Magnetic Properties of Heusler-Type Microwires and Thin Films

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In this paper, we studied magnetic properties of Heusler-type glass-covered microwires and thin films. The results have shown that we succeeded to prepare Ni–Mn–In thin films and Ni–Mn–Ga and Ni–Mn–In microwires that have martensitic and austenitic phases at room temperature.

***Index Terms*— Heusler alloys thin films and microwires, magnetic properties, magnetic refrigeration, pulsed laser deposition.**

I. INTRODUCTION

DISCOVERY of a large field-induced strain, ferromagnetic shape-memory effect, magnetic field induced martensitic transition (MT), substantial magnetocaloric effect (MCE), and half-metallic behavior gave rise to intensive studies of Heusler alloys within the last years [1]. Among applications of current importance are magnetic actuators and sensors, energy-harvesting devices, solid-state magnetic refrigeration, and other smart devices [2], [3].

Conventional refrigeration uses well-optimized vapor-compression cycle developed in 19th century. It is quite matured technology involving the specific refrigerants (ecologically and environmentally nonfriendly gases) as working substances. The way to change the refrigeration process is use of the magnetic refrigeration. First magnetic refrigerator demonstrating that magnetic refrigeration is a viable and competitive cooling technology in the near room temperature (RT) region with potential energy savings of up to 30% has been reported in [3]. The magnetic refrigeration allows using of solid environmentally friendly materials with high density and heat capacity. Key process in the magnetic refrigeration cycle is a variation of the entropy caused by the magnetic field change—MCE.

Refrigeration machine power depends on the heat exchange rate between the active material of the refrigerator and the heat-transfer medium. To increase the heat exchange rate, it is needed to enhance the surface to volume ratio. Therefore, certain efforts to prepare Heusler alloys with low dimensionality, like ribbons, films, or wires have been recently performed [4]–[10].

In this paper, we present our last results on magnetic properties and structure of two types of Heusler alloys: microwires and thin films. They both are characterized by a high surface to volume ratio, the property that is highly desirable for refrigeration.

II. EXPERIMENTAL DETAILS AND SAMPLES

Heusler-type NiMnGa and NiMnIn glass-coated microwires were produced by Taylor–Ulitovsky technique [6], [11] (see details in Table I). Microwires were annealed similarly to that has been recently reported [6]. We produced microwires with different ratio of metallic nucleus diameter d and total diameter D, i.e. with different ratios $\rho = d/D$. The internal stresses are originated from the fabrication process involving rapid solidification of the composite glass-coated microwires. The main source of the internal stresses is the difference in the thermal expansion coefficients between the glass coating and the ferromagnetic nucleus [11], [12]. The strength of the internal stresses depends on the ρ-ratio [11], [12] increasing with decreasing the ρ-ratio, i.e. with increasing of the relative volume of the glass coating. This allowed us to control residual stresses varying the $\rho-$ratio

For measurements the microwires bunch was used that is why the results on magnetic properties are presented either in emu or as normalized magnetization M/M_0 (where M, is the magnetic moment measured at highest magnetic field).

Thin films were grown on pre-oxidized Si(100) substrate by pulsed-laser deposition under co-deposition process for

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TABLE I
MICROWIRE AND THIN FILM PARAMETERS

sample	d, μm	D, μm	d/D	t, nm
$Ni_{50}Mn_{25}Ga_{25}$ glass-coated microwire	13.6	33.8	0.4	-
	10.4	16	0.65	-
$Ni_{50}Mn_{35}In_{15}$ glass-coated microwire	23	55	0.42	
$Ni_{66}Mn_{24}In_{10}$ film	-	-	-	31
$Ni_{73}Mn_{16}In_{11}$ film	-	-	-	34

