Structural and Magnetic Properties of Melt-Spun Ni-Mn(Fe)-Ga Ferromagnetic Shape Memory Ribbons

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We studied structural and magnetic properties of Fe doped $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$ ferromagnetic shape memory ribbons prepared by a melt-spinning method. Experimental results obtained indicate that martensitic phase transition temperatures of the ribbon strongly depend on annealing, hence on the degree of atomic ordering. Magnetic hysteresis loop of the as-prepared ribbons shows a feature that can be attributed to the coexisting ferro and antiferromagnetic interactions.

***Index Terms*— Heusler alloys, martensitic transformation, melt spinning.**

I. Introduction

Since the observation of giant magnetic field strains caused by reorientation of martensitic variants [1] and magnetic field-induced martensitic transformation [2] in ferromagnetic shape memory alloys (FSMAs), great efforts have been directed to the investigation of melt-spun ribbons of the FSMA [3].

These materials are considered as promising functional materials for sensor and actuator technology. They exhibit several specific features due to their small thickness and a non-equilibrium structure. Especially, recent interest in the study of rapidly quenched ribbons has been conditioned by the observation of peculiar magnetotransport properties [4] and potential use of magnetocaloric properties of these materials [5]–[7].

In this paper, we report on structural and magnetic properties of Ni–Mn(Fe)–Ga ribbons prepared from the master alloys of $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$ composition.

II. Samples Preparation and Measurements

Ribbon flakes were produced by a single roller melt spinning in an argon environment. Small rectangular samples cut from a bulk $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$ alloy by a diamond saw were placed into a quartz crucible with a circular nozzle of 0.5 mm and ejected by applying an argon overpressure on the polished surface of a copper wheel rotating at a linear speed of 48 ms^{-1} (4000 r/min). Typical dimensions of the ribbons were of ~1.2–1.5 mm in width, several centimeters in length, and thickness of ~10–14 μm.

Structural properties of the ribbons were examined by X-ray diffraction (XRD) and a scanning electron microscope (SEM).

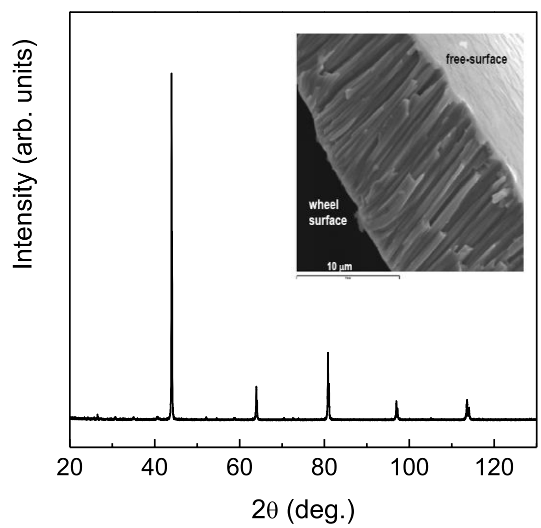

Fig. 1. XRD pattern of $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$ ribbon taken at room temperature. Inset: SEM picture of the ribbon.

Characteristic temperatures of the martensitic transformation were determined from differential scanning calorimetry (DSC) measurements. Temperature and field dependences of magnetization were measured by a vibrating sample magnetometer. Thermoelastic properties of the ribbons under bending stress were studied by a multipoint technique.

III. Experimental Results and Discussion

Fig. 1 shows the XRD pattern and SEM image of $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$ ribbon. The XRD pattern of the as-prepared ribbon suggests that the ribbon is crystalline. Microstructure of the as-prepared ribbons was found to be consisting of columnar grains grown perpendicularly to the ribbon plane (inset in Fig. 1).

