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Magnetocaloric effect in melt-spun MnCoGe ribbons

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Single-phase MnCoGe ribbons with an $NiIn_2$-type structure were produced by using the melt-spinning technique. We reduced the annealing time for stabilizing the lower-symmetry orthorhombic TiNiSi-type crystal structure by two orders of magnitude compared with that of the parent bulk alloy. Both phases exhibit a second-order magnetocaloric effect, with $\Delta S_M^{peak} \approx -2.8(-4.0) J\,kg^{-1}\,K^{-1}$ and $RC \approx 238$ (281) J kg^{-1} for the maximum isothermal magnetic entropy change and refrigerant capacity, respectively, for a magnetic field change of 5 T.

Keywords: MnCoGe melt-spun ribbon; Magnetocaloric effect; Magnetic entropy change; Refrigerant capacity

The stoichiometric MnCoGe compound exhibits polymorphism and can adopt either the hexagonal Ni_2In-type (space group $P6_3/mmc$) or the orthorhombic TiNiSi-type (space group $Pnma$) crystal structure at room temperature [1]. Both phases are ferromagnetically ordered, although the values for the Curie temperature, T_C, and saturation magnetic moment, m_S, differ: $T_C \approx 275$ and 355 K and $m_S \approx 2.8$ and 4.1 μ_B f.u.$^{-1}$ for the hexagonal and orthorhombic phases, respectively [2,3]. Both Mn and Co have magnetic moments, although the main contribution comes from the Mn atoms [2,4].

The orthorhombic variant, usually referred to as the low-temperature phase, is obtained after homogenization is achieved by thermal annealing at temperatures in the range of 773–1123 K [5–9], followed by slow or fast cooling to room temperature. However, a serious practical drawback in the homogenization process is the annealing time, which typically requires several days. On heating, this phase undergoes a first-order diffusionless structural phase transformation to the hexagonal phase (i.e. a martensitic-type transformation) with a large thermal hysteresis of $\sim \Delta T = 40$ K [3,10]. The temperature for the beginning of the structural transition T_{str} varies between 420 K [5] and 650 K [3,10]. Although the high-temperature stable phase is hexagonal (for $T > T_{str}$), it has also been reported that, when the alloy is annealed at a high temperature and rapidly quenched in water, this hexagonal phase can be obtained at room temperature in a metastable state [2,11].

An interesting feature of MnCoGe-based alloys is the strong interplay between structure and magnetism. Several factors, such as Co vacancies [8,12,13], Mn deficiency [14], the application of hydrostatic pressure [10,11,15], substitution of a small amount of Mn or Co by a fourth element [3,5,8,9,11,16,17] and the introduction of interstitial elements [18–20], may affect the intrinsic magnetic properties of both structural variants, as well as the value of T_{str}, considerably.

The magnetocaloric (MC) response of MnCoGe-based alloys has drawn considerable attention in the last few years. Large, and even giant, peak values of the isothermal magnetic entropy change ΔS_M^{peak} have been reported in pure [6,13] or doped alloys [8,9,15–20] with an orthorhombic crystal structure. In $MnCo_{0.95}Ge_{1.14}$ alloys a sizable ΔS_M^{peak} of -6.4 Jkg^{-1} K^{-1} is induced by a rather low magnetic field change of $\mu_o \Delta H = 1$ T [6]. The effect has been explained by the large, sharp drop

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in magnetization close to the ferromagnetic (FM) to paramagnetic (PM) transition as a consequence of the negative exchange striction of the lattice around T_C (i.e. due to the strong magneto-elastic coupling nature of the magnetic transition). More recently, a giant magnetic entropy change has been found in interstitially modified $MnCoGeB_x$ [16,19] and $MnCoGeC_x$ [19] alloys, or by partial replacement of Mn by Cr in $Mn_{1-x}Cr_xCoGe$ [15,16,19], by reducing the T_{str} to below the Curie point of the orthorhombic phase.

Until now, MnCoGe alloys have been produced as bulk samples by means of conventional melting techniques followed by lengthy thermal annealing. In view of the current interest and great potential of these compounds as MC materials near room temperature, here we report the synthesis of the equiatomic MnCoGe compound by rapid solidification using the melt-spinning technique, as well as characterizations of the crystal structure, the magnetic properties and the MC effect to a maximum magnetic field change up to $\mu_o \Delta H_{max} = 5$ T. To our knowledge, neither the synthesis of MnCoGe melt-spun ribbons nor their MC properties have been reported yet. Significantly, the use of rapid solidification to produce the orthorhombic variant of this compound results in a substantial reduction in the annealing time.

Rapidly solidified ribbons (with thicknesses $\approx$ 30–35 μm) were produced by melt spinning in an Ar atmosphere at a wheel linear speed of 20 ms^{-1} from as-cast pellets of nominal composition of MnCoGe previously obtained by arc melting from highly pure elements (>99.9%), also under an Ar atmosphere. Any Mn losses during arc melting were carefully compensated for by adding the appropriate excess of this element. Samples were annealed at 923 K for 1 h to stabilize the orthorhombic structure. Annealing was followed by water quenching. X-ray powder diffraction (XRD) patterns were obtained with a Bruker AXS model D8 Advance diffractometer using Cu K_α radiation. Microstructure and elemental composition were determined using a FEI/Philips XL30 field emission gun SEM equipped with an energy-dispersive analysis system (EDS).

