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The effect of step-like martensitic transformation on the magnetic entropy change of $Ni_{40.6}Co_{8.5}Mn_{40.9}Sn_{10}$ unidirectional crystal grown with the Bridgman-Stockbarger technique

F. Chen [a, *], Y.X. Tong [a], L. Li [a], J.L. Sánchez Llamazares [b, **], C.F. Sánchez-Valdés [c, d], P. Müllner [e]

[a] Institute of Materials Processing and Intelligent Manufacturing, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China
[b] Instituto Potosino de Investigación Científica y Tecnológica A.C., Camino a la Presa San José 2055, Col. Lomas 4ª sección, San Luis Potosí, S.L.P. 78216, Mexico
[c] Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, AP 14, Ensenada 22860, Baja California, Mexico
[d] División Multidisciplinaria, Ciudad Universitaria, Universidad Autónoma de Ciudad Juárez (UACJ), calle José de Jesús Macías Delgado #, 18100, Ciudad Juárez, Chihuahua, Mexico
[e] Micron School of Materials Science and Engineering, Boise State University, ID 83725, USA

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ABSTRACT

We report a step-like martensitic transformation and its effect on magnetocaloric properties in $Ni_{40.6}Co_{8.5}Mn_{40.9}Sn_{10}$ unidirectional crystal grown using the Bridgman-Stockbarger technique followed by vacuum annealing at 1173 K for 72 h. This alloy undergoes successive first-order phase transitions which are attributed to the monotonic compositional variation along the crystal growth direction; the latter results in the increase of the full-width at half-maximum of the magnetic entropy change as a function of temperature (δT_{FWHM}). For a magnetic field change of 2 and 5 T, the maximum magnetic entropy change are 9.7 and 16.0 J $kg^{-1}K^{-1}$ with an extended δT_{FWHM} of 11 and 23 K, respectively. The average hysteresis loss for a field change of 2 T is 19 J kg^{-1} reducing the refrigerant capacity by 17%.

1. Introduction

In recent years, ferromagnetic Ni-Mn-Z (Z: group IIIA–VA elements) Heusler alloys attracted interest as a group of promising refrigeration materials due to their giant and tunable inverse magnetocaloric effect (MCE) around room temperature (RT). The latter is originated by the large positive field-induced magnetization change across the first-order martensitic transformation. Krenke et al. reported the MCE for $Ni_{50}Mn_{50-x}Sn_x$ alloys with x = 13 and 15 [1]. Under a magnetic field change $\mu_0\Delta H$ of 5 T these authors reported a maximum magnetic entropy change ΔS_M^{peak} of 18 J $K^{-1}kg^{-1}$. The partial replacement of Ni or Mn in these Heusler alloys by Co leads to two important effects. First, the structural transition temperatures can be tuned in a wide range [2–6] and, second, the magnetization difference between martensite and austenite phases ($\Delta M_{M\text{-}A}$) increases providing more driving force to induce the structural transition at reduced magnetic fields [7,8]. The larger $\Delta M_{M\text{-}A}$ results in larger ΔS_M^{peak} values [9]. For example, in $Ni_{50}Mn_{38}Sb_{12}$, the substitution of 5 at.% Co for Ni increases the ΔS_M^{peak} value associated to the reverse martensitic transformation from 7 to 34 J K^{-1} kg^{-1} [3]. ΔS_M^{peak} of $Ni_{45}Mn_{37}In_{13}Co_5$ reaches ~34 J $kg^{-1}K^{-1}$ [4] which is nearly 4 times larger than 8.0 J $kg^{-1}K^{-1}$ for Co-free $Ni_{50}Mn_{34}In_{16}$ [5]. The substitution of Co for Mn in $Ni_{43}Mn_{46-x}Co_xSn_{11}$ considerably increases ΔS_M^{peak} from about 10 J $kg^{-1}K^{-1}$ to 19.1 J $kg^{-1}K^{-1}$ and raises its working temperature