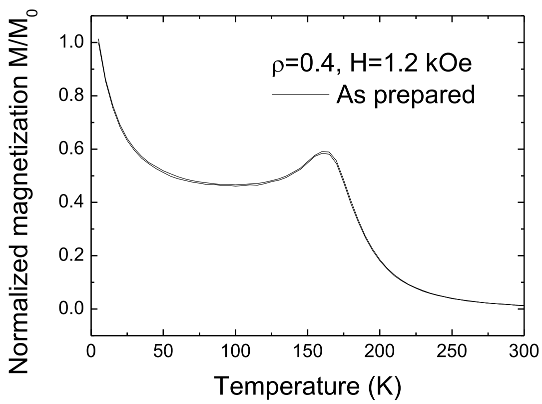

Fig. 1. Temperature dependence of normalized magnetization measured in as-prepared NiMnGa glass-coated microwire ($\rho = 0.4$) in the magnetic field of 1.2 kOe.

better composition control [13]. NiMnIn thin films have been prepared under high-vacuum ($\sim 10^{-9}$ torr) conditions by co-ablation of both $Ni_{50}Mn_{34}In_{16}$ and pure In targets. This technique is different from previously employed techniques for Heusler thin films preparation involving MBE and magnetron sputtering [1], [9]. The Heusler alloy thin films were annealed at 620 K for 30 min. The thicknesses t and compositions of the films are indicated in Table I. The structure has been studied by X-ray diffraction (XRD) at RT. In the case of NiMnIn microwire, high-energy X-ray powder diffraction measurements were performed at BW5 HASYLAB at DESY (Hamburg, Germany, $k = 0.12281$ A). For thin films, the Rutherford Back Scattering was used to check the composition and estimate the thickness. Magnetic properties have been measured with vibrating sample magnetometer by Lake Shore (7400 System), Magnetic Property Measurement System (MPMS) and Physical Property Measurement System (PPMS) by Quantum design. Magnetic field was in plane of the films and parallel to the microwire axis.

III. RESULTS AND DISCUSSION

A. NiMnGa Heusler-Type Microwires

Temperature T dependence of magnetization M/M_0 of as-prepared NiMnGa glass-coated microwire ($\rho = 0.4$) is shown in Fig. 1. As-prepared glass-coated microwires are paramagnetic at RT. Increasing of M/M_0 at T $\approx$ 150 K might be attributed to martensitic transformation around 150 K (Fig. 1). Recently has been reported that as-prepared NiMnGa microwires present crystalline structure [7].

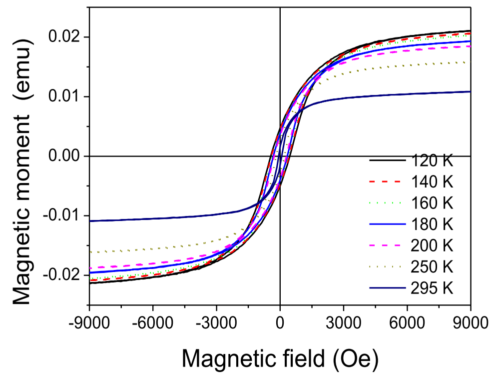

Fig. 2. Hysteresis loops at different temperatures for annealed at 773 K in NiMnGa glass-coated microwire with $\rho = 0.4$.

