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Enhanced magnetocaloric effect in a Co-doped Heusler $Mn_{50}Ni_{37}Co_3In_{10}$ unidirectional crystal

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ABSTRACT

A high-pressure optical zone-melting technique was employed to grow a Mn-rich Heusler $Mn_{50}Ni_{37}Co_3In_{10}$ unidirectional crystal in the present study. It was found that the Co-doped $Mn_{50}Ni_{37}Co_3In_{10}$ unidirectional crystal showed a low magnetic hysteretic loss and a widened working temperature interval in the vicinity of the martensitic transformation. The inverse magnetic entropy change (ΔS_M) reached 7.84 $Jkg^{-1}K^{-1}$ around 237.5 K under a magnetic field change of 30 kOe, and the corresponding effective refrigeration capacity (RC_{eff}) was about 127.2 Jkg^{-1}. The experimental results demonstrated a high potential to develop high-performance Mn-rich Heusler Mn–Ni–In magnetocaloric materials by means of Co doping in combination with the high-pressure optical zone-melting fabrication technique.

1. Introduction

Giant magnetocaloric effects (MCE) have been observed in Heusler Ni–Mn–X(X=Sn, In, Sb) materials, which resulted from both the first-order martensitic transformation and the second-order magnetic transition in austenite under an external magnetic field [1–5]. Therefore, Heusler Ni–Mn based materials attracted considerable attention, and plenty of reports related to this topic have been published in the literature during the past decades [6–11]. Generally, it was well accepted that the magnetic entropy change (ΔS_M) can be used to evaluate the refrigeration capacity for the magnetocaloric materials with a second-order transition, such as Gd [12], Gd–Si–Ge [13] and La–Fe–Si [14]. However, it was inappropriate to apply for the Heusler-type materials since it is inevitable that large hysteretic loss always occurs during the first-order magnetic-field-induced martensitic transformation. Another parameter, the effective refrigeration capacity (RC_{eff}) was proposed which comprehensively takes into account the magnetic entropy change, the refrigeration temperature interval and hysteresis loss as well. The refrigeration temperature interval was defined as $\Delta T_{FWHM}=T_{heat}-T_{cold}$, where T_{hot} and T_{cold} are the corresponding temperatures at full width at half maximum peak value of ΔS_M [15]. That is to say, enhancement of the cooling capability can be achieved by increasing ΔS_M and ΔT_{FWHM}; and meanwhile, it is necessary to reduce the magnetic hysteresis loss (HL) for the first-order martensitic transformation.

With regard to the Co alloying in Heusler Ni–Mn based magnetocaloric materials, lots of efforts have been made. Liu et al. found that with 5 at% Co substituting for Mn in $Ni_{46}Mn_{40}In_{14}$ ribbons, a Co-rich face-centered cubic secondary phase formed after annealing at 1173 K for 2 h. The secondary phase produced little impact on the hysteresis loss, but broadened the transformation interval and reduced the magnetic entropy change [16]. Yu et al. observed similar Co-rich face-centered cubic $Ni_{17}Sn_3$-type secondary phase in Ni–Mn–Sn–Co melt-spun ribbons [17]. Zhang et al. obtained a wide working temperature interval up to 22 K in Ni–Mn–In–Co alloy and they ascribed to the presence of an intermediate martensitic transformation [18]. Wu et al. found that Co doping in $Mn_{50}Ni_{40}In_{10}$ would result in a sharp magnetization discrepancy between austenite and martensite. For the increased magnetization in austenite, they contributed to the formation of strong ferromagnetic structure of Mn(B)–Ni–Mn(D), and as for the low magnetization in martensite, they proposed that significantly shortened distance between Mn(B)–Mn(D) led to the disappearance of the local ferromagnetic structure in a tetragonal martensitic structure [19]. Pathak et al. also found that the refrigeration capacity strikingly improved by introducing Co into Mn

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sites, and obtained a large RC_{eff} value across the martensitic transformation up to 167 Jkg^{-1} in $Ni_{50}Mn_{34}Co_1In_{15}$ under a magnetic field change of 50 kOe. The total effective refrigeration capacity on a complete refrigeration cycle (including the conventional magnetocaloric effect resulted from the second-order magnetic transition in the austenite) reached 396 Jkg^{-1} [20]. Therefore, in the present study we tentatively produced a Co-doped $Mn_{50}Ni_{37}Co_3In_{10}$ unidirectional crystal, and the main objective is to investigate the martensitic transformation and magnetocaloric effect so as to further clarify the doping effect of Co element.

2. Experimental procedure

Firstly, a polycrystalline button ingot with nominal chemical composition of $Mn_{50}Ni_{37}Co_3In_{10}$ (at%) was arc-melted from pure Mn, Ni, Co and In (purities higher than 99.99 wt%) in argon gas atmosphere and then mechanically removed the surface oxides. A rod with 8 mm in diameter and ~60 mm in length was prepared through the suction casting method. The unidirectional crystal was grown using the high-pressure optical zone-melting furnace with a growth rate of 7 mmh^{-1} (Quantum Design G2). More experimental details have been described elsewhere [21,22]. The produced crystal was annealed at 1073 K for 48 h in vacuum, followed by water quenching.

Microstructural observations were performed using an optical microscope (Zeiss Axio Imager A2m). A sample of ~16 mg with a rough size of 1 mm × 1 mm × 2 mm was taken from the stable zone for the magnetic measurements. Magnetic properties were studied using physical property measurement systems (Quantum Design PPMS−9) under a magnetic field change up to 30 kOe with heating and cooling rates of 2.5 $Kmin^{-1}$.