* Corresponding author. Institute of Materials Processing and Intelligent Manufacturing, College of Materials Science and Chemical Engineering, Harbin Engineering University, No. 145 Nan Tong Street, Nan-Gang District, Harbin 150001, China.
** Corresponding author. Instituto Potosino de Investigación Científica y Tecnológica A.C., Camino a la Presa San José 2055, Col. Lomas 4ª sección, San Luis Potosí, S.L.P. 78216, Mexico.
E-mail addresses: chenfeng01@hrbeu.edu.cn (F. Chen), jose.sanchez@ipicyt.edu.mx (J.L. Sánchez Llamazares).

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range to around room temperature [6]. Ito et al. [7] suggested that to significantly enhance the ferromagnetic coupling between the Mn atoms, the Co content should exceed about 6 at. %. However, the addition of Co also spurs the formation of a second phase [10,11]. In fact, our previous work on Ni-Co-Mn-Sn bulk alloys shows that if Co exceeds 10 at.%, a large amount of γ phase particles form [12]. In $Ni_{37.7}Co_{12.7}Mn_{40.8}Sn_{8.8}$ melt-spun ribbon ΔS_M^{peak} decreased from 15 J $K^{-1}kg^{-1}$ to 2.2 J K^{-1} kg^{-1} because of the formation of γ phase particles [13]. Liu et al. [4] suggested that the γ phase widens the range of transformation temperatures and, thus, smears the magnetic-field induced transformation reducing the MCE. Thus, the Co content must be controlled to avoid the formation of the γ phase as a precondition to keep a high magnetization for the austenitic phase in the quaternary alloy system (i.e., the Co content has to be chosen between 6% and 10 at.%).

For ideal Ericsson cycle based magnetic refrigeration, magnetocaloric material should possess a constant ΔS_M in the working refrigeration temperature range [14]. This means the full-width at half-maximum of $\Delta S_M(T)$ curve (δT_{FWHM}) should be large. A composite material [15,16] showing two or more sucessive magnetic phase transitions is, from the experimental point of view, a promising approach to this problem. The starting point is the selection of an appropriate synthesis method. Considering that in Ni-Mn-Z Heusler alloys the structural transition temperatures are highly sensitive to small composition changes the attainment of successive martensitic transformations can be obtained by creating chemical segregation or composition gradient. Segregations typically occur with directional solidification, most prominently in the growth of unidirectional [17] crystal or single crystal [18,19].

With this idea in mind, a unidirectional crystal of $Ni_{40.6}Co_{8.5}Mn_{40.9}Sn_{10}$ was expected to be grown using the Bridgman-Stockbarger method, which leads to chemical segregation [18,19]. It was found that the prepared sample had a crystallographic growth direction of [110] and exhibited a step-like phase transition resulting in a remarkable increase in δT_{FWHM}. The effect of such a transformation on various magnetocaloric properties is also discussed.

2. Experimental procedure

The unidirectional crystal was fabricated from an induction melted polycrystalline alloy with the nominal composition $Ni_{41}Co_9Mn_{40}Sn_{10}$. The alloy was hand-grounded into a powder that was re-melted in a custom-made furnace and a crystal with 6.3 mm diameter was grown by means of the Bridgman-Stockbarger technique; we used as seed a Ni-Mn-Ga single crystal with [001] parallel to the growth direction [19]. After growth, the sample was homogenized at 900 °C for 72 h under an argon atmosphere.

Microstructural studies were carried out on slices cut from the same ingot next to the samples used for the magnetic measurements. The average composition determined by energy dispersive X-ray spectroscopy (EDS) in a LEO model 1430VP scanning electron microscope was $Ni_{40.6}Co_{8.5}Mn_{40.9}Sn_{10}$. The microstructure was characterized with an optical microscope. XRD analysis was performed at room temperature using copper K_α radiation.