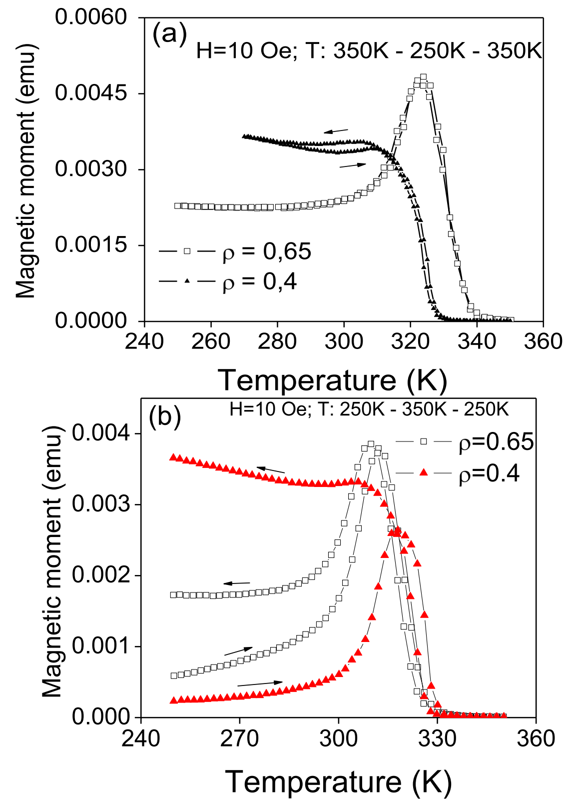

Fig. 3. Temperature dependence of the magnetic moment for annealed at 773 K glass-coated NiMnGa microwires ($\rho = 0.4$ and $\rho = 0.65$) measured in the magnetic field of 10 Oe during cooling from paramagnetic state. (a) Heating and (b) heating–cooling of previously demagnetized samples.

Annealing at 773 K results in a drastic change of magnetic properties: we were able to observe a magnetization curve up to 295 K (Fig. 2), although the saturation magnetization measured at magnetic field of 9 kOe drops with temperature indicating proximity to Curie temperature. Annealed microwire ($\rho = 0.4$) presents weak hysteresis on temperature dependence of magnetic moment $M(T)$ measured at magnetic field $H = 10$ Oe [Fig. 3(a)], while the other microwire (with $\rho = 0.65$) presents magnetization growth in vicinity of Curie temperature [Fig. 3(b)]. $M(T)$ dependence shown in Fig. 3 has been measured from demagnetized state of the samples first decreasing the temperature from 350 to 250 K and then increasing it back to 350 K [Fig. 3(a)]. We observed

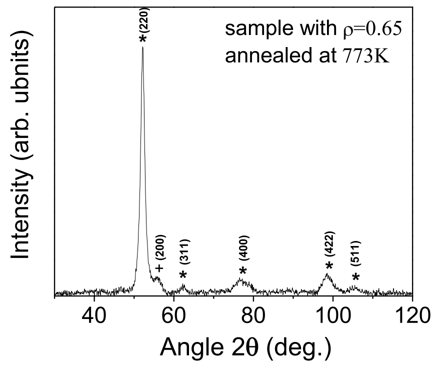

Fig. 4. XRD pattern of annealed at 773 K NiMnGa microwire with $\rho = 0.65$.

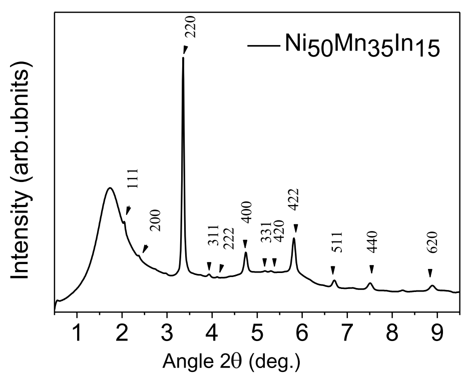

Fig. 5. XRD pattern of annealed at 823 K NiMnIn microwire with $\rho = 0.42$.

considerable hysteresis when the samples have been heated and cooled in demagnetized state [from 250 to 350 K and back, Fig. 3(b)] in magnetic field of 10 Oe.

Annealed NiMnGa microwires generally present two crystalline phases: martensitic and austenitic (Fig. 4). Thus, sample with $\rho = 0.65$ annealed at 773 K (30 min) consists of two phases: cubic Fm-3m with lattice parameter $a = 0.5823$ nm (marked by stars in the figure) and some amount of tetragonal I4/mmm phase with lattice parameters $a = 0.3865$ nm, $c = 0.4283$ nm (marked by crosses, see Fig. 4) [14].