3. Results and discussion

Fig. 1(a) shows the longitudinal optical image of the $Mn_{50}Ni_{37}Co_3In_{10}$ unidirectional crystal. There are a large number of equiaxed grains at the initial zone (left side) with an average grain size of 60 μm, as shown in Fig. 1(b). A few columnar grains are remained to grow parallel along the crystal growth direction in the stable zone, as shown in Fig. 1(c).

Fig. 2 shows the thermomagnetic curve (*M–T*) measured under a magnetic field of 1 kOe within the temperature range from 100 K to 380 K (recorded at 2.5 $Kmin^{-1}$). The magnetic field was applied parallel to the crystal growth direction. The martensitic and austenitic transformation starting and finishing temperatures are determined to be M_s=234 K, M_f=183 K, A_s=210 K, and A_f=270 K, respectively, as marked in Fig. 2. The hysteresis ($\Delta T = A_f - M_s$) of martensitic transformation is about 36 K, wider than that of $Mn_{50}Ni_{40}In_{10}$ unidirectional crystal (18.6 K) [23]. One can observe that the magnetization at first rises sharply upon heating due to reverse martensitic transformation from antiferromagnetic martensite to ferromagnetic austenite. With further increasing temperature, the magnetization remains stable and then drops at 375 K owing to the ferromagnetic→paramagnetic transition in austenite. The magnetostructural transition behavior is completely reversible upon cooling. The insert in Fig. 2 is the *dM/dT vs. T* curves. One can observe clear peak splitting upon heating where two peaks appear at 248.8 K and 257.2 K, respectively. It may be resulted from the local chemical compositional microsegregation. Further work is required to clarify this point.

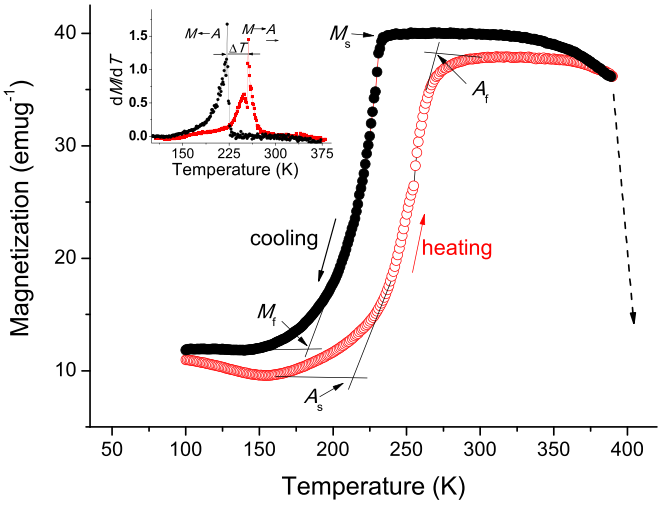

Fig. 2. Thermomagnetic curves measured under a magnetic field of 1 kOe for the $Mn_{50}Ni_{37}Co_3In_{10}$ unidirectional crystal. Insert: *dM/dT vs. T* curves.

Fig. 3 shows several selected field-up and field-down magnetization isotherms (*M–H*) between 170 K and 270 K under a magnetic field change of 30 kOe. Magnetization isothermals were recorded as follows: the sample was first zero-field cooled to 170 K, and afterwards the magnetic field strength was increased to 30 kOe and then decreased to zero. After the *M–H* curve was

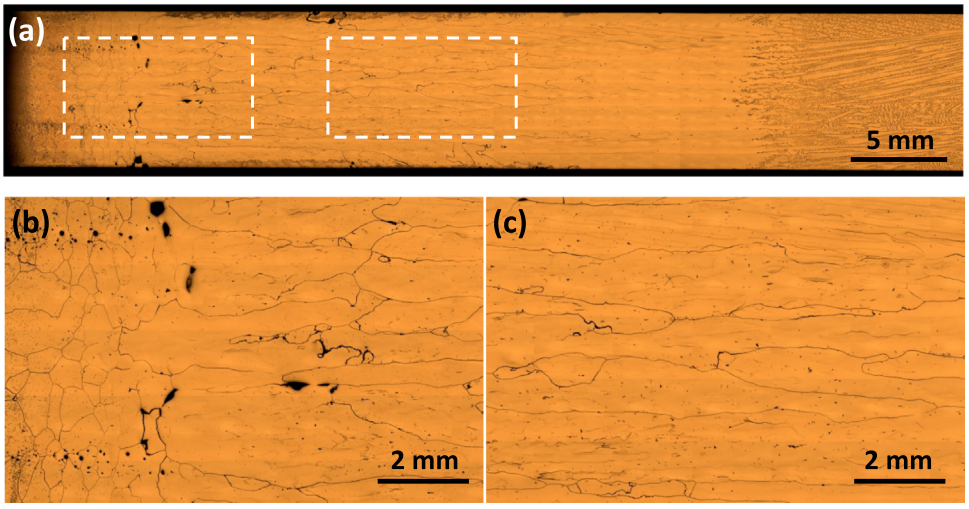

Fig. 1. (a) Longitudinal optical image of the $Mn_{50}Ni_{37}Co_3In_{10}$ unidirectional crystal growing at a rate of 7 mmh^{-1}. (b, c) Enlarged images, as marked by white frames in (a).