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Gd–Dy–Al–Co bulk metallic glasses with large magnetic entropy change and refrigeration capacity

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ABSTRACT

Novel $Gd_{56-x}Dy_xAl_{24}Co_{20}$ (x = 0, 14, 17) bulk metallic glasses (BMGs) were prepared by copper mold casting. They exhibit magnetic entropy changes (ΔS_M) comparable to that of $Gd_{53}Al_{24}Co_{20}Zr_3$ BMG and crystalline Gd. Moreover, these glassy alloys have broad entropy change peaks, resulting in the refrigeration capacities of 751.4 J kg^{-1}, 702.8 J kg^{-1}, and 682.3 J kg^{-1} for $Gd_{56}Al_{24}Co_{20}$, $Gd_{42}Dy_{14}Al_{24}Co_{20}$, and $Gd_{39}Dy_{17}Al_{24}Co_{20}$ at 5 Tesla. The large magnetocaloric effect makes these BMGs attractive candidates as magnetic refrigerant in temperature range of 50–140 K. It is also found that the Curie temperature of this kind of metallic glass linearly declines with the increase of Dy. The ΔS_M of metallic glasses reaches maximum at certain content of Dy. These findings are expected to provide a meaningful guidance for the composition design of rare earth based glassy alloys for refrigeration application.

1. Introduction

The magnetocaloric effect (MCE) arises from the reorientation of magnetic moments when exposed to an external varying magnetic field. The adiabatic magnetization gives rise to an increase of the temperature of a material, *vice versa*, it is cooled as the adiabatic demagnetization is proceeded [1]. This magnetization/demagnetization cycles are similar to compression/expansion of gas and can be used for refrigeration. Compared with conventional gas refrigeration, the magnetic refrigeration technology has advantages of both in high efficiency and environmentally friendliness. During the past two decades, magnetic refrigeration techniques based on MCE have attracted extensive attention. Recently, with the discovery of the giant magnetocaloric effect (GMCE) materials, *e. g.*, Gd–Si–Ge [2], Mn–As–Sb [3], La–Fe–Si [4], Mn–Fe–P–As [5], the interest in the magnetic refrigeration technology has further been enhanced.

Metallic glasses possess special merits such as tailorable ordering temperature, high electrical resistivity and high corrosion resistance [6]. In addition, the broadness of magnetic transition from paramagnetic to magnetically ordered state also results in the improvement of refrigeration capacity [7]. Very recently, some scholars began to concentrate their efforts on amorphous materials with large MCE. It has been shown that rare earth (RE) based bulk metallic glasses (BMGs) are attractive due to their large magnetic moments and intricate spin structure. Erenow, heavy rare earth (HRE) Gd-based [8–11], Ho-based [12], Dy-based [13], and Er-based [14,15] BMGs have been measured to have large MCE, indicating their promising future as candidate for magnetic refrigeration.

We have reported our findings of the excellent magnetic entropy changes of 15.78 J kg^{-1} K^{-1}, 13.86 J kg^{-1} K^{-1} and 9.64 J kg^{-1} K^{-1} in $Gd_{40}Dy_{16}Al_{24}Co_{20}$, $Gd_{36}Dy_{20}Al_{24}Co_{20}$, and $Gd_{34}Dy_{22}Al_{24}Co_{20}$, respectively [16]. In this work, we further investigate the MCE of Gd–Dy–Al–Co bulk metallic glasses by changing the content of Dy in these glassy alloys. We detected excellent refrigeration capacities in this system. Here we present the new experimental data and investigate the feature of magnetic properties of this system.

2. Experimental

The master alloys with nominal composition of $Gd_{56-x}Dy_xAl_{24}Co_{20}$ (x = 0, 14, and 17) were prepared by arc melting the mixture of high-purity Gd (99.95%), Dy (99.95%), Al (99.95%) and Co (99.95%) under a Ti-gettered argon atmosphere in a watercooled copper crucible. Each ingot was remelted for four times to ensure the homogeneity of composition. The master alloy was then remelted and suctioned into a copper mold to obtain cylindrical rod of 2 mm in diameter. The amorphous structure of the as-cast rods was ascertained by using a Rigaku D/max-3B diffractometer with Cu Kα radiation at 40 keV. Thermal analysis of the specimen was carried out by a Netzsch STA 449C differential scanning calorimeter (DSC) at the rate of 20 K min^{-1}. The temperature and magnetic field dependences of magnetization were measured in physical properties measurement system, PPMS 9, of Quantum Design Company.

