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Research Article

Tailoring of Magnetocaloric Effect in $Ni_{45.5}Mn_{43.0}In_{11.5}$ Metamagnetic Shape Memory Alloy

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We investigate the direct and inverse magnetocaloric effect in $Ni_{45.5}Mn_{43.0}In_{11.5}$ Heusler alloy ribbons comparing the results obtained for the as-quenched sample with the ones after different annealing procedures. An enhancement and shift of the entropy maximum to near room temperature is observed in all annealed samples. A remarkable magnetocaloric effect is observed in samples with short-time treatment (10 minutes) and at the lowest annealing temperature. We show that the suppressing of uncompensated martensitic transition and thermal hysteresis are both influenced by the heat treatment. Also, an improvement on Curie's temperature is observed and, at low magnetic field, it has been risen up to 310 K. Our results demonstrate that the martensitic transformation is highly sensitive to the applied magnetic field and also to the annealing treatment, which means that the magnetocaloric effect can be tuned showing different behaviors for each sample.

1. Introduction

Many first-order phase transition materials have been found to exhibit giant magnetocaloric effect (MCE) [1–3]. Currently, the search for a cheap magnetic material which exhibit a large MCE that works in the temperature range of 100 up to 300 K for a magnetic field variation of ΔH = 10 kOe is carried out. The most extensively studied Heusler alloys have those of the Ni-Mn-Ga system, nevertheless to overcome some of the problems related with practical applications (such as the high cost of Gallium and the usually low martensitic transformation temperature), the search for Ga-free alloys has been recently attempted. In order to reduce such costs and to improve the martensitic transition temperature, the substitution of Ga is proposed and, in particular, by introducing In or Sn [4–7].

These ferromagnetic shape memory alloys (FSMA) exhibit ferromagnetic and shape memory effect simultaneously. The ferromagnetic shape memory effect can be controlled by temperature, stress, and by magnetic field. Recently, Ni-Mn-In Heusler alloys have drawn much attention due to their potential as ferromagnetic shape memory alloys, which undergo a thermoelastic martensitic transformation (MT) from parent austenitic phase to a martensitic one on cooling [8]. These alloys exhibit notable sensitivity of MT to the applied magnetic field, they seem to be among the most suitable for the room temperature (RT) applications for example, in micro and nanomechanics devices and in alternative energy technologies, due to the giant magnetocaloric effect (MCE) observed in this alloys [9, 10]. Moreover, some authors have reported that such FSMAs also present giant magnetoresistance (GMR) due to the first-order phase transition, which can undergo a GMR variation of around 80% [11].

In this work, we present the influence of different annealing treatments on the martensitic transition and magnetic entropy change in a nonstoichiometric Ni-Mn-In Heusler alloy ribbon in order to tailor the MCE around RT. These alloys are of particular interest due to the existence of both direct and inverse magnetocaloric effect in a rather narrow temperature interval. The value of the entropy change depends on the difference in the magnetic state of the sample corresponding to the austenite and martensite phases and consequently is determined by the magnetic phase diagram. Along with the scientific interest of the results, these materials could be exploited in refrigeration by using positive and negative magnetic entropy changes.

2. Experimental

Polycrystalline $Ni_{45.5}Mn_{43.0}In_{11.5}$ alloy was produced by arc-melting with the appropriate amounts of high purity (99.99%) Ni, Mn, and In. Then, the master alloy was induction melted in quartz tubes and ejected in argon environment onto the polished surface of a copper wheel rotating at an elevated linear speed of 48 m/s. Rapid quenching by melt spinning offers two potential advantages for the fabrication of these magnetic shape memory alloys: the avoiding or reduction of the annealing to reach a homogeneous single phase alloy and the synthesis of highly textured polycrystalline ribbons. During the solidification process, the ribbon is continuously fragmented due to high crystallization kinetics and brittleness of the alloy. The crystal structure was checked by X-ray pattern diffraction technique and additionally the microstructure and elemental chemical composition analyses were performed by means of scanning electron microscope (SEM, JEOL 6100) equipped with electron dispersive X-Ray spectroscopy detector (EDX, Inca Energy 200). From these analyses, we obtain an average composition of $Ni_{45.5}Mn_{43.0}In_{11.5}$ ($e/a = 7.91$) for the produced ribbon. Taking the EDX error into concern, the Heusler alloy ribbons are very close to the nominal alloy value. The magnetic properties were measured using a quantum design VersaLab VSM in the temperature range of 50–400 K and up to 30 kOe applied magnetic field. Martensitic transition (MT) was characterized from the thermomagnetic measurements, which means zero-field cooling (ZFC), field cooling (FC), and field heating (FH) routines that were performed using different applied magnetic fields. The temperature ramping rate used was 4 K/min.