Magnetic properties were measured by vibrating sample magnetometry in a Quantum Design PPMS® EverCool®-9T platform. The sample studied had a parallelepiped shape with dimensions 0.8 × 4.5 × 4.0 mm^3; the major length was parallel to the axial direction of the ingot (i.e., [110]). The magnetic field $\mu_0 H$ was applied along the latter in order to reduce the influence of the demagnetizing field. The low-field (5 mT) and high-field (5 T) magnetization as a function of temperature, $M(T)$, curves were measured between 10 and 400 K (data were obtained by first cooling the sample from room temperature in zero applied magnetic field to an initial measuring temperature of 10 K). Then, the magnetic field was applied and the variation of magnetization was continuously measured while the temperature was increased continuously up to 400 K (ZFC process) at a rate of 1.0 K/min. After the last point was measured, the sample is cooled to 10 K keeping the same static field (FC process). Finally, the M vs T data were measured again for increasing temperatures under a constant magnetic field (FH process). The phase transformation and magnetic transition temperatures were obtained from the differential scanning calorimetric (DSC) curves measured in a TA Instruments model Q200 with a heating/cooling rate of 10 K/min and the minimum of the dM/dT vs. T curve measured under $\mu_0 H = 5$ mT. The temperature dependence of magnetic entropy change $\Delta S_M(T)$ was determined by numerical integration of the Maxwell relation (i.e., $\Delta S_M(T, \mu_0 H) = \mu_0 \int_0^{\mu_0 H} \left[\frac{\partial M(T,\mu_0 H')}{\partial T}\right]_{\mu_0 H'} dH'$). For such a purpose, a set of isothermal magnetization curves, $M(\mu_0 H)$, were measured in increasing the temperature across MST → AST phase transition [temperature steps are indicated in Fig. 4(a)]. Taking into account that in the temperature range where phase transformation occurs the shape of the $M(\mu_0 H)$ curves may strongly depend on the thermal history, we applied a fixed thermal protocol throughout MST → AST as follows: (1) heating to 400 K to stabilize austenite, (2) cooling to 210 K to completely form martensite, and (3) heating to the selected measuring temperature T_{meas}. This procedure was repeated for each T_{meas} to ensure that, prior to applying the magnetic field at a given T_{meas}, the sample consistently had the phase constitution corresponding to the thermally induced structural transition.

3. Results and discussion

Fig. 1 shows an XRD pattern and optical image taken at room temperature from the cross section of the rod-shaped sample. The XRD result indicates that the sample has a preferred orientation of [110] parallel to the solidification direction. It is different from the seed orientation, [001], indicating that the preferred growing direction of the Ni-Co-Mn-Sn unidirectional crystal is [110]. The inset shows three domains with two different martensite variants. The martensite laths in the top left corner of the image have the same orientation as the martensite laths in the bottom right corner. No

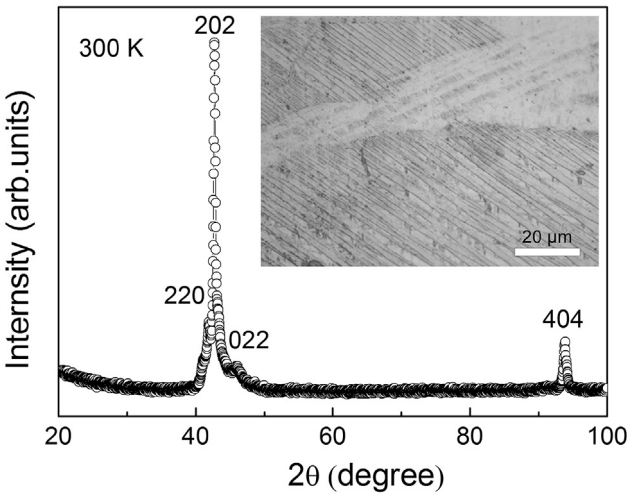

Fig. 1. XRD trace and optical image (inset) obtained at room temperature. The XRD trace shows a strong 202 reflection. The microstructure presents three domains containing two martensite variants.