Magnetocaloric Effect in Uncoated Gd$_{35}$Al$_{20}$Co$_{25}$ Amorphous Wires


School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, People’s Republic of China

School of Materials Science and Engineering, Inner Mongolia University of Technology, Hohhot 010051, People’s Republic of China

Institute for Composites Science and Innovation – InCSI, College of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

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The Gd$_{35}$Al$_{20}$Co$_{25}$ amorphous wires exhibit a relatively strong magnetocaloric effect (MCE). These melt-extracted amorphous wires display second-order magnetic transition (SOMT) and the value of maximal magnetic entropy ($\Delta S_m$) for the melt-extracted wires is calculated to be ~9.7 J kg$^{-1}$ K$^{-1}$ around the Curie point ($T_c$) of ~110 K with applied field of 5 T. Moreover, the melt-extracted amorphous wires show a high refrigerating efficiency with a relatively large cooling power (RCP, ~804 J kg$^{-1}$) and refrigeration capacity (RC, ~580 J kg$^{-1}$) under an applied magnetic field of 5T due to the broad paramagnetic-ferromagnetic (PM-FM) region associated with amorphous alloys. These favorable properties make melt-extracted Gd-based amorphous wires to be the potential refrigerant for magnetic refrigeration (MR) of liquid oxygen.

Keywords: melt-extraction, amorphous microwires, magnetic entropy change, refrigerating efficiency

1. Introduction

Magnetic refrigeration (MR) based on the magnetocaloric effect (MCE) of refrigerant has attracted more increasing interests of international research communities for its high-efficiency, energy saving and the possibility for replacement of traditional vapor compression refrigerators used at room temperature. The MCE and corresponding working temperature of the magnetic refrigerants are two key parameters in the MR applications. At the very low temperatures such as hydrogen and helium liquefaction range or even mK range, paramagnetic salts i.e. Dy$_2$Ga$_5$O$_{12}$ and Gd$_2$Ga$_5$O$_{12}$ have been used as refrigerants in MR. Moreover, the series of refrigerants with first-order magnetic transition (FOMT) such as La(Fe,Si)$_3$, Gd(FeSi)$_3$, and MnFePAs alloys and with second-order magnetic transition (SOMT) e.g. pure Gd, Gd-based and Dy-based alloys are developed for MR which applied in liquid nitrogen or room temperatures.

The Gd-based amorphous alloys possess more interesting characteristics in MR applications among these refrigerants mentioned above. Gd is a unique member of the lanthanide series with large magnetic moment and its ground-state electronic configuration is 4f$^{7}(5d6s)^{1}$. In contrast to other rare earth metals, Gd has no orbital momentum, leading to a relatively small magnetocrystalline anisotropy and a wide composition range which is possible by alloying predominantly magnetic 3d transition elements. Gd-based amorphous magnetic refrigerants also show some advantages over the crystalline materials due to their larger temperature range of paramagnetic-ferromagnetic (PM-FM) which leading to large relatively cooling power (RCP) and refrigeration capacity (RC). This characteristic renders the amorphous alloys as the attractive candidates for magnetic refrigerators although their entropy change is much lower than that of crystalline materials. Moreover, Gd-based amorphous materials display many excellent properties due to their unique long-range disorder structure, i.e. relatively higher electrical resistivity thus reducing eddy currents, higher corrosion resistance for absence of grain boundaries, higher cost effectiveness, more excellent softly magnetic properties and outstanding mechanical properties.

In this paper, an improved rapid quenching method named melt-extraction technique is applied for fabricating Gd-based amorphous wires. In comparison with the conventional methods, the melt-extraction method has a larger cooling rate of ~10$^4$–10$^5$ K s$^{-1}$, thus the melt-extracted amorphous wires exhibit higher degree of amorphization than the components of bulk metallic glasses (BMGs) or amorphous ribbons. A variety of amorphous wires with excellent giant magneto-impedance (GMI) effects and mechanical properties were fabricated with this method. Herein, the MCE properties of melt-extracted Gd$_{35}$Al$_{20}$Co$_{25}$ (at%) amorphous microwires are systematically investigated and these results display the melt-extracted Gd-based amorphous wires as a great promising refrigerant for magnetic refrigeration (MR) applications in liquid oxygen range.
2. Experimental