Magnetization measurements were performed using a PPMS platform equipped with a vibrating sample magnetometer module. The magnetic field $\mu_o H$ was applied along the major length of the ribbon samples (typically, ~4 mm) to minimize the demagnetizing field effect. Magnetization vs. temperature ($M(T)$) curves were recorded under a low applied magnetic field of 5 mT with the aim of accurately determining the value of T_C. The magnetic entropy change as a function of the temperature curves, $\Delta S_M(T)$, was obtained by numerical integration of the Maxwell relation $\Delta S_M(T) = \mu_o \int_o^{\mu_o H_{max}} \left(\frac{\partial M}{\partial T}\right)_{\mu_o H} dH$ from a set of isothermal magnetization curves $M(\mu_o H)$ measured up to $\mu_o H_{max} = 5$ T. The refrigerant capacity RC, which measures the thermal efficiency of the material on the energy transfer from cold to hot reservoirs for an ideal thermodynamic cycle, was estimated using the following three well-established methods: $RC\text{-}1 = \Delta S_M^{peak} \times \delta T_{FWHM}$ [20], $RC\text{-}2 = \int_{T_{hot}}^{T_{cold}} [\Delta S_M(T)]_{\Delta B} dT$ [21] and $RC\text{-}3$ by maximizing the product $|\Delta S_M| \times \Delta T$ below the $\Delta S_M(T)$ curve (referred to as the Wood and Potter method) [22,23]. In the case of $RC\text{-}1$ and $RC\text{-}2$, T_{hot} and T_{cold} are the temperatures that define the temperature interval of the full width at half maximum of the $\Delta S_M(T)$ curve (i.e. $\delta T_{FWHM} = T_{hot} - T_{cold}$).

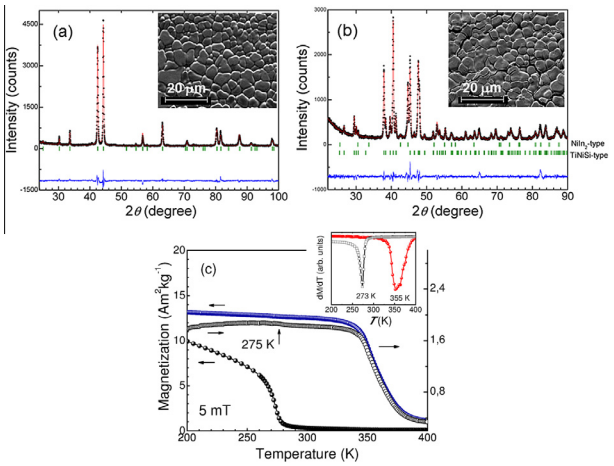

Figure 1. Experimental (red dots) and calculated (violet line) XRD patterns using the Rietveld method for (a) as-quenched and (b) annealed MnCoGe alloy ribbons. Vertical lines indicate the positions of the Bragg reflections for the hexagonal and orthorhombic phases. Insets: typical microstructure observed at the free ribbon surface. (c) $M(T)$ and dM/dT vs. T curves (inset) at 5 mT for aq (open squares) and annealed (full circles) MnCoGe ribbons. The horizontal arrows indicate the heating/cooling regime. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 1(a and b) shows the room-temperature XRD patterns obtained for the as-quenched (aq) and annealed samples, respectively. Both patterns were refined using the FullProf analytical package based on the Rietveld method [24], with good reliability factors from the refinements (aq sample: $R_B = 9.3\%$, $R_f = 9.3\%$ and $\chi^2 = 2.2$; annealed sample: $R_B = 3.6\%$, $R_f = 3.3\%$, and $\chi^2 = 2.0$).

As-quenched ribbons crystallize as a single-phase hexagonal $NiIn_2$-type structure with lattice parameters $a = 4.083(1)$ Å and $c = 5.313(1)$ Å, which roughly agree with those reported for bulk alloys [3]. The homogeneous distribution of chemical elements and the single-phase character of the ribbons were also confirmed by SEM examinations in the backscattered electron emission mode (i.e. no minor or secondary phases were detected). Numerous EDS analyses performed on both cross-section and ribbon surfaces for different ribbon flakes confirmed that the average chemical composition of the samples is close to the nominal one (i.e. 1:1:1) within experimental error (~0.1% wt.). The XRD pattern corresponding to the annealed sample (Fig. 1b) reveals the formation of an orthorhombic TiNiSi-type structure as the major phase (98% wt.), with lattice parameters $a = 5.958(2)$ Å, $b = 3.822(1)$ Å and $c = 7.059(2)$ Å (in agreement with Refs. [3,4]). A residual amount of the hexagonal phase (~2% wt.; $a = 4.060(1)$ Å; $c = 5.344(1)$ Å) is also present in the sample.