Ribbon flakes were annealed using different thermal treatments, 873, 973, and 1073 K, which it will lead to distinct magnetic behaviors. The annealing was performed under a vacuum chamber with a base pressure of 5×10^{-6} mbar. In addition, we have used different annealing times; in the cases of 873, and 1073 K we let the sample inside the heat chamber for 10 minutes and in the other treatment (973 K) for 20 minutes.

3. Results and Discussion

Figure 1 shows the martensitic transition for the as-quenched ribbon. As one can note, two different peaks are observed (and marked) in ZFC-FC-FH measurements. These peaks are related to uncompensated martensitic transitions and can also be directly affect by the applied magnetic field. For magnetic fields below 5 kOe, the predominant peak is the one denoted with number 1, and above this value, we can note that the peak 2 rules above the other. For an applied small magnetic field (50 Oe), we are also able to observe negative susceptibility during cooling the ribbon bellow some critical temperature around 125 K. Such a behavior disappears at higher applied field values. This quasidiamagnetism effect has been recently attributed by Prudnikov et al. [12] to a strong nonequilibrium of the system due to the presence of magnetic and structural disorders and exchange anisotropy. The origin of this anisotropy is related to the existence of antiferromagnetic interactions, characteristic in the system under study due to the presence of Mn atoms in In-sites, which means that at low temperature, an exchange bias effect should be appreciable and expected [13]. This could be experimentally demonstrated by the exchange shift of the hysteresis loop of the field-cooled sample at low temperature.

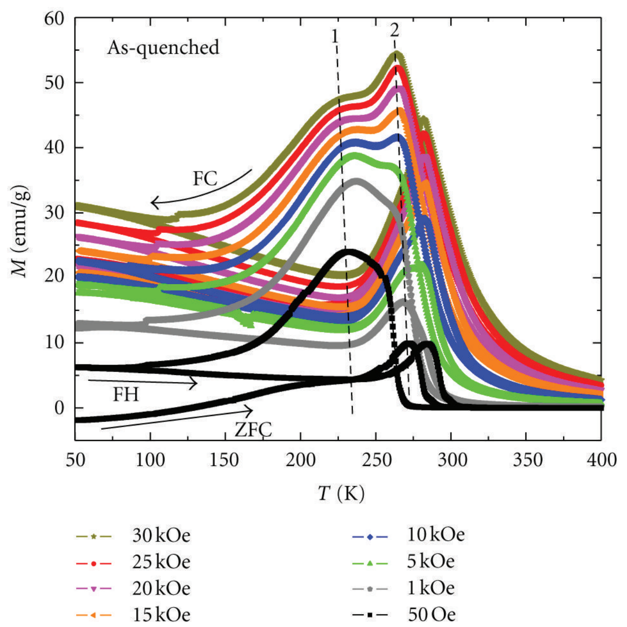

Figure 1: ZFC, FC, and FH thermomagnetic curves of as-quenched $Ni_{45.5}Mn_{43}In_{11.5}$ ribbon obtained at different magnetic field. Arrows indicate cooling and heating regimes in ZFC, FC, and FH protocols.

Figure 2(a) shows a comparison among the thermomagnetic measurements at 50 Oe for different ribbons. As we can note, a short time annealing can improve the magnetic response in a temperature interval close to RT, whereas a twice-larger annealing time and higher annealing treatment can dramatically decrease the magnetic moments, as a consequence of the shifting induced by the annealing on the martensitic phase transformation to a higher temperature. Besides, the annealing procedure has an important role on the properties of the martensitic transition. It's remarkable that by annealing the $Ni_{45.5}Mn_{43.0}In_{11.5}$ ribbons, we are able to suppress those uncompensated martensitic transitions (see Figure 1). The annealing has relaxed the residual structural stress originating from the melt spinning fabrication.

The annealing temperatures can be related with the shifting to RT of the first-order transition (see Figure 2(b)), even at high annealing temperature, the magnetic transition

