Large magnetocaloric effect and enhanced magnetic refrigeration in ternary Gd-based bulk metallic glasses

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The magnetocaloric effect and refrigeration capacity (RC) of Gd₅₅Co₂₀Al₂₅ and Gd₅₅Ni₂₅Al₂₀ bulk metallic glasses (BMGs) have been investigated. Large magnetic entropy changes ΔSM of 11.2 and 10.8 J kg⁻¹ K⁻¹ and large RC values of 846 and 920 J kg⁻¹ are obtained for Gd₅₅Co₂₀Al₂₅ and Gd₅₅Ni₂₅Al₂₀, respectively, at a field change of 7 T. The RC value (640 J kg⁻¹ at 5 T or 920 J kg⁻¹ at 7 T) of Gd₅₅Ni₂₅Al₂₀ BMG is larger than that reported for all magnetocaloric materials, including crystalline and amorphous materials measured under the same conditions. The large RC value is due to the broad ΔSM peak (more than 100 K), which is caused by the disordered structure of an amorphous material. The large ΔSM and RC values make these Gd-based ternary BMGs attractive candidates for magnetic refrigeration applications. © 2008 American Institute of Physics.

I. INTRODUCTION

The application of magnetic refrigeration has been extensively studied since the discovery of the magnetocaloric effect (MCE) in 1881. Magnetic refrigeration is a promising technology that has been applied in low temperatures. Materials used for magnetic refrigeration at low temperatures (T < 20 K) mainly concentrate on paramagnetic salts. However, never has a technology of the magnetic refrigeration been practically employed in the temperature region between 20 K and room temperature. The challenges for the application of magnetic refrigeration at high temperatures are to reduce the magnetic fields applied and to enhance the magnetic refrigeration efficiency. Therefore, one of the most important topics is to discover a magnetic refrigeration material with a practical value at a comparatively low magnetic field and high temperatures. The basic requirement for magnetic refrigeration materials is a large magnetic entropy change. However, a material with a large magnetic entropy change does not necessarily have high refrigeration efficiency. At present, an accepted criterion to evaluate refrigeration efficiency is refrigeration capacity (RC). In order to obtain a high refrigeration capacity, a broad ΔSM peak is also needed, as well as a high magnetic entropy change.

Usually, the study of magnetic refrigeration has been focused on crystalline materials and less work has been done on amorphous materials. Recently, the MCE was observed in transition-metal-based and rare-earth-based amorphous materials. Previous studies verified that amorphous magnetic materials can have large magnetic entropy changes comparable to (or even larger than) that of the known crystalline magnetic refrigerants. In addition, they have advantages over the crystalline magnetic refrigerants because the amorphous materials may have a larger temperature range of the half maximum peak ΔSM, as well as larger magnetic entropy changes. Furthermore, their unique properties, such as high electrical resistivity (thus small eddy current heating), tailorable nature associated with disordered structure, outstanding mechanical properties, and high thermally stability, make them good candidates for magnetic refrigeration materials. Rare-earth-based crystalline materials, such as Gd₅₅Si₂Ge₂, RCo₂, and RAl₂, have a large MCE because of the large magnetic moment of rare earth ions. In this paper, the MCE and RC of two Gd-based bulk metallic glasses (BMGs), Gd₅₅Co₂₀Al₂₅ and Gd₅₅Ni₂₅Al₂₀, are investigated.

II. EXPERIMENT

Gd₅₅Co₂₀Al₂₅ and Gd₅₅Ni₂₅Al₂₀ BMGs with nominal composition were prepared by arc melting pure Gd, Co (or Ni), and Al in a purified argon atmosphere. The ingots were remelted and suck cast into a Cu mold to obtain a cylindrical rod 2 mm in diameter. The glassy structure of the BMG alloy was ascertained by mean of x-ray diffraction (XRD) using Cu Kα radiation in a D/max-γA diffractometer with a graphite crystal monochromator. Thermal analysis was carried out in a Perkin–Elmer DSC-7 differential scanning calorimeter (DSC) under flowing purified argon. The values of glass transition temperature, Tg, and the onset crystallization temperature, Tx, were determined from the DSC traces with the accuracy of ±1 K. The temperature and field dependences of magnetization were measured by using a superconducting quantum interference device (SQUID) magnetometer.

III. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns taken from the cross-sectional surface of Gd₅₅Co₂₀Al₂₅ and Gd₅₅Ni₂₅Al₂₀ as-cast rods 2 mm in diameter. The typical broad diffraction maximum of amorphous phases for the as-cast Gd-based BMGs illustrates the glassy character of the alloys. No appreciable
peaks, corresponding to a crystalline phase, can be seen within the resolution limit of XRD. These indicate that fully amorphous rods can be obtained for these two alloys at least 2 mm in diameter. The glass nature of Gd$_{55}$Co$_{20}$Al$_{25}$ was also confirmed by the continuous DSC at a heating rate of 20 K min$^{-1}$ (as shown in the inset of Fig. 1). A clear endothermic event characteristic of a glass transition followed by a sharp exothermic crystallization peak was observed. The values of glass transition temperature, $T_g$, and the onset crystallization temperature, $T_x$, are 594 and 649 K, respectively, resulting in a supercooled liquid region $\Delta T_x (\Delta T_x = T_x - T_g)$ of 55 K. These results are consistent with those previously reported.\(^{20,21}\) The distinctive glass transition and sharp crystallization event as well as the large value of $\Delta T_x$ further confirm the excellent glass forming ability of these alloys.

Figure 2 shows the temperature dependence of magnetization at an applied field of 0.02 T for the Gd$_{55}$Co$_{20}$Al$_{25}$ and Gd$_{55}$Ni$_{25}$Al$_{20}$ alloys. The Curie temperature ($T_C$) defined by the maximum of the “absolute value” of $dM/dT$, are 105 and 80 K for Gd$_{55}$Co$_{20}$Al$_{25}$ and Gd$_{55}$Ni$_{25}$Al$_{20}$, respectively. They are much lower than that of the crystalline Gd (293 K). The reduced $T_C$ in Gd-based BMGs may be attributed to the structural disordering and the addition of alloying elements. Even though a strong disorder exists in the BMG alloys, the magnetization varies rapidly at the magnetic-ordering temperature as the crystalline magnetic material at its magnetic transition temperature. According to the Maxwell relation,

$$\frac{\partial S}{\partial H} = \frac{\partial M}{\partial T} H,$$

a large magnetic entropy change may be expected for Gd-based BMGs near $T_C$.

Isothermal magnetization curves for Gd$_{55}$Co$_{20}$Al$_{25}$ BMGs with an increasing field in a wide temperature range are shown in Fig. 3. In the vicinity of $T_C$, a temperature step of 5 K was chosen and 10 or 20 K for the regions far away from $T_C$. The sweeping rate of the field was slow enough to ensure that the data were recorded in an isothermal process. For an isothermal process, the magnetic entropy change $\Delta S_M$ can be calculated by integrating the Maxwell relation, Eq. (1),

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_{0}^{H} \left( \frac{\partial S_M}{\partial H} \right)_T dH$$

$$= \int_{0}^{H} \frac{\partial M}{\partial T} dH,$$

where $S_M(T,H)$ is the magnetic entropy in a magnetic field $H$ at temperature $T$. $S_M(T,0)$ is the magnetic entropy in the absence of the magnetic field at temperature $T$. In the case of magnetization measurements performed at a small field and temperature intervals, the numerical approximation of integral is usually applied, which is expressed as