An ingot with nominal composition of Gd$_{55}$Al$_{20}$Co$_{25}$ was firstly prepared in argon atmosphere by arc melting and then suction casted into an alloy rod with diameter of ~10 mm. The raw materials are high-pure Gd (99.50%), Al (99.99%) and Co (99.99%) crystals. Subsequently, the rod was re-melted in a boron nitride (BN) pot by electro-magnetic induction and the melt was extracted by a copper wheel with high-speed rotation. The specific processing parameters are as follows: 1) the diameter and knife-edge of copper wheel are 320 mm and 60°, respectively; 2) linear velocity of the copper wheel is fixed at around 30 m/s; 3) the feeding rate of the melt is fixed at 20 μm/s.\textsuperscript{[12]} The morphology of melt-extracted Gd$_{55}$Al$_{20}$Co$_{25}$ amorphous microwires was observed on a field-emission scanning electron microscope (SEM-Helios Nanolab600i) at 20 kV. The phase structure information of these as-extracted wires was identified by X-ray diffraction (XRD) method and the pattern was obtained on a D/max-rb (Rigaku) with Cu Ka radiation at room temperature. The glass transition temperature ($T_g$) and initial temperature of crystallization ($T_x$) of the as-extracted wires were confirmed by exploring the thermo analysis on a differential scanning calorimeter (DSC) with heating rate of 20 K/min. The magnetocaloric effect (MCE) of the Gd-based microwires was evaluated by measuring isothermal magnetizations ($M-H$) curves on a commercial magnetic property measurement system (SQUID-VSM) performed by Quantum Design, the external magnetic field change ($\Delta H$) and the pattern was defined as glass transition temperature ($T_g$). The temperature of ~637 K marked by purple unidirectional arrow is denoted as temperature range of super-cooled liquid can be calculated by $\Delta T_g = T_{x1} - T_g$ and the result is ~52 K.

3. Results and Discussions

3.1. Structure characteristics

As shown in inset of Figure 1a, the Gd$_{55}$Al$_{20}$Co$_{25}$ microwires fabricated by the melt-extraction method are of high quality for their smooth surfaces and uniform diameters from ~20-30μm. The micro-size of the wires means a large specific surface area which benefits the heat exchange in cooling system. As shown in Figure 1a, only a broad diffuse peak appears at ~33° in the XRD pattern, indicating the amorphous characteristic of these Gd-based microwires.

Further to explore the thermal stability and confirming the amorphous feature of melt-extracted microwires, differential scanning calorimeter (DSC) analysis is performed over a temperature range of 400-800 K. As shown in Figure 1b, the DSC curve has an obvious endothermic reaction peak appearing at ~585 K (marked by green unidirectional arrow, defined as glass transition temperature ($T_g$)), then followed by several exothermic peaks owing to the crystallization of the amorphous phase. The result is consistent with that of BMGs, and the several endothermic peaks display a complex and multi-step crystallization of the wires during the heating process. The temperature of ~637 K marked by purple unidirectional arrow is denoted as temperature range of crystallization ($T_x$), then the temperature range of super-cooled liquid can be calculated by $\Delta T_x = T_{x1} - T_x$ and the result is ~52 K.

3.2. Magnetocaloric properties

The temperature dependence of magnetization ($M-T$) of the melt-extracted Gd$_{55}$Al$_{20}$Co$_{25}$ microwires was therefore measured in the applied field of 200 Oe from 20 to 200 K, as illustrated in Figure 2a. It clearly shows the ferromagnetic-paramagnetic transition with the temperature increasing. The derivative of $M-T$ curve is shown in the inset of Figure 2a and the Curie temperature ($T_C$) defined as the minimum value of $dM/dT$ curve is ~110 K and marked in green arrow. For exploring the PM-FM transition of the as-extracted wires, the $H/M (H=200$ Oe) ratio of the $M-T$ curve as a function of the temperature is calculated. As exhibited in Figure 2b, the Gd$_{55}$Al$_{20}$Co$_{25}$ amorphous microwires obey the Curie-Weiss law above $T_C$ and the predominant exchange interaction of the as-extracted wires is ferromagnetic below $T_C$ owing to the positive paramagnetic Curie points\textsuperscript{[14]}. The temperature data were fitted to the Curie-Weiss law and by this way, the Curie (C) and Weiss (θ) constants are determined. As shown in Figure 2b, the values of C and θ are calculated as ~5.07 emu·K/mol and ~121 K, respectively. Furthermore, the effective magnetic moments ($\mu_{eff}$) are calculated as $\mu_{eff}=6.4 \mu_B$. The large $\mu_{eff}$
is considered as the strong interaction of magnetic moment between transition metal (TM) element Co with 3d-electrons and rare-earth (RE) element Gd with 4f-electrons in the disordered amorphous wires, thus the excellent MCE of wires can be expected and obtained\textsuperscript{17}.