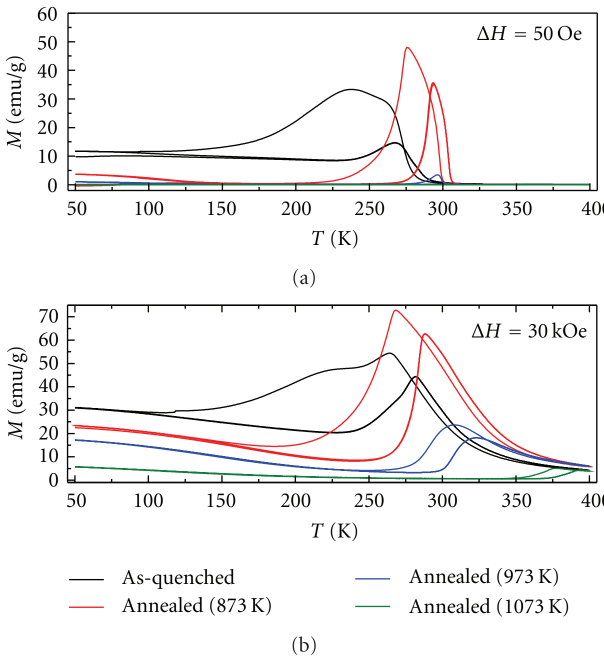

FIGURE 2: Temperature dependence of magnetization of as-quenched and annealed $Ni_{45.5}Mn_{43.0}In_{11.5}$ ribbons at 873 K, 973 K, and 1073 K obtained at a field of 50 Oe (a) and 30 kOe (b).

cannot be observed in the temperature range of 50–400 K for an applied magnetic field of 30 kOe. Other feature related to the different annealing temperatures is the reduction of the thermal hysteresis. In this case, as higher the annealing temperature, smaller is the thermal hysteresis.

This behavior could be explained by the annealing influence due to the increase in the grain size and crystal defects, along with the variation of internal stresses induced during the quenching process. It is also worth mentioning that the excess of Mn atoms, in this non stoichiometric Heusler alloy, are located in different sites leading to exchange interactions very sensitive to the Mn—Mn distance that could be modified by the annealing process.

The evaluation of the magnetocaloric effect has been estimated by the entropy variation, which was calculated using the Maxwell's relation [14]

$$\Delta S_M(T)_H = \int_0^H \left[\frac{\partial M(T)}{\partial T}\right]_H dH, \quad (1)$$

where $\partial M/\partial T$ is obtained directly from thermomagnetic measurements (ZFC-FC-FH). Such route to perform the calculations makes their accuracy improved since there is no need to extrapolate points, like in the case of isothermal curves, therefore the derivatives of thermomagnetic measurements are directly proportional to the entropy variation.

Figure 3 shows the entropy variation for ribbons with different annealing procedures. A very remarkable improvement is seen in the ribbon annealed for 10 minutes at 873 K. The entropy variation in this case had shown an enhancement on the order of 5 times higher than in the as-quenched ribbon, which is a dramatic feat. In addition, the temperature value at which the inverse magnetocaloric effect achieves its maximum is shifted from 276 K up to 284 K in this case. Thus, this first annealing is proved to be able to enhance the inverse magnetocaloric effect and shift the temperature where its maximum occurs by 8 K. The annealed ribbon at 973 K presents practically the same entropy variation as the as-quenched one, nonetheless, the temperature where the inverse magnetocaloric effect achieves its maximum is, in this case, in the range of RT achieving a value of 307 K. Hence, we obtain using such annealing procedure an impressive temperature shift by 31 K, nevertheless, the inverse magnetocaloric effect is not enhanced like in the previous case. Finally, at 1073 K, it is observed that the entropy variation decreases drastically and the inverse magnetocaloric effect reaches its maximum at 386 K, well above the RT, but the effect is not improved comparing with the other cases. Other feature that is also observed in the sample annealed at 1073 K is the fact that the magnetic phase transition from ferromagnetic to paramagnetic is not displayed since such thermal treatment shifts the Curie temperatures to a higher value, which is found to be above 400 K and, then, we are not able to see this transition due to our equipment limitation.

The refrigerant capacity (q) is defined by [15]

$$q = \int_{T_1}^{T_2} \Delta S(T)_H \, dT, \quad (2)$$

where T_1 and T_2 are the temperatures of cold and hot reservoir of the refrigeration cycle, respectively. The value of q can be obtained by performing the integration over the full width at half maximum (FWHM) in a ΔS-T curve, according to literature [16]. The different thermally treated ribbons display different refrigerant capacities being 54.8 J/kg (as-quenched), 163.6 J/kg (873 K), 44.6 J/kg (973 K), and 17.6 J/kg (1073 K). Comparing the entropy variation for as-quenched and annealed at 973 K, one should expect that the refrigerant capacities would be similar. However, the presence of uncompleted martensitic transformation in as-quenched ribbon produces a broader entropy peak and thus the increasing in the refrigerant capacity in such sample. In fact, this reduction in the refrigerant capacity for the sample annealed at 973 K is also due to the range of working temperatures T_1 and T_2 that, in such specific case, is narrower than all the previous samples, reducing the working temperature interval. For another annealed ribbon (873 K), the refrigerant capacity was rather increased comparing to the other two. An improvement of around 70% has been observed.