$$\Delta S_M = \sum_{i} \frac{M_i - M_{i+1}}{T_i - T_{i+1}} \Delta H_i,$$

where $M_i$ and $M_{i+1}$ are the magnetizations measured at temperatures $T_i$ and $T_{i+1}$ in a field of $H$, respectively. By Eq. (3), the temperature dependence of $\Delta S_M$ for Gd$_{55}$Co$_{20}$Al$_{25}$ and Gd$_{55}$Ni$_{25}$Al$_{20}$ BMGs in the applied field of 7, 5, and 2 T are obtained (shown in Fig. 4). The peak values of $-\Delta S_M$ are 11.2 and 10.8 J kg$^{-1}$ K$^{-1}$ at 7 T for Gd$_{55}$Co$_{20}$Al$_{25}$ and
Gd$_5$Ni$_{25}$Al$_{20}$ BMGs, respectively. The $\Delta S_M$ values are comparable with that of Gd (13.3 J kg$^{-1}$ K$^{-1}$ in an applied field of 7 T), which has been considered as a good magnetic refrigerant.\cite{4} Table I lists the magnetic entropy changes and related parameters of various magnetic refrigeration materials. The large MCE in Gd-based BMGs is due to the large magnetic moment of Gd.

The temperature range of half maximum of the entropy change peak is 100 K for Gd$_{55}$Co$_{20}$Al$_{25}$, and 111 K for Gd$_{55}$Ni$_{25}$Al$_{20}$ alloys in a field change of 7 T (as seen in Fig. 4). These values are much larger than those of other well-known crystalline magnetic refrigeration materials. For example, the temperature range of the half maximum of the entropy change peak of Gd$_3$Si$_2$Ge$_2$ (Ref. 6) and MnFe$_{0.45}$As$_{0.55}$ (Ref. 7) is less than 30 K and that of (Mn$_{0.8}$Fe$_{0.2}$)$_3$Si$_2$Ge$_2$ (Ref. 9) and Ni$_2$Mn$_{1-x}$Cu$_x$Ga (Ref. 22) is less than 5 K. Another relevant parameter characterizing the refrigerant efficiency of the material is the RC, which is measured by different methods in literature.\cite{4,5} Usually, a large refrigerant efficiency of the material is the RC, which is measured less than 5 K. Another relevant parameter characterizing the magnetic moment of Gd.

The temperature range of half maximum of the entropy change peak is 100 K for Gd$_{55}$Co$_{20}$Al$_{25}$, and 111 K for Gd$_{55}$Ni$_{25}$Al$_{20}$ alloys in a field change of 7 T, respectively. The large MCE in Gd-based BMGs is due to the large related parameters of various magnetic refrigeration materials. For example, the temperature range of half maximum of the entropy change peak of Gd$_3$Si$_2$Ge$_2$ (Ref. 6) and MnFe$_{0.45}$As$_{0.55}$ (Ref. 7) is less than 30 K and that of (Mn$_{0.8}$Fe$_{0.2}$)$_3$Si$_2$Ge$_2$ (Ref. 9) and Ni$_2$Mn$_{1-x}$Cu$_x$Ga (Ref. 22) is less than 5 K. Another relevant parameter characterizing the magnetic refrigeration cycle operating between temperatures $T_1$ and $T_2$ of the hot and cold reservoirs is defined as $RC=\Delta S_M\Delta T$, where $\Delta S_M$ is the magnetic entropy change at the hot and cold ends of the cycle (defined equal) and $\Delta T=T_2-T_1$. For a given magnetic refrigerant, the optimum refrigeration cycle occurs when the product of $\Delta S_M\Delta T$ is at its maximum. The other method is to integrate numerically the area below the $\Delta S_M-T$ curve by using the temperatures at half maximum of the peak as the integration limits,\cite{5} which has been widely used in community. For the RC value, it is necessary to take into account the hysteresis loss. The effective refrigeration capacity is the RC that minus the hysteretic loss. But for our Gd-based BMGs, there is almost no hysteresis loss (see the hysteresis curves at the temperatures around the maximum magnetic entropy change in Fig. 5). It is expected because Gd (unlike other rare earth metals) has no orbital momentum with a relatively small magnetocrystalline anisotropy. The RC for Gd$_{55}$Co$_{20}$Al$_{25}$ is 846 J kg$^{-1}$ (7 T) or 541 J kg$^{-1}$ (5 T) obtained by the latter method. It is 920 J kg$^{-1}$ (7 T) or 640 J kg$^{-1}$ (5 T) for Gd$_{55}$Ni$_{25}$Al$_{20}$ BMG. Both of the RC values are much larger than those of most classical crystalline magnetic refrigeration materials, such as Gd$_3$Si$_2$Ge$_2$.