B. NiMnIn Heusler-Type Microwires

The second group of studied microwires is NiMnIn Heusler-based microwire. To achieve stable microstructure, the microwire has been annealed at 823 K for 30 min. Similarly, the ratio of external and internal diameters has been chosen to be $\rho = 0.4$. Fig. 5 shows the XRD patterns of $Ni_{50}Mn_{35}In_{15}$ microwire. Single cubic phase with a lattice constant 0.4997 nm has been recognized without traces of any other phases. Fig. 6 shows temperature dependence of magnetization measured at low (50 Oe) and high (10 kOe) fields. The highfield magnetization monotonously decreases with temperature confirming a singlephase nature of NiMnIn microwires. In contrary to NiMnGabased microwires, NiMnIn does not show any hysteresis in the temperature dependence of magnetization. Small maximum is observed just below the Curie temperature ($T_c \sim 225$K) by measuring at low field (50 Oe) that could be assigned to the Hopkinson maximum similarly as in the case of NiMnGa microwires. Hysteresis loop (Fig. 7) also confirms a single ferromagnetic phase with a coercivity of 113 Oe.

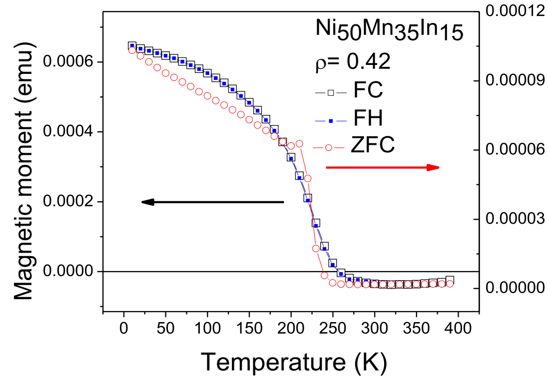

Fig. 6. Temperature dependence of magnetization for NiMnIn microwire [zero field cooling (ZFC) at 50 Oe, field cooling (FC) and field heating (FH) at 10 kOe].

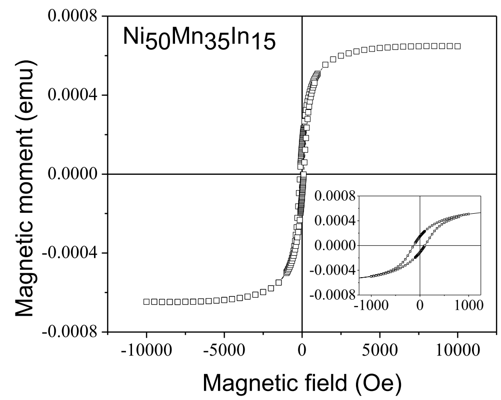

Fig. 7. Hysteresis loops for NiMnIn microwire measured at 10 K. Inset shows a low-field measurement.

Qualitatively observed $M(T)$ dependences are similar to that observed in bulk Heusler-type alloys [15], [16]. For NiMnIn and NiMnGa alloys produced by conventional arc melting the $M(T)$ dependences are explained considering three phase transition temperatures: T_{CM}—Curie temperature of martensitic phase, T_M—temperature of MT, and T_C—Curie temperature of the austenitic (high temperature) phase (AP). The AP is generally in a ferromagnetic state below its Curie temperature T_C, and $T_C > T_M$ [15], [16]. In the case of studied NiMnIn and NiMnGa microwires, the T_C values are rather smaller (for example, $T_C \approx 270$ K estimated from Fig. 6). The magnetization increasing observed in bulk NiMnIn and NiMnGa alloys at about $T_M \approx 270$–290 K was associated with a MT from the magnetic state characterized by low magnetic moment (antiferromagnetic or paramagnetic state) to a ferromagnetic AP state. The change in the ZFC magnetization in the low-temperature region ($T < T_{CM}$) previously reported for bulk NiMnIn has been attributed to the magnetic heterogeneity in this temperature range [15]. Consequently, hysteresis observed in Fig. 3 must be attributed to the coexistence of two crystalline phases. On the other hand, considerable magnetization increase in vicinity of Curie temperature can be related also either to the Hopkinson effect (see hysteresis loops in Fig. 2) or to an MT.