Generally, the MCE is assessed by calculating the magnetization $M$ as a function of the temperature $T$ and the applied field $H$. Thus isothermal magnetization ($M$-$H$) curves of Gd$_{55}$Al$_{20}$Co$_{25}$ microwires at different temperatures of 20-200 K, which interval is 10 K while near $T_C$ reduced to 5 K, were measured with the external magnetic fields up to 5 T ($\Delta H$=0-5 T) and the results are shown in inset of Figure 3a. To clarify the predominant exchange interactions of these microwires, the Arrott plots ($H/M$ vs. $M^2$) of the $M$-$H$ curves were calculated. As shown in Figure 3a, all the slopes of $M^2$-$H/M$ curves display positive values, also confirming that the PM-FM transition of these melt-extracted amorphous microwires is SOMT\textsuperscript{18}. In addition, the $M$-$H$ loops of these microwires at 20 K were measured and shown in Figure 3b. The low coercivity ($H_c$=30 Oe) and remanence ($M_r$=7 emu/g) indicate a soft ferromagnetic characteristic of these wires which is favorable for MR applications. Furthermore, $M$-$H$ loop at 20 K also exhibits small anisotropic field and large saturation magnetization ($M_s$), combined with the characteristics of negligible thermal hysteresis and reduced magnetic hysteresis for SOMT materials, suggesting that low magnetic fields would lead to a large magnetic entropy change ($-\Delta S_m$)\textsuperscript{19}.

The magnetic entropy change ($-\Delta S_m$) of the as-extracted wires is evaluated from $M$-$H$ curves as shown in inset of Figure 2a through Maxwell relationship\textsuperscript{9} as follows:

$$-\Delta S_m(T,\Delta H) = S(T, H_2) - S(T, H_1) = \int_{H_1}^{H_2} \frac{\partial M}{\partial T} \, dH$$

And the result is calculated by a numerical approximation of the integral in Equation 1\textsuperscript{20}:

$$-\Delta S_m(T_n) = \sum \frac{\Delta(M_{i+1} - M_i)}{\Delta(T_{n+1} - T_n)} \Delta H_i$$

where $S$ is the magnetic entropy under given temperature $T_n$, $M_i$ and $M_{i+1}$ represent the values of the magnetization at $T_n$ and $T_{n+1}$ under the applied field $H_i$, respectively.

**Figure 2.** Magnetization as a function of temperature ($M$-$T$) from 20-200 K at applied field of 200 Oe for Gd$_{55}$Al$_{20}$Co$_{25}$ metallic glass microwires (a), the inset is the derivative result of $M$-$T$ curve, (b) the ratio of applied field $H$ and magnetization $M$ as a function of temperature result ($H/M$-$T$) of the wires.

**Figure 3.** (a) Arrott plots ($H/M$ vs. $M^2$) of Gd$_{55}$Al$_{20}$Co$_{25}$ amorphous microwires constructed from isothermal magnetization ($M$-$H$) curves and the inset is the $(M$-$H$) curves at different selected temperatures from 20 K to 200 K with applied magnetic field of 0-5 T, (b) the hysteresis loop ($M$-$H$) of the as-extracted microwires measured at 20 K.
The $-\Delta S_m$ values of the melt-extracted Gd$_{25}$Al$_{25}$Co$_{25}$ amorphous microwires at different temperatures from 25 to 195 K and under the varying applied magnetic field from 0 to 5 T are shown as three-dimensional (3D) image in Figure 4. It is well-known that the value of $-\Delta S_m$ increases with the applied field increasing and maximum value ($-\Delta S_m^{\max}$) reaches as large as ~9.7 J·kg$^{-1}$·K$^{-1}$ near the Curie temperature of ~110 K under $\Delta H$=5 T. This value is slightly larger than that (~9 J·kg$^{-1}$·K$^{-1}$ at ~115 K) of its components in BMG$^{[21]}$ and almost similar to the value (~9.7 J·kg$^{-1}$·K$^{-1}$ at ~100 K) of Gd$_{25}$Al$_{25}$Co$_{25}$ metallic glass fibers$^{[22]}$ at $\Delta H$=5 T, which suggests the excellent magnetocaloric properties of melt-extracted Gd$_{25}$Al$_{25}$Co$_{25}$ amorphous microwires. But the result is smaller than that of Gd$_{25}$Al$_{25}$Co$_{25}$Zr$_3$ amorphous wires (~10.3 J·kg$^{-1}$·K$^{-1}$ at ~94 K).$^{[8]}$