The results obtained from the DSC measurements revealed that the as-prepared ribbons transform to the

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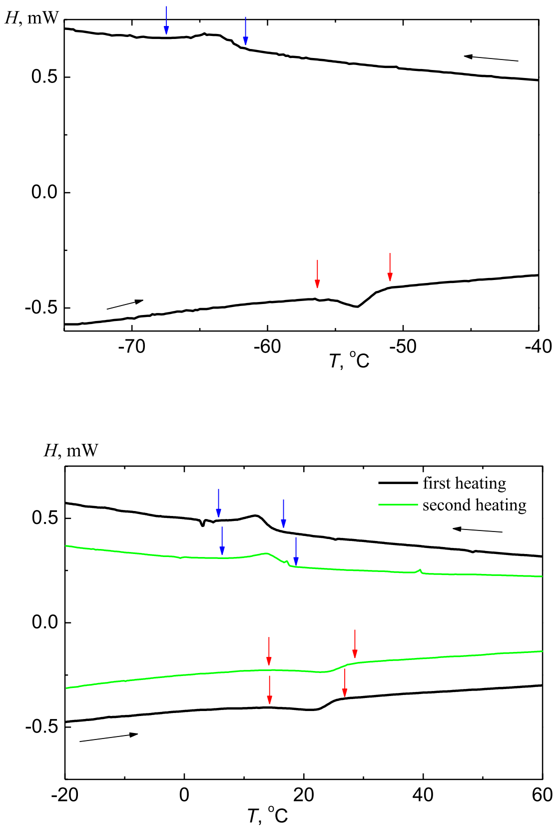

Fig. 2. Direct and reverse martensitic transition temperatures in as-prepared (top) and annealed at 200 °C for 2 h (bottom) ribbons of $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$.

low-temperature martensitic state at $T_m \approx -63$ °C (Fig. 2, top). These phase transition temperatures are significantly lower than those observed in the bulk $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$. This difference is presumably due to the structural disorder. Such a scenario is supported by the further DSC measurements. As shown in Fig. 2, annealing of the as-prepared ribbons results in a marked increase of the martensitic transformation temperatures. Particularly, for a ribbon annealed at 200 °C for 2 h, the martensitic transition was found to increase to $T_m \sim -3$ °C. The increase in the transformation temperature is related to annealing-induced ordering of the ribbons. It is interesting to note that the ordering process seems to be incomplete after annealing at 200 °C for 2 h. This is evident from the comparison of first and second DSC scans of the annealed $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$ ribbon (Fig. 2, bottom). Especially, a noticeable increase in the characteristic temperatures of the martensitic transformation is observed after the second DSC cycle. Considering that the first cycle was completed at 100 °C, this increase can be attributed to further ordering process, which takes place even at rather a low temperature 100 °C.

Results of the thermoelastic properties measurements under bending stress studied by a multipoint technique are shown in Fig. 3. In the case of as-prepared ribbon (curve 1), bending deformation of the ribbon in the studied temperature interval is a linear function of temperature. This is in accordance with the results of the DSC measurements, which have shown that martensitic transformation temperature in the as-prepared

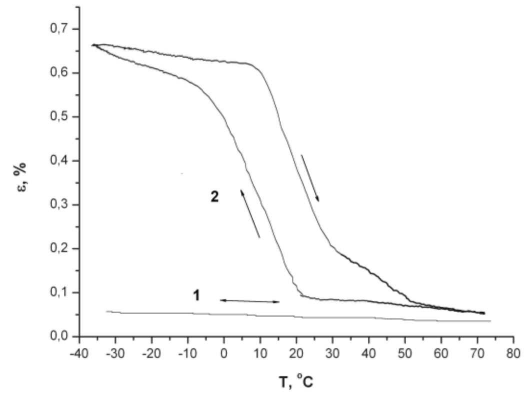

Fig. 3. Strain-temperature dependences measured in as-prepared (curve 1) and annealed at 200 °C for 2 h (curve 2) $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$ ribbons.

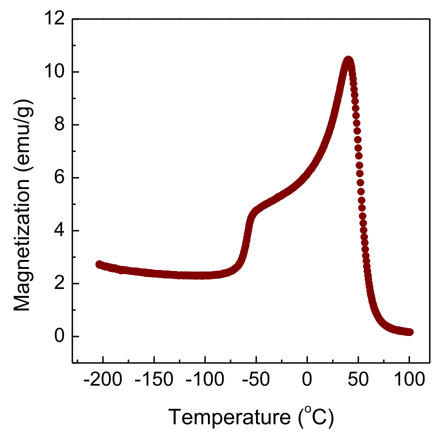

Fig. 4. Temperature dependence of the magnetization in the as-prepared $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$ ribbon.

ribbon occurs at approximately −63 °C. Thus, in the studied temperature interval, the ribbon is in the austenitic state and does not undergo a martensitic transformation, which explains linear dependence of the deformation as a function of temperature.

