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Effect of thermal cycling on the martensitic transformation in Ni-Mn-In alloys

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The influence of thermal cycling on the characteristics of the martensitic transformation in $Ni_{45.4}Mn_{40.9}In_{13.7}$ alloy was investigated. It was shown that after 1000 repeated thermal cycles trough temperature interval of the martensitic transformation, application of magnetic field of 1.1 T resulted in higher transformation temperatures shift of 10 K/T compared to 7 K/T before cycling. On the other hand, the measurements display a steady increase of electric resistivity with the number of cycles that along with decrease of the transformation latent heat indicate the phase hardening. The means to prevent functional degradation of magnetocaloric materials due to phase hardening are suggested. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4895585]

I. INTRODUCTION

In recent years, extensive attention was paid to the study of materials that exhibit the giant magnetocaloric effect (MCE), as they can be utilized for magnetic refrigeration. A series of new materials showing large MCE was found.[1–4] Ni-Mn-In based alloys are among them demonstrating metamagnetic behavior as well.[5] The martensitic transformation in these alloys is accompanied by a considerable drop in magnetization on cooling because the martensitic phase is non-ferromagnetic.

In accordance with the Clausius-Clapeyron equation,

$$dT_m/dH = -\Delta M/\Delta S, \tag{1}$$

effect of magnetic field H on the characteristic temperatures T_m of martensitic transformation depends on ΔM and ΔS, which are the differences in magnetization and entropy between the high- and low-temperature phases.

The ability to control the T_m value is a key issue in the development of materials for a magnetic refrigerator. Increase in ΔM, which can be achieved by addition of Co,[6–8] leads to an increase of dT_m/dH. In this study, we report on another possibility to increase dT_m/dH: by variation of ΔS.

When Ni-Mn-In is used as a magnetocaloric material, it undergoes a forward and reverse martensitic transformation. Taking into account that the martensitic transformation in this alloy is accompanied by a substantial change of the specific volume,[9] one can expect an increase of dislocation density during the phase transformation. This, in turn, implies that the martensitic transformation occurs in the material exhibiting phase hardening with the characteristics of transformation changing during repeated thermal cycles. In particular, a variation of the entropy ΔS occurs. Our investigations demonstrate that after many thermal cycles, the decrease in ΔS will increase the sensitivity of the phase transformation to the magnetic field, which results in a more pronounced metamagnetic behavior of the alloy. It should be noted that effect of repeated thermal cycles on physical properties of magnetocaloric rare earth and Heusler materials has been investigated in a number of studies. In Gd5 (Si1.95Ge2.05)[10] as well as in metamagnetic Ni–Co–Mn–Sb,[11] thermal cycling leads to an increase in electrical resistance and a weak change in transformation temperatures. It has been suggested to occur due to an increase in the number of defects and a change in the degree of atomic ordering introduced by redistribution of atomic positions. In Ni-Mn-Ga,[12] transformation temperatures and the latent heat were found to remain almost constant after 1000 thermal cycles through the interval of martensitic transformation.

II. EXPERIMENTAL DETAILS

In the present study, Ni-Mn-In alloy of nominal composition Ni-45.4 at. %, Mn-40.9 at. %, In-13.7 at. % has been studied. A vibration sample magnetometer (VSM) was used for the magnetization measurements in the range from 50 to 400 K. A calorimeter scan was performed using Netzsch 204 F1 differential scanning calorimeter (DSC) at a rate of 10 K/min. In addition, resistivity measurements were carried out by a four terminal sensing method. Ni-Mn-In ingot was homogenized at 1173 K for 48 h in a vacuum furnace.

III. RESULTS AND DISCUSSION

After homogenization, magnetic measurements were performed in different magnetic fields to determine their influence on the phase transformations (Fig. 1).

The characteristic temperatures obtained from the magnetization curves corresponding to a magnetic field of 50 Oe were found to be: the Curie temperature $T_C = 323$ K, characteristic

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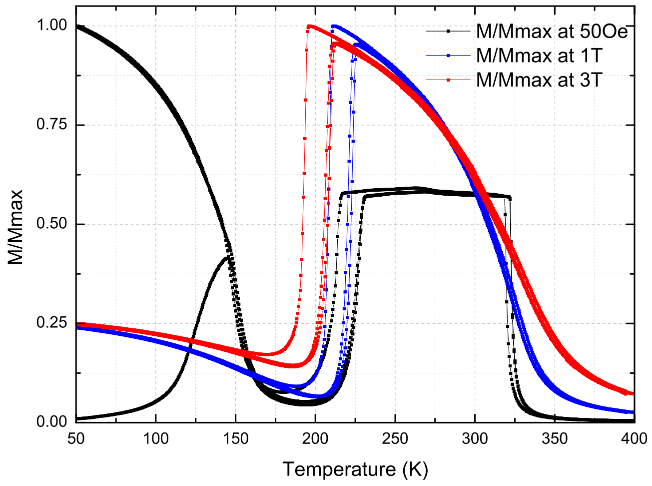