We can assume that the main peculiarity of the glass-coated microwires is the appearance of strong internal stresses distributed in complex way within the microwires. Moreover,

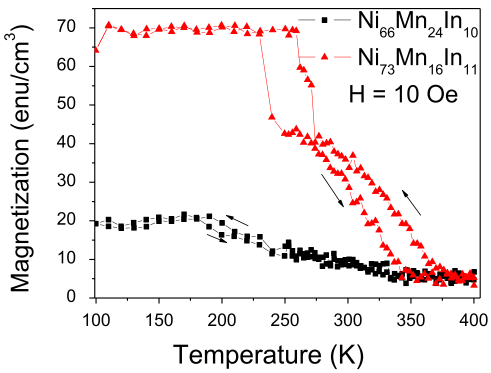

Fig. 8. Temperature dependence of magnetic moment of $Ni_{66}Mn_{24}In_{10}$ and $Ni_{73}Mn_{16}In_{11}$ thin films measured at 10 Oe.

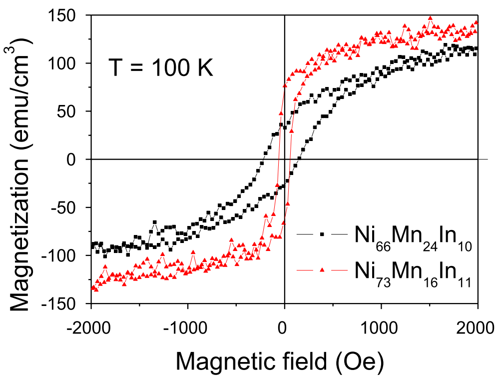

Fig. 9. Hysteresis loops of $Ni_{66}Mn_{24}In_{10}$ and $Ni_{73}Mn_{16}In_{11}$ thin films at 100 K.

the internal stresses distribution along the microwire's radius is not homogeneous: near the axis of the metallic nucleus the tensile stresses are the strongest one. However, closer to the interlayer between the metallic nucleus and glass coating the compressive stresses are dominant [12].

C. Magnetic Properties of Ni–Mn–In Heusler Alloys Thin Films

Both prepared thin films show ferromagnetic behavior at low temperature and RT (Figs. 8 and 9). Considerable difference in magnetization M versus temperature T dependence observed at 10 Oe (Fig. 8) must be attributed to softer magnetic character of $Ni_{73}Mn_{16}In_{11}$ samples (Fig. 9).

Observed hysteresis on $M(T)$ dependences (more appreciated for $Ni_{73}Mn_{16}In_{11}$, see Fig. 8) must be attributed to MT Crystalline structure was checked by XRD (not shown): samples at RT were found to be a mixture of structural phases.

IV. Conclusion

We successfully prepared Heusler-type NiMnGa and NiMnNi glass-coated microwires and Ni–Mn–In thin films. Large internal stresses, originated from the difference in thermal expansion coefficients of the glass and metal, affect the properties and crystalline structure of the microwires. Annealing of microwires considerably affect magnetic properties at RT. Magnetic behavior of NiMnGa microwires has been explained considering two-phase crystalline structure (martensitic and austenitic) of prepared microwires. NiMnIn microwires present single-phase structure.

Magnetic properties of NiMnIn thin films are affected by the preparation conditions and composition.

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References

[1] M. Acet, L. Manosa, and A. Planes, "Magnetic-field-induced effects in martensitic Heusler-based magnetic shape-memory alloys," in *Handbook of Magnetic Materials*, vol. 19, K. H. J. Buschow, Ed. Amsterdam, The Netherlands: Elsevier, 2011.

[2] E. Liu *et al.*, "Stable magnetostructural coupling with tunable magnetoresponsive effects in hexagonal ferromagnets," *Nature Commun.*, vol. 3, p. 873, May 2012.

