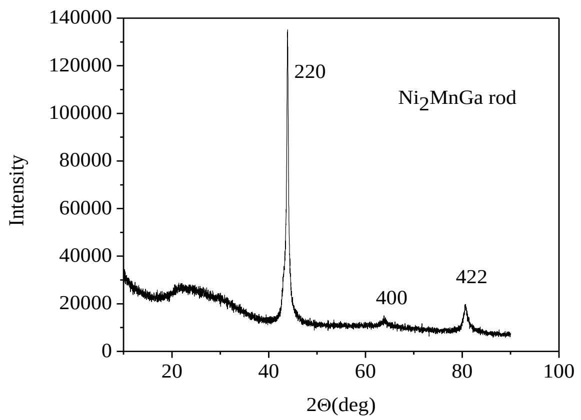

Fig. 3. X-ray diffraction patterns for Ni_2MnGa rapidly quenched rod

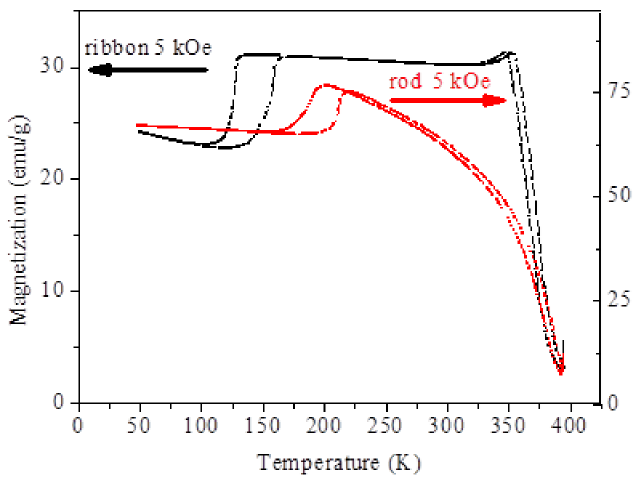

Fig. 4. Temperature dependence of magnetization for rapidly quenched Ni_2MnGa rod and ribbon

SEM/EDX reveals high homogeneity of composition in both samples, the rod and the ribbon. However, real composition slightly varies from the stoichiometric 2:1:1 (Ni_2MnGa) being Ni = 48.34 %, Mn = 29.12 %, Ga = 22.53 % for the rod and Ni = 48.17 %, Mn = 25.69 %, Ga = 26.14 % for the ribbon. The difference in the real composition could be ascribed to the preparation method. The ribbon has been prepared from the same master alloy by its remelting with follow causes the partial decrease and rapid quenched on the rotated wheel. Each melting process results in the decrease of the relative Mn content due to its evaporation.

XRD diffraction analysis of the ribbon at the room temperature (see Fig.2) reveals single B2 phase with the space group F and lattice parameter a = 0.585 nm. The lattice parameter has very similar value to that of other authors (a = 0.584 nm) [9]. XRD diffraction analysis of the rod at the room temperature (see fig.3) shows single B2 phase with the lattice parameter a = 0.583 nm. No presence of other phases is observed. This is typical feature of the rapidly quenched Heusler alloys where single Heusler phase is observed even in the as-quenched state and no other annealing is necessary [7, 8].

Although, the structural properties of the rapidly quenched rod and ribbon are almost the same, magnetic characterization reveals some differences. The measurements of the temperature dependence magnetization of Ni_2MnGa rod show structural transition (characterized by A_s - austenite start temperature, A_f - austenite finish temperature, M_s – martensite start temperature, M_f - martensite finish temperature) at the temperature close to 190 K (more precisely: A_s = 193 K, A_f = 218 K, M_s = 199 K, M_f = 161 K) with a temperature hysteresis of about 32 K (see Fig.4). It has been shown that Ni_2MnGa alloy shows such structural transition from martensitic structure at low temperatures to austenitic structure at higher temperatures [5, 10]. The austenitic phase is characterized by the higher saturation magnetization which is demonstrated by the increase of magnetization with temperature at around 200 K. The Curie temperature of Ni_2MnGa rod was estimated at 390 K. The measurements of temperature dependence magnetization of Ni_2MnGa ribbons show the structural transition at lower temperature as compared to the rods: A_s = 105 K, A_f = 186 K, M_s = 139 K, M_f = 91 K with a temperature hysteresis of about 25 K (see Fig.4). This difference is probably the result of lower Mn content in the ribbon samples as compared to the rods (see EDX analysis). Similarly, the Curie temperature of ribbons sample (375 K) is a slightly lower than that of rod. Moreover, magnetization decreases slightly with temperature (above 160 K) and starts to decrease steeply just below the Curie temperature.

