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Table-like magnetocaloric effect and enhanced refrigerant capacity in crystalline $Gd_{55}Co_{35}Mn_{10}$ alloy melt spun ribbons

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ABSTRACT

$Gd_{55}Co_{35}Mn_{10}$ ribbons were prepared by melt-spinning and subsequent crystallization treatment. Crystallization resulted in the precipitation of the Gd_3Co-type and $Gd_{12}Co_7$-type phases in the amorphous matrix. Under a magnetic field change of 0–5 T, a table-like magnetocaloric effect, with a maximum magnetic entropy change $(-\Delta S_M)^{max}$ of 5.46 J kg^{-1} K^{-1} in the temperature range of 137–180 K and enhanced refrigerant capacity (RC) of 536.4 J kg^{-1}, was achieved in $Gd_{55}Co_{35}Mn_{10}$ ribbons crystallized at 600 K for 30 min. The table-like $(-\Delta S_M)^{max}$ feature and enhanced RC values make $Gd_{55}Co_{35}Mn_{10}$ crystallized ribbons promising for Ericsson-cycle magnetic refrigeration in the temperature range from 137 to 180 K.

1. Introduction

Magnetic refrigeration (MR) based on the magnetocaloric effect (MCE) is expected to overcome the limitations of vapor-compression refrigeration. MR technology has several advantages over conventional vapor-compression refrigeration technology, such as improved energy efficiency, environmental friendliness and compactness [1–3]. Therefore, the working material for MR technology has been intensively investigated and a number of magnetocaloric materials (MCMs) have been developed in recent years. The properties of MCMs must meet the performance requirements of the thermodynamic cycles. As a regenerative cycle, the Ericsson cycle (composed of two isothermal and two isomagnetic field processes) is well suited for large temperature-span magnetic refrigerators and has been widely applied in room temperature magnetic refrigeration [4]. For efficient operation of an Ericsson cycle, a constant magnetic entropy change (ΔS_M) over the operating temperature range (known as "table-like" MCE) is required, hence it is essential to develop suitable MCMs by tailoring their magnetocaloric properties to broaden the $(-\Delta S_M) - T$ curves [5,6]. Furthermore, the broadened $(-\Delta S_M) - T$ curve usually brings about concomitant improvement in the refrigerant capacity (RC) [7], which is also crucial for MCMs used in an Ericsson thermodynamic cycle.

To achieve a table-like $(-\Delta S_M) - T$ curve in a single-phase crystalline material is a difficult task, since such materials usually have narrow $(-\Delta S_M) - T$ curves. To overcome this obstacle, a natural idea is to manufacture materials consisting of several ferromagnetic compounds with appropriate mass fraction and appropriately "close" Curie temperatures (T_Cs). The similar values of $(-\Delta S_M)$ and tunable T_C in $La(Fe_{1-x}Co_x)_{11.44}Al_{1.56}$ alloys ($x = 0.04, 0.08, 0.12$) can yield table-like characteristics in the $(-\Delta S_M) - T$ curve [8]. Therefore, the composite system composed of these compounds can act as MCMs [8]. Using the experimental data of $LaFe_{10.7}Co_{0.8}Si_{1.5}$ and $La_{0.6}Pr_{0.4}Fe_{10.7}Co_{0.8}Si_{1.5}$ alloys, a $(LaFeCoSi)_{1-x}/(LaPrFeCoSi)_x$ composite system was designed and fabricated based on the rule of mixtures, which exhibited the desired table-like $(-\Delta S_M) - T$ curve for $x = 0.45$ [9]. A sintered layer structural composite, composed of three kinds of $RA1_{2.15}$ (R = Rare earth) layers, has also been shown to be suitable for the Ericsson cycle at low temperatures [5]. $Eu_8Ga_{16}Ge_{30}$-EuO composites, prepared by repetitive grinding and appropriate mass fraction of the two component alloys, exhibit table-like MCE and large RC value of ~ 665 J/kg for a field change of 5 T in the temperature range of 20–80 K [10]. Two types of composite materials with varying Ce content were obtained by assembling the ribbons in a layer by layer fashion or mixing the powders of amorphous $Fe_{78-x}Ce_xSi_4Nb_5B_{12}Cu_1$ ($x = 0, 1, 3, 5, 10$) alloy ribbons [11]. These materials exhibited a nearly constant value of $(-\Delta S_M)$ over a temperature span of ~ 80 K and enhanced RC values (273–317 J/kg, $\Delta\mu_0 H = 5$ T) [11]. Recently, Zhong et al. [12] reported multilayer