FIG. 1. Temperature dependence of the relative magnetization M/M_{max}, measured in different applied fields. M/M_{max} at $H = 50$ Oe was determined using the FC protocol (upper black curve) and ZFC protocol (lower black curve). See main text for details.

temperatures of the forward and reverse transformations $M_s = 214$ K, $M_f = 205$ K, $A_s = 217$ K, and $A_f = 231$ K. As shown in Fig. 1, a magnetic field of $\mu_0 H = 3$ T shifts characteristic temperatures by 21 K (or by 7 K/T) towards lower temperatures. Without a superimposed field (zero field cooling (ZFC)), magnetization shows a spike at a temperature of 145 K in the martensitic phase. By contrast, for the field cooling (FC) protocol, transformation results in a steady increase of the relative magnetization upon cooling below 145 K. These features can be attributed to the formation of ferromagnetic ordered regions in the martensite as reported earlier for Ni-Mn-In alloys of different composition.[13]

After the initial annealing, equilibrium atomic order was not achieved in the alloy upon cooling. Thus, an additional annealing (1023 K/50 h) was employed to provide higher level of a long range order of the $L2_1$ type in the austenitic phase. As demonstrated in Fig. 2, this brought about a noticeable change of the transformation temperatures: $M_s = 225$ K, $M_f = 210$ K, $A_s = 220$ K, and $A_f = 235$ K. Although the characteristic phase transformation temperatures increased, the width of temperature hysteresis decreased after the additional annealing.

The formation of martensite is accompanied by a rise of resistivity, and resistivity measurement was employed as effective means to track the changes in phase transformation during thermal cycling. As seen in Fig. 2, the repeated austenite-martensite transformations lead to an increase in resistivity of both the low-temperature and the high-temperature phases; and after 1000 cycles, the resistivity is approximately doubled. The effect of increasing with number of cycles is attributed to a notable build-up of dislocation density in both phases. Microstructural observations of Ni-Ti alloys[14,15] during thermal cycling revealed that similar increase in electrical resistance was accompanied by introduction of appreciable amount of dislocations. As outlined before, the difference in the specific volumes of martensite and austenite can give rise to the generation of dislocations upon movement of phase transformation front. Indeed, in Ni-Mn-In alloys, the change in the specific volume upon the martensitic transformation is considerable and amounts to 0.6%.[9]

Fig. 3 shows a calorimeter scan recorded during cooling of the sample. It is important to note that these measurements were taken on exactly the same specimen before and after cycling to avoid any differences between calorimetric properties of alloy except for those introduced by cycling. The curves demonstrate an influence of the repeated martensitic transformations on the latent heat L. Clearly, thermal cycling causes a drop in the heat release from 3.4 J/g in the virgin sample to 2.8 J/g upon completion of 1000 cycles. Since $L = T\Delta S$, the difference in entropies also diminishes after cycling. Thus, the characteristics of the martensitic transformation change as a result of phase hardening. Similarly, electrical resistivity is affected and Fig. 4 summarizes the effect of thermal cycling on the temperature dependence of electrical resistivity. The data shown were recorded without a magnetic field and with a superimposed field of 1.1 T. The application of the magnetic field reduces the phase transition temperatures by 11 K,

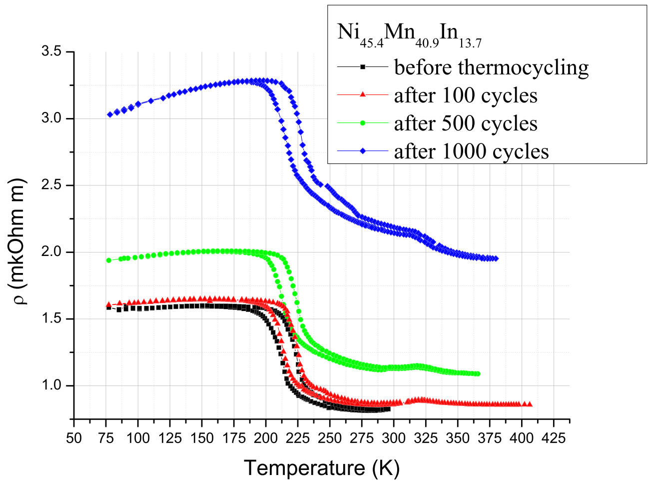

FIG. 2. Influence of repeated martensitic transformations on the electrical resistivity of the $Ni_{45.4}Mn_{40.9}In_{13.7}$ alloy.