<table>
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<tr>
<th>Materials</th>
<th>State</th>
<th>$\Delta S_M$ (J kg$^{-1}$ K$^{-1}$)</th>
<th>Temperature (K)</th>
<th>Field (T)</th>
<th>RC (J/kg)</th>
<th>Reference</th>
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<tr>
<td>Gd$<em>{55}$Co$</em>{20}$Al$_{25}$</td>
<td>BMG</td>
<td>11.2</td>
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<td>7</td>
<td>846</td>
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<td>7</td>
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<td>5</td>
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<td>15</td>
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<td>94</td>
<td>5</td>
<td>...</td>
<td>10</td>
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<tr>
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<td>1.65</td>
<td>588</td>
<td>1.5</td>
<td>74</td>
<td>12</td>
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<td>12</td>
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<tr>
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<td>10</td>
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<tr>
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<td>5</td>
<td>360</td>
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FIG. 4. (Color online) Magnetic entropy changes $\Delta S_M$ of Gd$_{55}$Co$_{20}$Al$_{25}$ (triangle) and Gd$_{55}$Ni$_{25}$Al$_{20}$ (square) BMGs in magnetic field changes of 0–2, 0–5, and 0–7 T.

FIG. 5. (Color online) Hysteresis curve of Gd$_{55}$Co$_{20}$Al$_{25}$ BMG at 90, 95, 100, and 105 K. The inset shows the hysteresis curve of Gd$_{55}$Ni$_{25}$Al$_{20}$ at 80 K. Curves with open (or solid) symbols are measured during increasing (or decreasing) field.
Gd55Co20Al25 and Gd55Ni25Al20 BMGs, respectively. The RC value [640 J kg⁻¹ (5 T)] of Gd53Ni25Al20 BMG is even much larger than that of Gd52Al24Co20Zr3 BMG [which has the largest RC value of 590 J kg⁻¹ (5 T)] among the magnetocaloric materials reported]. These RC values are also listed in Table I.

As mentioned earlier, all the peaks for our Gd-based alloys are broad in the $\Delta S_M - T$ curve. Ikeda and Ichikawa proposed a model to explain the broadened magnetic transition observed in amorphous alloys. This model suggested that the broadened magnetic transition observed in amorphous alloys is caused by a local concentration fluctuation and the existence of a large enough local concentration fluctuation will lead to distribution in ordering temperature. Another model suggested by Liu et al. argued that the magnetic transition in all amorphous materials would be broadened because the fluctuation of exchange integrals as a result of structural disorder will always exists in amorphous alloys. In our study, the reducing of $T_C$ and the broadening peak of $\Delta S_M$ may be attributed to the structural disorder because the fluctuation of exchange integral which was caused by local concentration fluctuations always exists in amorphous alloys.

IV. CONCLUSIONS

In conclusion, Gd55Co20Al25 and Gd55Ni25Al20 BMGs with a diameter of 2 mm have been prepared by conventional copper mold suction casting. Large $\Delta S_M$ values of 11.2 and 10.8 J kg⁻¹ K⁻¹ have been achieved for Gd55Co20Al25 and Gd55Ni25Al20 BMGs, respectively, which are comparable to that of Gd [13.3 J kg⁻¹ K⁻¹ (7 T)]. In addition, for a magnetic field of 7 T, the RC values are 846 and 920 J kg⁻¹ for Gd55Co20Al25 and Gd55Ni25Al20 BMGs, respectively. The RC value of Gd55Ni25Al20 BMG is the largest among the reported values for all crystalline and amorphous materials measured under the same experimental conditions (5 T). Both Gd-based BMGs have not only a large $\Delta S_M$ but also a wide temperature range of a large $\Delta S_M$ peak. Therefore, it is expected that these BMG alloys are ideal candidates for the magnetic refrigerant application in the temperature range of 50–150 K.

ACKNOWLEDGMENTS

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