REPETITIVE PHASE TRANSITION MEASUREMENTS IN Ni$_{50}$Mn$_{26}$Ga$_{24}$

Andrea Chudíková* — Tomáš Ryba* — Zuzana Vargová**
— Sergej Ilkovič*** — Marian Reffers *** — Vladimir Kománický*
— Róbert Gyepes*** — Rastislav Varga*

We have performed basic characterization of rapidly quenched Ni$_{50}$Mn$_{26}$Ga$_{24}$ Heusler ribbon. It is characterized by austenitic phase Fm-3m in B2 modification at room temperature and by structural transition to martensitic phase around 200 K. Rapid quenching results in the metastable state that is demonstrated by the variation of four characteristic transition temperatures $A_s$, $A_m$, $M_s$, and $M_f$. However after 6th training cycle, the transition temperatures and hysteresis becomes stable. This proves, that rapid quenching can be potentially interesting method of production of Heusler alloys that could be suitable for practical magnetocaloric application.

Keywords: Heusler alloys, magnetocaloric effect, resistance dependence on temperature

1 INTRODUCTION

Magnetocaloric effect is a thermodynamic process, which presents the change of temperature during configuration of magnetic moments of the paramagnetic or ferromagnetic material which is influenced by outer magnetic field. The idea of magnetocaloric cooling enabled in past an energy-efficient approach to lowering temperatures in the order of hundreds to tens milli Kelvin above absolute zero. The physical principle of magnetic cooling is based on the fact that the magnetic part of entropy of the magnetic material at a constant temperature is a decreasing function of magnetic field. Maximum temperature change occurs with maximum change in magnetization, which happens at the Curie temperature. The entropy change can further be increased when the material changes its crystallographic phase from less ordered one to another phase with higher symmetry. These features are typical for selected Heusler alloys.

Almost two decades ago, magnetic refrigeration has been confirmed to be efficient enough for applications even at room temperatures. One of the goals for application of magnetocaloric effect in industry is refrigeration. The advantage of magnetocaloric effect is its speed. Moreover, these new types of alloys could be used to create more silent, more ecological and more energy efficient refrigerators. Heusler alloy consisting of Ni$_3$MnGa should be the long awaited material to replace traditional cooling based on cyclic compression and expansion of gasses. The material has Curie temperature close to the room temperature and it is also characterized by the structural transition from less ordered tetragonal phase to highly ordered cubic phase. However, one of disadvantage of the Heusler alloy is the necessity for a long term post annealing process at quite high temperatures. This problem can be solved by using rapid quenching method that allows for rapid production of a large amount of materials with enhanced homogeneity and correct short range ordering. However, rapid quenching results in a metastable state which could disqualified the materials from practical application.

In the given paper, we deal with production of Ni$_{50}$Mn$_{26}$Ga$_{24}$ Heusler alloy using rapid quenching. Due to the fast production process, the sample is in metastable state. Hence, we applied the repetitive training of the sample to see how long it takes to obtain stable phase transition.

2 EXPERIMENTAL

The Ni$_{50}$Mn$_{26}$Ga$_{24}$ alloy was prepared out of elements with chemical purity Ni of (99.999%) and Mn,Ga of (99.99%) in the form of bulk (10 g), by Arc-melting method. Later on, ribbons with length of 3-20 mm and thickness 37 μm are prepared from the master alloy by melt- spinning technique.

Chemical composition and microstructure of the ribbon are characterized by scanning electron microscopy (SEM) equipped with EDX option. The crystalline phase was verified by X-ray diffraction. X-ray diffraction of the Ni$_{50}$Mn$_{26}$Ga$_{24}$ Heusler alloy was measured on a diffractometer with copper electrode using the photon wavelength of 1.541Å.

Temperature dependence of saturation magnetization was measured by vibrating sample magnetometer (VSM) VERSALAB in Presov in the temperature range from 50 to 400 K under applied magnetic field of 0.5 T.

One of the simplest methods for ascertaining the phase transformation is by determining resistance dependence on temperature. For the measurement of electric resistance dependence on temperature, samples with length of 1 cm were used (see Fig. 1).

The crucial point for the electric resistance measurement are good contacts. Silver contacts have not a good mechanical resistance so we used a different method: the
ends of the ribbon is firstly soaked in a solution of copper sulfate (SurTek 867) which creates copper surface with low surface tension. Later on, tin contacts were applied, which are mechanically better (see Fig. 2).