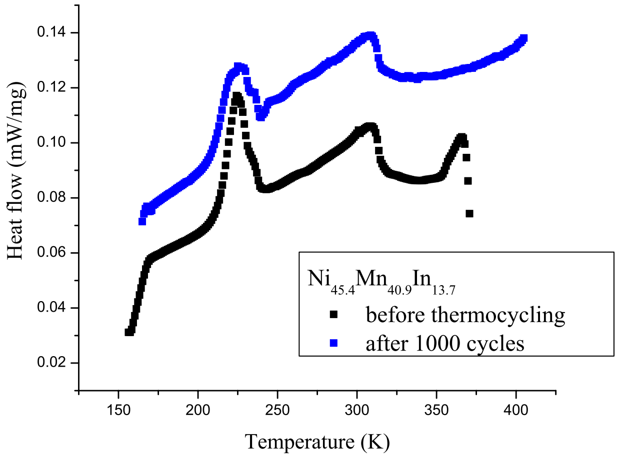

FIG. 3. Differential scanning calorimetry of $Ni_{45.4}Mn_{40.9}In_{13.7}$ in cooling mode: (a) before thermal cycling, (b) after 1000 thermal cycles between 150 and 340 K.

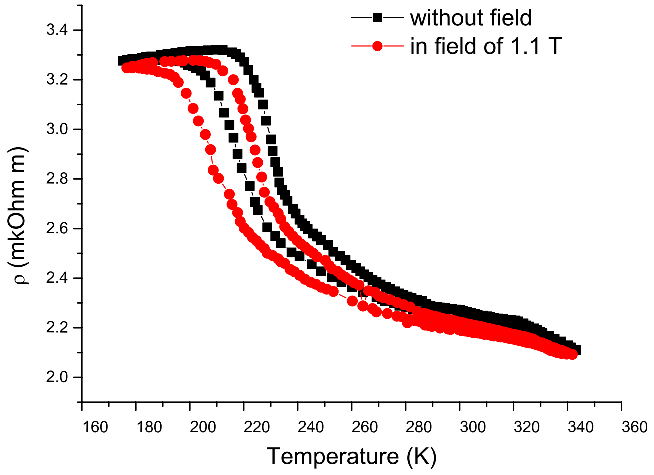

FIG. 4. Electrical resistivity of the $Ni_{45.4}Mn_{40.9}In_{13.7}$ alloy as a function of temperature in a magnetic field and without field.

resulting in $dT_m/dH = 10$ K/T. This value exceeds the ones reported in literature for Ni-Mn-Co-In.[16] It is also higher than the 7 K/T obtained in the virgin samples, i.e., before additional annealing and thermal cycling (Fig. 1). Modification of the temperature dependence of electrical resistivity by magnetic field results in significant magnetoresistance in the temperature interval of the martensitic transformation. Indeed, the maximal value of magnetoresistance is about 15% exceeding the obtained earlier[17] in the magnetic field of 1.1 T.

It should be noted that the decrease in the latent heat brought about by the repeated martensitic transformations introduces difficulties in realization of the idea of magnetic refrigeration using the metamagnetic transition in Ni-Mn-In alloys. In contrary to conventional MCE, the cooling capability of the inverse MCE materials relies on the amount of the latent heat absorbed during metamagnetic transition since magnetic contribution to MCE is smaller and opposite in sign. Sensitivity of characteristic temperatures to magnetic field improves after thermal cycling that is favorable for MCE applications but in the process of the repeated structural transformations, this material undergoes phase hardening due to the large volume changes accompanying them. It reduces the latent heat of the phase transition. To restore the latent heat to the original value, high-temperature annealing could possibly be used. As mentioned above, the extent of phase hardening is proportional to the volume effect of martensitic transformation. In its turn, the volume effect depends on the difference in the lattice parameters between parent and martensitic phases. Therefore, in order to decrease the phase hardening and prevent fast functional degradation of the magnetocaloric material, the lattice parameters can be modified by variation of composition as well as by alloying with additional element.

IV. SUMMARY

The results can be summarized as follows:

(1) The substantial volume change associated with the martensitic transformation results in an increase of dislocation density upon repeated thermal cycling of the alloy.
(2) The structural changes, in particular, the generation of dislocations and their accumulation in the course of repeated martensitic phase transformations affect both the electrical and calorimetric properties of the alloy.
(3) The phase hardening brings about an increase of electrical resistivity and a drop in the latent heat of the transformation.
(4) The magnetocaloric properties of the alloy can be adjusted by proper choice of composition and doping element or restored after phase hardening by an appropriate heat treatment to provide prolonged service life of material for magnetic refrigeration.

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