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and bulk $Gd_{65}Mn_{25}Si_{10}$-Gd (weight ratio of 7:3) composite materials composed of amorphous $Gd_{65}Mn_{25}Si_{10}$ and crystalline Gd. Under a magnetic field change of 0–5 T, a table-like MCE in a wide temperature span over 73 K (220–293 K), enhanced ΔT_{FWHM} and large RC values were obtained for both composites. However, there are some limitations of these composite systems, such as low density and the formation of an intermediate layer from the solid-state reaction between adjacent layers [13].

Alternatively, composites formed by multiple successive magnetic phase transitions could also broaden the $(-\Delta S_M) - T$ curves and overcome the above disadvantages. Two examples of alloys with table-like MCE are Gd-Co-Al alloys prepared by arc-melting and suction-casting [14] and the $(Gd_{1-x}Er_x)$NiAl series of alloys [15]. Multiphase composites obtained by crystallization of amorphous alloys can be more useful than alloys exhibiting multiple successive magnetic phase transitions. Gd-Ni-Al amorphous-nanocrystalline composites produced by the melt-spinning method exhibit double magnetocaloric effect (MCE) plateaus [16]. A similar table-like MCE was found in $Gd_{56}Ni_{15}Al_{27}Zr_2$ composites prepared by suction-casting, which is attributed to the coexistence of crystalline and amorphous phases [17]. In our previous works [18,19], partially crystalline $Gd_{65}Mn_{25}Si_{10}$ alloy ribbons consisting of an amorphous matrix, α-Gd and $GdMn_2$ nanocrystals [18] as well as fully crystallized $Gd_{55}Co_{35}Ni_{10}$ alloy ribbons with $Gd_{12}Co_7$-type and Gd_4Co_3-type crystalline phases [19] were shown to possess table-like MCE and enhanced RC values.

However, only a few studies investigated the influence of heat-treatment of amorphous MCMs to obtain an in-situ amorphous-nanocrystalline structure with multiple successive magnetic phase transitions and table-like $(-\Delta S_M) - T$ curves. In our previous work, the thermal stability, magnetic and magnetocaloric properties of $Gd_{55}Co_{35}M_{10}$ (M = Mn, Fe, and Ni) amorphous alloys were systematically investigated [20]. Up to now, the effect of heat treatment on the magnetic and magnetocaloric properties of $Gd_{55}Co_{35}Mn_{10}$ amorphous alloys has not been studied. It is unclear whether crystallized $Gd_{55}Co_{35}Mn_{10}$ alloy ribbons will also show a table-like MCE like crystallized $Gd_{55}Co_{35}Ni_{10}$ alloy ribbons. In this paper, the effect of crystallization treatment on the structure, magnetic and magnetocaloric properties of $Gd_{55}Co_{35}Mn_{10}$ melt-spun ribbons was investigated. The results show that a nearly table-like MCE, with $(-\Delta S_M)^{max}$ of 5.46 $J\,kg^{-1}\,K^{-1}$ (5 T) in the temperature range from $\sim$137 to 180 K and enhanced refrigerant capacity (RC) of 536.4 $J\,kg^{-1}$ was achieved in $Gd_{55}Co_{35}Mn_{10}$ alloy ribbons crystallized at 600 K for 30 min. This temperature range of 120–180 K has been used in a wide range of fields such as liquefied natural gas, military projects, space technology, medicine, biology, life sciences, and so on. Therefore, these experimental results can be used for such application.

2. Experimental details

$Gd_{55}Co_{35}Mn_{10}$ alloy was prepared by arc melting pure Mn, Co (> 99.95 wt% in purity) and Gd (> 99.98 wt% in purity) in argon atmosphere. Additional 5.0 wt% of Mn was added to compensate the volatilization of Mn in arc-melting. In the process of melting, the ingot was turned over and re-melted four times to ensure homogeneity. After arc-melting the weight loss was less than 1.5 wt%. Then the ingot was crushed into small pieces and put into a quartz tube. After vacuuming and argon gas flushing, induction heating was used to melt the pieces. The ribbons were obtained by a copper single-roller melt spinning technique with a circumferential speed of 50 m/s. The widths and thicknesses of the ribbons were $\sim$1 mm and $\sim$15 µm, respectively. The as-spun $Gd_{55}Co_{35}Mn_{10}$ alloy ribbons were sealed in a quartz tube with argon atmosphere, and crystallization heat treatment was carried out at a temperature determined from the DSC results.