In order to study the magnetic anisotropy of both samples, hysteresis loops in different directions have been measured. The measurements of hysteresis loops for Ni_2MnGa rod in parallel (H_C = 16 Oe) and perpendicular (H_C = 17 Oe) direction with respect to the rod axis at 300 K (see Fig.5) are almost identical which points to highly isotropic character of rapidly quenched rod.

In contrary to the rod sample, hysteresis loops of the Ni_2MnGa ribbon shows different behaviour depending on the direction of applied fields (Fig. 6). The saturation is reached at lower fields in the parallel direction (H_C = 2.1 Oe) to the ribbon axis. This point to the direction of easy magnetization is lying in the parallel direction to the ribbon axis. Such behaviour is most probably causes by anisotropic crystal growth in the ribbon during its melt spinning. In contrary to the rod sample, where crystal growth direction is radial (see Fig. 1), the crystal growth in ribbon sample is perpendicular (H_C = 3.7 Oe) to the ribbon surface.

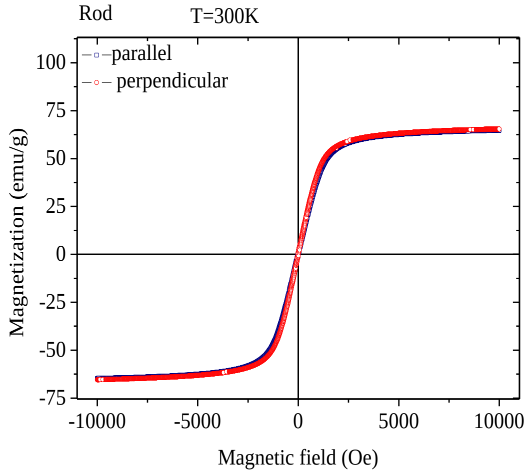

Fig. 5. Hysteresis loops of Ni_2MnGa rod in parallel and perpendicular direction at T = 300 K

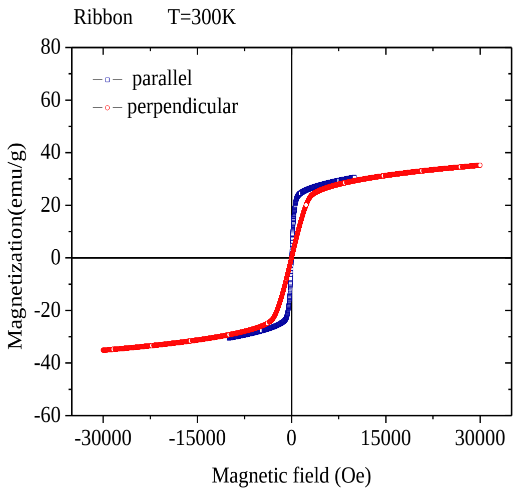

Fig. 6. Hysteresis loops of Ni_2MnGa ribbon in parallel and perpendicular direction at T = 300 K

4 CONCLUSIONS

In conclusion, we report on fabrication of the Ni_2MnGa Heusler alloy by different rapid quenching methods. Two samples have been prepared: the rod by suction casting of molten master alloy and the ribbon by melt-spinning method. Although the structural analysis shows the same B2 structure at room temperature with lattice parameter a = 0.585 nm for both shape, they are characterized by different structural and magnetic properties. The Ni_2MnGa rod shows crystal growth in radial direction, while ribbon demonstrates growth in perpendicular direction to the ribbon surface as a result of different stresses applied on the samples during rapid quenching.

Both alloy shows structural transition between martensitic and austenitic structure close to 190 K (rod) and 150 K (ribbon). The variation of the structural transition temperature for different shapes is most probably a result of slight variation in chemical composition.

Finally, magnetic measurements reveal isotropic behavior for rod shape sample, while there is a strong anisotropy for ribbon shape The Heusler alloy with easy magnetization axis lying in the direction of the ribbon axis.

Acknowledgement

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