3. Results and discussion

The XRD patterns and DSC traces obtained from the as-cast $Gd_{56-x}Dy_xAl_{24}Co_{20}$ (x = 0, 14, and 17) rods with 2 mm in diameter are shown in Fig. 1. A typical broad halo without appreciable

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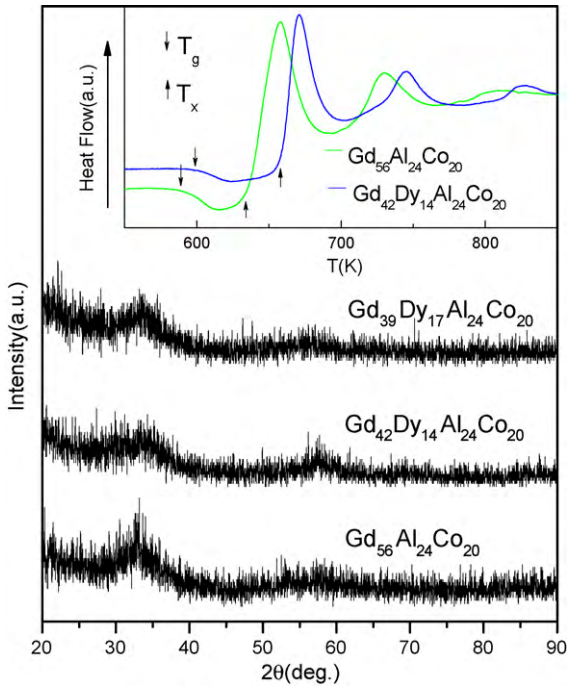

Fig. 1. XRD patterns of as-cast $Gd_{56-x}Dy_xAl_{24}Co_{20}$ (x = 0, 14, and 17) rods with 2 mm in diameter. The DSC traces correspond to x = 0 and x = 14.

crystalline peak is observed, indicating that a fully amorphous state is formed. The glassy feature of the specimen can be further confirmed by their DSC traces. As shown in the inset of Fig. 1, the traces exhibit obvious endothermic reactions in $Gd_{56}Al_{24}Co_{20}$ and $Gd_{42}Dy_{14}Al_{24}Co_{20}$ due to the glass transition. The glass transition temperature, T_g, and first crystallization temperature, T_x, are 589 K, 634 K for $Gd_{56}Al_{24}Co_{20}$, and 599 K, 658 K for $Gd_{42}Dy_{14}Al_{24}Co_{20}$, respectively, resulting in the supercooled liquid region, ΔT_x (=$T_x - T_g$), of 45 K and 59 K. Obviously, the addition of Dy not only increases the thermal stability *via* T_g and T_x but also the ΔT_x. The decrease of Al in $Gd_{56}Al_{24}Co_{20}$ by 1% as compared with $Gd_{55}Al_{25}Co_{20}$ [11,16–18], does not change T_g obviously, but increases the T_x by 20 K.