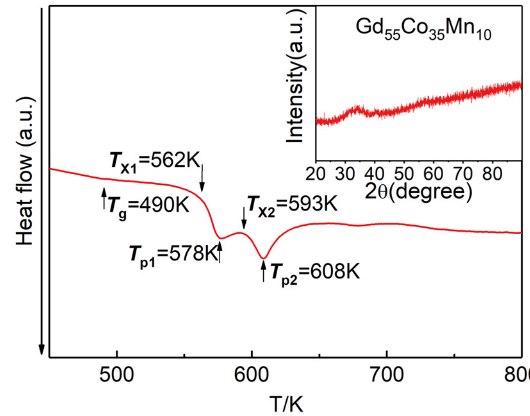

Fig. 1. DSC curve of the as-spun $Gd_{55}Co_{35}Mn_{10}$ alloy ribbons, measured at a heating rate of 20 K/min. The inset shows the XRD pattern of the as-spun $Gd_{55}Co_{35}Mn_{10}$ alloy ribbons.

To characterize the structure of $Gd_{55}Co_{35}Mn_{10}$ ribbons, X-ray diffraction (XRD) measurements were performed with a Philips diffractometer using Cu K_α radiation. Differential scanning calorimetry (DSC) data were collected at a heating rate of 20 K/min under a protective atmosphere using a Netzsch STA449C Thermal Analyzer. Magnetic measurements were carried out over a temperature range from 10 to 300 K on a Quantum Design Physical Property Measurement System (model PPMS-9).

3. Results and discussion

The inset of Fig. 1 shows the XRD pattern of the as-spun $Gd_{55}Co_{35}Mn_{10}$ alloy ribbons. The broad diffraction peaks illustrate the fully amorphous characteristics of the as-spun $Gd_{55}Co_{35}Mn_{10}$ alloy ribbons. The DSC curve of the as-spun $Gd_{55}Co_{35}Mn_{10}$ alloy ribbons is shown in Fig. 1. The as-spun ribbons exhibit two exothermic peaks corresponding to crystallization during heating. The glass transition temperature (T_g), the onset temperature of the first and second crystallization peaks (T_{x1}, T_{x2}), marked on the DSC trace, are 490 K, 562 K and 593 K, respectively. The T_g and T_{x1} of the ribbons are far higher than room temperature, which indicates that the structure and magnetocaloric properties are stable at room temperature. The crystallization peak temperatures T_{p1} and T_{p2} are 578 K and 608 K, respectively.

The effect of crystallization time on the crystallization behavior of the as-spun $Gd_{55}Co_{35}Mn_{10}$ alloy ribbons is shown in Fig. 2, which displays the XRD patterns of the $Gd_{55}Co_{35}Mn_{10}$ ribbons crystallized at 600 K for 20 and 30 min, respectively. When the as-spun ribbons was crystallized at 600 K for 20 min, only the Gd_3(Co, Mn) phase, with space group Pnma, precipitated in the amorphous matrix, indicating that a two phase structure, consisting of the Gd_3(Co, Mn) phase and the amorphous matrix phase, was obtained. A small mass fraction of the $Gd_{12}(Co, Mn)_7$ phase with space group $P2_1/c$ also precipitated in the amorphous matrix when the ribbons were crystallized at 600 K for 30 min. As a result of the finite heating rate of 20 K/min, T_{x1}, T_{p1}, T_{x2}, and T_{p2} can shift to higher temperatures. Therefore, samples crystallized at 600 K (T_{x2} < 600 K < T_{p2}) for 30 min can show precipitates corresponding to the second crystallization peak [19]. Gd_3(Co, Mn) is the first crystalline phase and $Gd_{12}(Co, Mn)_7$ is the second crystalline phase to form, corresponding to the first and second exothermic peaks displayed in Fig. 1, respectively. No $Gd_{12}(Co, Mn)_7$ phase was detected in the XRD patterns of samples annealed at 600 K for 20 min, which may be caused by the longer incubation time for nucleation of the $Gd_{12}(Co, Mn)_7$ phase.

Fig. 3 presents the temperature dependence of magnetization of the as-spun and as-annealed $Gd_{55}Co_{35}Mn_{10}$ alloy ribbons un-