[3] K. A. Gschneidner, Jr. and V. K. Pecharsky, "Thirty years of near room temperature magnetic cooling: Where we are today and future prospects," *Int. J. Refrigeration*, vol. 31, no. 6, pp. 945–961, Sep. 2008.

[4] A. M. Aliev *et al.*, "Magnetocaloric effect in ribbon samples of Heusler alloys Ni-Mn-M (M=In, Sn)," *Appl. Phys. Lett.*, vol. 97, no. 21, p. 212505, Nov. 2010.

[5] J.-P. Ahn, N. Cheng, T. Lograsso, and K. M. Krishnan, "Magnetic properties, structure and shape-memory transitions in Ni-Mn-Ga thin films grown by ion-beam sputtering," *IEEE Trans. Magn.*, vol. 37, no. 4, pp. 2141–2143, Jul. 2001.

[6] R. Varga, T. Ryba, Z. Vargova, K. Saksl, V. Zhukova, and A. Zhukov, "Magnetic and structural properties of Ni-Mn-Ga Heusler-type microwires," *Scripta Mater.*, vol. 65, no. 8, pp. 703–706, Oct. 2011.

[7] A. Zhukov *et al.*, "Magnetic properties and magnetocaloric effect in Heusler-type glass-coated Ni-Mn-Ga microwires," *J. Alloys Compounds*, vol. 575, pp. 73–79, Oct. 2013.

[8] C. Gómez-Polo, J. I. Pérez-Landazábal, V. Recarte, V. Sánchez-Alarcos, G. Badini-Confalonieri, and M. Vázquez, "Ni-Mn-Ga ferromagnetic shape memory wires," *J. Appl. Phys.*, vol. 107, no. 12, p. 123908, Jun. 2010.

[9] A. Sokolov, L. Zhang, I. Dubenko, T. Samanta, S. Stadler, and N. Ali, "Evidence of martensitic phase transitions in magnetic Ni-Mn-In thin films," *Appl. Phys. Lett.*, vol. 102, no. 7, pp. 072407-1–072407-3, Feb. 2013.

[10] P. Klaer *et al.*, "Electronic structure of the austenitic and martensitic state of magnetocaloric Ni-Mn-In Heusler alloy films," *Phys. Rev. B*, vol. 88, no. 17, p. 174414, Nov. 2013.

[11] M. Vázquez, J. M. García-Beneytez, J. M. García, J. P. Sinnecker, and A. Zhukov, "Giant magneto-impedance in heterogeneous microwires," *J. Appl. Phys.*, vol. 88, no. 11, pp. 6501–6505, Sep. 2000.

[12] H. Chiriac, T.-A. Óvári, and A. Zhukov, "Magnetoelastic anisotropy of amorphous microwires," *J. Magn. Magn. Mater.*, vols. 254–255, pp. 469–471, Jan. 2003.

[13] A. Grunin, A. Goikhman, and V. Rodionova, "Ni-Mn-In Heusler alloy thin films grown by pulsed laser deposition," *Solid State Phenomena*, vol. 190, pp. 311–314, Jun. 2012.

[14] P. J. Webster and K. R. A. Ziebeck, "Magnetic and chemical order in Heusler alloys containing cobalt and titanium," *J. Phys. Chem. Solids*, vol. 34, no. 10, pp. 1647–1654, Oct. 1973.

[15] K. Y. Mulyukov and I. I. Musabirov, "Influence of magnetic field intensity on the temperature dependence of magnetization of $Ni_{2.08}Mn_{0.96}Ga_{0.96}$ alloy," *J. Electromagn. Anal. Appl.*, vol. 2, no. 7, pp. 431–435, Jul. 2010.

[16] A. Kazakov *et al.*, "Phase transitions, magnetotransport and magnetocaloric effects in a new family of quaternary Ni-Mn-In-Z Heusler alloys," *J. Nanosci. Nanotechnol.*, vol. 12, no. 9, pp. 7426–7431, Sep. 2012.