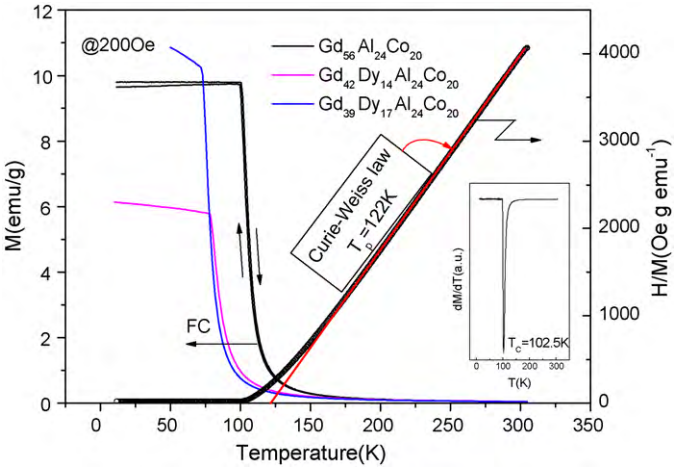

Fig. 2. Temperature dependence of the magnetization for $Gd_{56}Al_{24}Co_{20}$, $Gd_{42}Dy_{14}Al_{24}Co_{20}$ and $Gd_{39}Dy_{17}Al_{24}Co_{20}$ metallic glasses. The plot in right hand is the temperature dependence of the ratio H/M (the dash line is the fit for the linear part of H/M curve) for $Gd_{56}Al_{24}Co_{20}$. The inset shows the T_C of $Gd_{56}Al_{24}Co_{20}$ as an example.

Fig. 2 shows the temperature dependence of the magnetization (M–T curve) of specimen in field cooling (FC) mode in a field of 200 Oe at the temperature range of 305–2 K. The Curie temperature (T_C), which is defined by the minimum in the temperature dependence of the first order derivative of the magnetization (dM/dT, where M is the magnetization and T is the temperature), have been determined from the M–T curve (as shown in the inset of Fig. 2). For $Gd_{56}Al_{24}Co_{20}$, the T_C is measured to be about 102.5 K and 103.5 K during cooling and heating. Instead of showing a large thermal hysteresis in crystalline magnetocaloric substances [19], the cooling and heating magnetization curves of $Gd_{56}Al_{24}Co_{20}$ metallic glasses almost overlap, meaning that the thermal hysteresis can be eliminated. Such feature can be also considered as one of the merits of amorphous alloys. For $Gd_{42}Dy_{14}Al_{24}Co_{20}$ and $Gd_{39}Dy_{17}Al_{24}Co_{20}$, their cooling Curie temperatures are 81.5 K and 76 K, respectively. The resulting T_C indicates that the addition of Dy decreases the T_C because the T_C of Dy is much lower than that of Gd [20]. From Fig. 2, one can get the plot of the ratio H/M (H is the external field) as a function of the temperature. It is shown that $Gd_{56}Al_{24}Co_{20}$ alloy obeys the Curie–Weiss law at temperature above 170 K, with a paramagnetic Curie temperature T_p = 122 K. $Gd_{42}Dy_{14}Al_{24}Co_{20}$ and $Gd_{39}Dy_{17}Al_{24}Co_{20}$ also exhibit the same behavior. Below the T_C, their magnetic states are ferromagnetic, which also can be confirmed from the magnetization curve in the following test. The discrepancy of magnetization per unit mass between $Gd_{42}Dy_{14}Al_{24}Co_{20}$ and $Gd_{39}Dy_{17}Al_{24}Co_{20}$ is almost 5.5 emu g^{-1} below their T_Cs although their mole mass is similar. Considering the difference in the magnetic structure between Gd and Dy (ferromagnetic and helimagnetic), this result indicates that the magnetic structure of these two alloys are somewhat different.

In order to explore the magnetic transition, we performed the measurement of the isothermal magnetizations (M–H) in the magnetic field of 0–50 kOe at different temperatures. Fig. 3(a) displays the M–H curve of $Gd_{39}Dy_{17}Al_{24}Co_{20}$ in temperature range of 33–112 K. In the vicinity of T_C, the temperature step of 2 K was chosen. For the regions far away from their T_C, the steps are 4 K or 7 K. The magnetization of $Gd_{39}Dy_{17}Al_{24}Co_{20}$ BMG rises abruptly at a rather low critical field and below its transition temperature, and then shows a tendency of rapid saturate, indicating that the alloy is in the ferromagnetic state. In contrast, the curves gradually changes to straight lines above the T_C, suggesting that it gradually switches from ferromagnetic to paramagnetic state. In this work, it has been also proved that $Gd_{56}Al_{24}Co_{20}$ and $Gd_{42}Dy_{14}Al_{24}Co_{20}$ exhibit the same magnetic behavior near their T_C where a second order phase transition occurs.