The annealed, at 200 °C for 2 h, ribbon exhibits marked anomaly at the deformation versus temperature curves measured upon heating and cooling (Fig. 3, curve 2). Upon cooling bending deformation of the ribbon starts to increase rapidly at 20 °C. This rapid increase is followed by a less steep dependence at ∼2 °C. Upon subsequent heating, the deformation starts to decrease at 20 °C and exhibits an inflection at 32 °C. These temperatures are in a good accordance with the martensitic transformation temperatures measured by the DSC (Fig. 2). Thus, deformation as a function of temperature shows a well-defined temperature hysteresis, which is directly linked to the temperature hysteresis of the martensitic transformation. Therefore, hysteretic feature of the deformation is a manifestation of a shape memory effect. It is shown in Fig. 3 that the annealed $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$ ribbon demonstrates ≈0.65% bending strain upon transformation from austenitic to martensitic state.

Temperature dependence of magnetization measured upon heating of as-prepared $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$ ribbon points to a number of anomalies, which correspond to magnetic

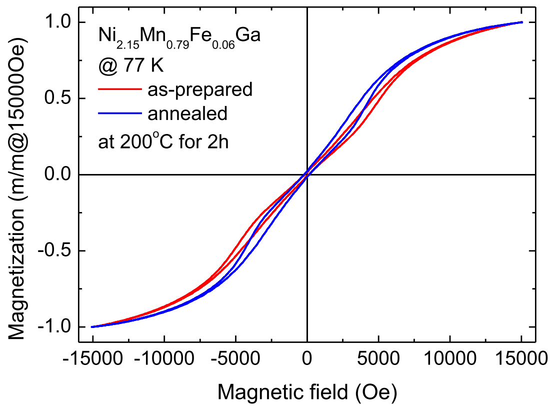

Fig. 5. Hysteresis loops measured at liquid nitrogen temperature in as-prepared (red curve) and annealed at 200 °C for 2 h (blue curve) $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$ ribbons.

and structural transitions (Fig. 4). Upon heating from low temperatures, a rapid increase in magnetization is detected at approximately −63 °C. According to the results of the DSC measurements [Fig. 2(a)], this temperature corresponds to the reverse martensitic transformation from the low-temperature martensitic to the high-temperature austenitic state. Upon further heating, magnetization rapidly increases up to ∼42 °C. Heating above this temperature is accompanied by the drastic decrease of the magnetization, which is due to the transition to paramagnetic state. Curie temperature determined from this measurement was found to be $T_C \approx 52$ °C.

Hysteresis loops measured at $T = -196$ °C in the as-prepared and annealed ribbons exhibit a feature typical for materials with coexisting magnetically soft and magnetically hard phases (Fig. 5). This feature can be explained as caused by the coexisting ferro and antiferromagnetic interactions. The structural inhomogeneity of the as-prepared ribbon can lead to the formation of a local region with dominating antiferromagnetic and ferromagnetic interactions, hence to the formation of magnetically soft and magnetically hard regions, which coexist with each other. The fact that after annealing at 200 °C for 2 h, the hysteresis loop still possesses complex character indicates that such annealing is not sufficient to complete crystallization process and to remove completely structural and chemical inhomogeneity of the ribbons prepared by melt-spinning method. Similar behavior of the magnetization has recently been reported for $Ni_{51}Mn_{28.5}Ga_{20.5}$ polycrystalline melt-spun ribbons [8].

IV. Conclusion

We have studied ribbons of $Ni_{2.15}Mn_{0.79}Fe_{0.06}Ga$ FSMA prepared by a melt-spinning method. The DSC and thermoelastic test under bending stress revealed that martensitic phase transition temperatures are sensitive to the thermal treatment. The annealed ribbon demonstrates ≈0.65% bending strain upon martensitic transformation. Magnetic hysteresis loops measured at $T = -196$ °C in as-prepared and annealed ribbons exhibit a feature typical for materials with coexisting magnetically soft and magnetically hard phases. This can be explained as caused by the coexisting ferro and antiferromagnetic interactions.

Acknowledgment

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