For understanding the MCE response to the magnetic field of the studied wires at Curie temperature, the peak entropy change $-\Delta S_m^{\max}$ at applied field $H$ was plotted in Figure 5a and followed the relationship for SOMT materials$^{[23]}$:

$$-\Delta S_m^{\max} \propto H^n$$  \hspace{1cm} (3)

The fitting curve of $-\Delta S_m^{\max}$ points was plotted dashed line in Figure 5a and leads to $n=0.718$, which is slightly lower than ~0.74 of Gd$_{25}$Al$_{25}$Co$_{25}$Zr$_3$ amorphous microwires$^{[24]}$ and ~0.738 of Gd$_{25}$Al$_{25}$Co$_{25}$ metallic glass microfibers$^{[22]}$. Commonly, the value $n$ is 2/3 (~0.667) corresponding to mean field theory$^{[25]}$, the deviation of the value for the studied wires is considered resulting from the inhomogeneous distribution on the amorphous matrix of nano-crystals in these wires. These nano-crystals formed during the melt-extracted process were considered for improving magnetic and mechanical properties of the amorphous alloys$^{[13]}$.

The relatively cooling power (RCP) of the melt-extracted Gd$_{25}$Al$_{25}$Co$_{25}$ amorphous microwires was calculated by the product between $-\Delta S_m^{\max}$ and full width at half-maximum of the calculated $-\Delta S_m$ peak ($\delta$FWHM$^{[2]}$)

$$RCP = -\Delta S_m^{\max} \times \delta_{\text{FWHM}} = -\Delta S_m^{\max} \times (T_2 - T_1)$$  \hspace{1cm} (4)

where $T_1$ and $T_2$ are the onset and offset temperatures of $\delta$FWHM and the related results are shown in Figure 5b. The $\delta$FWHM and maximal RCP value are 83 K and ~804 J·kg$^{-1}$ respectively at $\Delta H$=5 T. The value is larger than that (~800 J·kg$^{-1}$) of its component in BMG$^{[21]}$. Cooling efficiency of the studied wires is also evaluated by using refrigeration capacity (RC):

$$RC = \int_{T_1}^{T_2} -\Delta S_m(T) dT$$  \hspace{1cm} (5)

where $T_1$ and $T_2$ are same as those in Equation 4, and generally RC is ~3/4 of RCP$^{[25]}$ due to the broad triangular shape of $-\Delta S_m$ vs. $T$ peaks in these amorphous wires. The calculated results were also displayed in Figure 5b and for $\Delta H$=5 T, the RC of studied wires is ~580 J·kg$^{-1}$, and this result is larger than that (541 J·kg$^{-1}$) of Gd$_{25}$Al$_{25}$Co$_{25}$ BMG$^{[20]}$, but less than that (652 J·kg$^{-1}$) of Gd$_{25}$Al$_{25}$Co$_{25}$ metallic glass fibers$^{[22]}$. Thus, the large RCP and RC values display the excellent cooling efficiency and MCE of Gd$_{25}$Al$_{25}$Co$_{25}$ amorphous microwires.

The large degree of amorphization due to the large cooling speed during the melt-extracted process and shape effect of the wires are considered for resulting in the excellent MCE of these Gd-base wires. As well-known, the long-range disorder microstructure of the amorphous alloys results in the fluctuation of exchange integrals, thus leading to broaden the PM-FM region of magnetic transition.
in the amorphous wires\(^{26}\). In addition, when the axis of all measured melt-extracted Gd-based microwires are arranged parallel to the magnetic field direction, the demagnetizing factor (N) is determined to be ~0 due to the shape effect. Compared with its component in BMG or ribbon shape with \(n=0\), the \(-\Delta S_m\) increased significantly when temperatures are below \(T_C\), while the \(-\Delta S_m\) almost remained unchanged as temperatures above \(T_C^{[27]}\).

4. Conclusions

Gd\(_{55}\)Al\(_{20}\)Co\(_{25}\) amorphous microwires with excellent magnetocaloric effect were fabricated by a melt-extraction method with high quenching speed (~10\(^{-8}\) K/s). The predominant exchange interaction of as-extracted wires is SOMT around Curie temperature and the \(-\Delta S_m\) is calculated to be ~9.7 J·kg\(^{-1}\)·K\(^{-1}\) at ~110 K as \(\Delta H=5\) T. The RCP and RC of the wires are ~804 J·kg\(^{-1}\) and ~580 J·kg\(^{-1}\) respectively when \(\Delta H=5\) T. The excellent MCE of the melt-extracted Gd\(_{55}\)Al\(_{20}\)Co\(_{25}\) amorphous microwires is considered due to the high degree of amorphization and their size effect.

References


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