The isothermal magnetic entropy change (ΔS_M) can be calculated from the magnetization curves, which can be derived from Maxwell relation by integrating over the magnetic field

$$\Delta S_M(T,H) = S(T,H) - S(T,0) = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T}\right)_H dH \quad (1)$$

where $H_{\max}$ represent the maximum value of magnetic field. From Eq. (1), it is clear that a large MCE can be observed near the transition temperature when the magnetization changes distinctly in a constant field. The sign of ΔS_M is determined by the sign of $\partial M/\partial T$. If it is negative, a traditional MCE will be observed. Here we calculated the ΔS_M by a numerical approximation of integral introduced elsewhere [8]. Fig. 3(b) shows $-\Delta S_M$ as a function of temperature under 50 kOe. The peak values of ΔS_M are 8.84 J kg^{-1} K^{-1} at 106.5 K, 9.37 J kg^{-1} K^{-1} at 83.5 K, and 9.22 J kg^{-1} K^{-1} at 78 K for $Gd_{56}Al_{24}Co_{20}$, $Gd_{42}Dy_{14}Al_{24}Co_{20}$ and $Gd_{39}Dy_{17}Al_{24}Co_{20}$, respectively. These peak values of $-\Delta S_M$ are comparable to those of $Gd_{53}Al_{24}Co_{20}Zr_3$ [8] and pure Gd [21] and much larger than that of $Pd_{40}Ni_{22.5}Fe_{17.5}P_{20}$ [22].

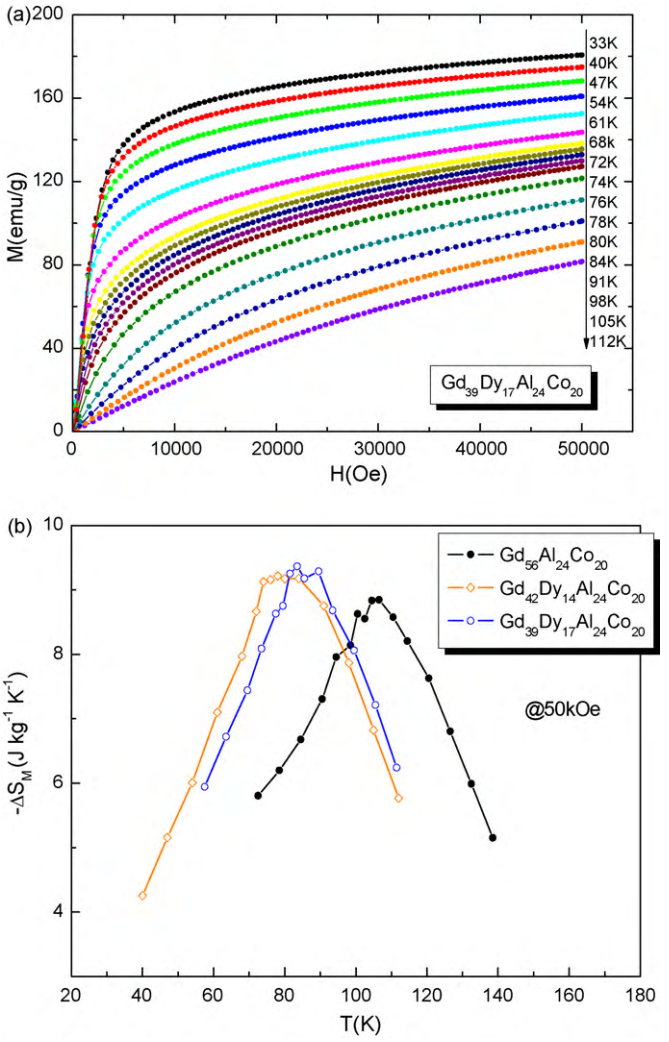

Fig. 3. (a) Isothermal magnetization as a function of magnetic field at various temperatures for $Gd_{39}Dy_{17}Al_{24}Co_{20}$, and (b) the magnetic entropy changes calculated *via* Maxwell relation under 50 kOe.