![Fig. 1. Heusler alloy in the form of a ribbon](image)

![Fig. 2. The prepared sample with tin contacts](image)

### 3 RESULTS AND DISCUSSION

SEM analysis shows that the ribbon is polycrystalline with small crystals (0.62 - 1.57 µm) – (see Fig. 3). A columnar growth of crystals can be observed on section of the ribbon, reflecting the gradient stress induced during production due to the gradient of temperature during melt-spinning.

![Fig. 3. SEM micrograph of the Ni\textsubscript{50}Mn\textsubscript{26}Ga\textsubscript{24} ribbon](image)

X-ray diffraction at room temperature reveals three peaks in intensity from planes (220), (400), (422) – (see Fig. 4) – that correspond to single austenite phase (Fm-3m) of the ribbon Ni\textsubscript{50}Mn\textsubscript{26}Ga\textsubscript{24} with Mn-Ga disorder (B2 modification of ordered Heusler structure).

![Fig. 4. X-ray diffraction patterns for Ni\textsubscript{50}Mn\textsubscript{26}Ga\textsubscript{24} rapidly quenched ribbon](image)

\textit{Ni}_{50}\textit{Mn}_{26}\textit{Ga}_{24} is characterized by a phase transition less ordered tetragonal to a more ordered cubic structure. Such transition is proved by measured temperature dependence of saturation of magnetization (see Fig. 5). For the measurements of magnetization dependence on temperature showing phase transformation from tetragonal-martensit to the cubic-austenit structure at the temperature close to (194-234 K).

![Fig. 5. Temperature dependence of saturation magnetization of Heusler alloy Ni\textsubscript{50}Mn\textsubscript{26}Ga\textsubscript{24}](image)

In order to study the training effect on the structural transition, we measured temperature dependence of resistance in the vicinity of the transition (173 – 353 K). The structural transition from martensitic to austenitic phase is characterized by the decrease of resistance just below 200 K with increasing temperature (see Fig. 6). Such transition is characterized by the temperature hyste-
resis when the sample is heating and cooling. Therefore, four characteristic temperatures are used to describe the transition: martensite start temperature, \( M_s \), and martensite final temperature, \( M_f \), for cooling and austenite start temperature, \( A_s \), and austenite final temperature, \( A_f \), for heating. In Ni\(_{50}\)Mn\(_{25}\)Ga\(_{25\text{rib}}\), the transition from martensite to austenite starts at \( A_s = 210 \text{ K} \) and is finished at \( A_f = 250 \text{ K} \). During cooling, the transition from austenite to martensite starts at \( M_s = 240 \text{ K} \) and finished at \( M_f = 190 \text{ K} \).

![Fig. 6. Resistance dependence of Heusler alloy on temperature](image)

**Fig. 6.** Resistance dependence of Heusler alloy on temperature

However, preparation of samples by rapid quenching method results in a metastable state. This implies change in physical properties over time- aging. We made cyclic measurements of temperature dependence of resistance in order to see the training effect on aging. Fig. 7 shows the dependence of four characteristic temperatures \( A_s, A_t, M_s, \) and \( M_f \) on the training cycle. The metastable state of as-cast polycrystalline Ni\(_{50}\)Mn\(_{25}\)Ga\(_{25}\) ribbon results in the variation of characteristic temperatures in the way that temperature hysteresis of the structural transition as well as the transition interval decrease. However, the characteristic temperatures become stable after 6th cycle showing that structural transition and its hysteresis have reached the stable state.

![Fig. 7. Dependence of four characteristic temperatures](image)

**Fig. 7.** Dependence of four characteristic temperatures \( A_s, A_t, M_s, \) and \( M_f \) on the training cycle dependence

5 CONCLUSIONS

We have performed basic characterization of rapidly quenched Ni\(_{50}\)Mn\(_{25}\)Ga\(_{25}\) Heusler ribbon. It is characterized by austenitic phase Fm-3m in B2 modification at room temperature and by structural transition to martensitic phase around 200 K. Rapid quenching results in the metastable state that is demonstrated by the variation of four characteristic transition temperatures \( A_s, A_t, M_s, \) and \( M_f \). However after 6th training cycle, the transition temperatures and hysteresis becomes stable. This proves, that rapid quenching can be potentially interesting method of production of Heusler alloys that could be suitable for practical magnetocaloric application.

Acknowledgement

This work was Support by the project NanoCEXmat Nr. ITMS26220120035, Slovak grant APVV-0266-10, APVV-0027-11 and VEGA grant Nos. 1/0060/13 and 2/0070/12.

REFERENCES


Received 30 November 2015