4. Conclusions

In conclusion, we have studied the magnetostructural and magnetocaloric properties of a $Ni_{45.5}Mn_{43.0}In_{11.5}$ ferromagnetic shape memory alloy with ribbon shape and the effect of different annealing treatments. The short annealing at 873 K proved to be the best choice to achieve a high entropy variation, however, the other annealings, at 973 and 1073 K, showed to be very efficient to shift the martensitic transition

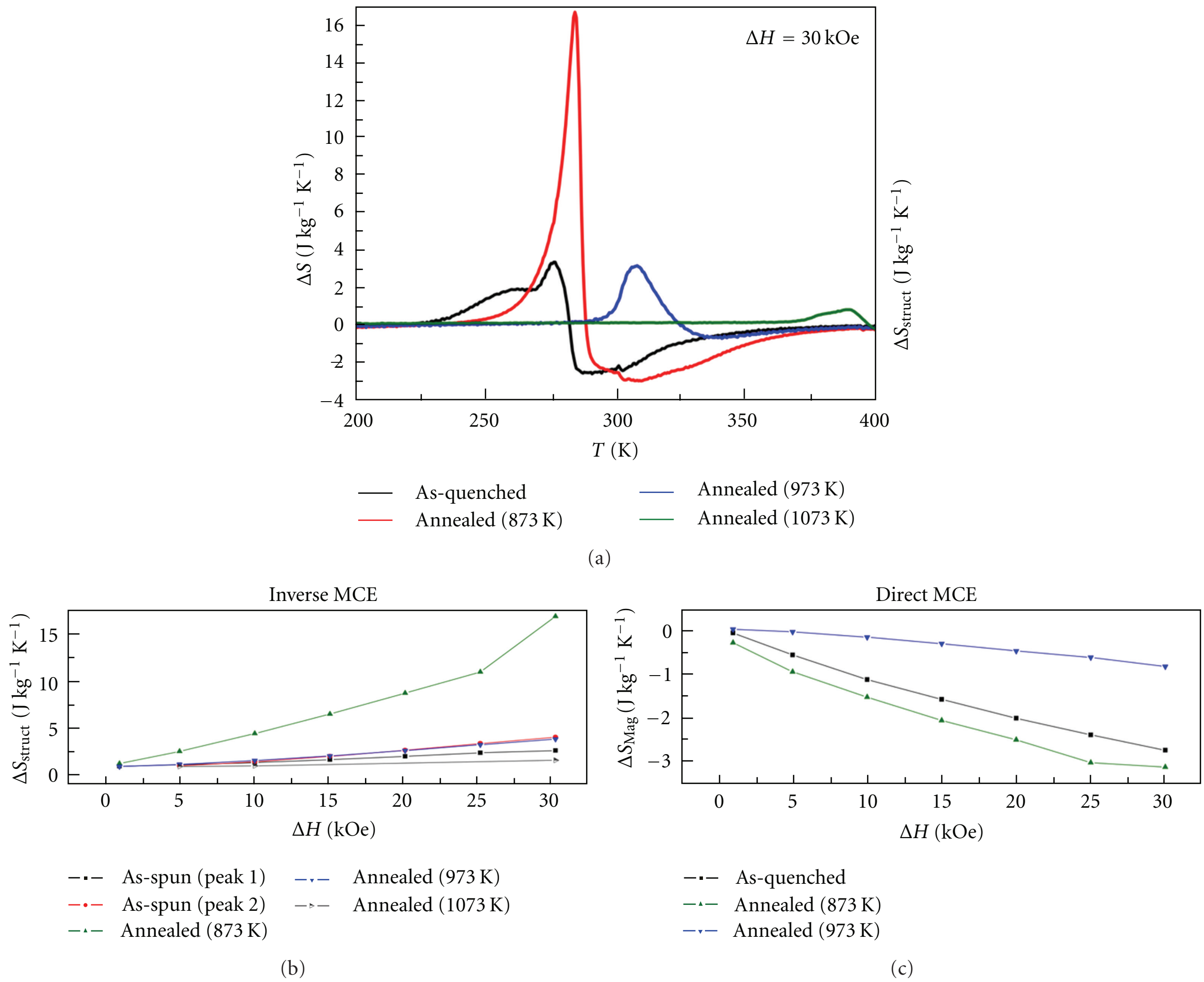

Figure 3: Magnetic entropy changes of as-quenched and annealed $Ni_{45.5}Mn_{43}In_{11.5}$ ribbons at 873 K, 973 K and 1073 K obtained at a field of 30 kOe (a). Magnetic entropy change maxima versus field change obtained at the structural transformation (b) and at the magnetic transition (c).

towards a temperature higher than the room temperature (above 300 K), which leads to a entropy variation in the range of potential applications as magnetic coolant. The problem still lies in the working temperature range and the low refrigerant capacity that needs to be enhanced in the future.

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