The refrigeration capacity (RC) is also an important parameter to evaluate the integrated MCE of a substance. This parameter can be accounted by different methods [23]. Here we calculated the RC by the product of the peak entropy change and the full width at half maximum of the peak (δT_{FWHM}). It is seen that the δT_{FWHM} values of these alloys reach 85 K, 75 K and 74 K, resulting in the RC values of 751.4 J kg^{-1}, 702.8 J kg^{-1}, and 682.3 J kg^{-1} for $Gd_{56}Al_{24}Co_{20}$, $Gd_{42}Dy_{14}Al_{24}Co_{20}$ and $Gd_{39}Dy_{17}Al_{24}Co_{20}$, respectively. These RC values are much larger than those of $Gd_5Si_2Ge_2$ [2] and $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ [24]. The broadened magnetic transition observed in this system can be explained by dispersing in transition temperature induced from a local concentration fluctuation [25].

Fig. 4 shows the variation of ΔS_M and magnetic transition temperatures with the content of Dy in Gd–(Dy)–Al–Co bulk metallic glasses. Some data are collected from other references [14,16]. As mentioned before, the amount of Dy contributes to the decline of the transition temperature of this system. According to the Weiss's mean field theory [26], the T_C from paramagnetic to ferromagnetic state can be expressed as

$$T_C = 2ZA_{ex}J\frac{(J+1)}{3k_B} \quad (2)$$

where Z is the coordination number, A_{ex} the exchange integral, J the total angular momentum, and k_B is the Boltzmann constant.

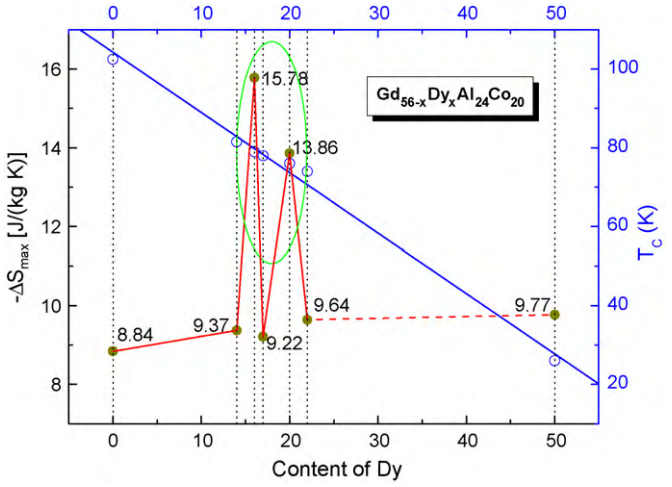

Fig. 4. The variation of ΔS_M and magnetic transition temperatures with the content of Dy in $Gd_{56-x}Dy_xAl_{24}Co_{20}$ (x = 0, 14, 16, 17, 20, and 22) bulk metallic glasses, in which x = 50 corresponds to $Gd_7Dy_{50}Al_{23}Co_{20}$. The dash line from x = 22 to x = 50 shows the uncertainty of $-\Delta S_M$.

The value of Z of amorphous alloy is similar to or even larger than that of crystalline alloy, which is often fixed to 12 [27]. Therefore, the disappearance of long-range order in amorphous alloy strongly weakens the exchange interaction between electrons, *i.e.* the structural disorder results in the derogation and fluctuation of exchange integral. From Fig. 4, it can be also seen that there are some peaks in ΔS_M at certain compositions. This may imply that the realignment of moment can be easier at special composition in the system. From this point of view, we may deduce that on the side where Dy as the master element in alloy, there is special composition which also exhibits excellent MCE. Although there is the similarity among rare earth elements, the composition where peak appears is usually unsymmetrical. It is expected that the ΔS_M for the alloy with more Dy will be larger than that with more Gd.

4. Summary

Large MCE have been obtained in $Gd_{56-x}Dy_xAl_{24}Co_{20}$ (x = 0, 14, 17). The glassy structure makes them exhibit wide breath of ΔS_M peak, leading to excellent RC among the reported magnetic materials. Their high RC combined with high electrical resistivity, outstanding mechanical properties, and tunable nature makes them attractive candidate for magnetic refrigerants in the temperature range of 50–140 K. The occurrence of maximum ΔS_M at certain composition of this system indicates that an optimal MCE can be acquired by tuning the content of Dy, providing a guidance for the composition design of rare earth based glassy alloys.

Acknowledgements

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