Magnetocaloric effect and critical behavior of amorphous \((\text{Gd}_4\text{Co}_3)_{1-x}\text{Si}_x\) alloys

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The amorphous alloys \((\text{Gd}_4\text{Co}_3)_{1-x}\text{Si}_x\) \((x=0, 0.05, \text{and} 0.10)\) were prepared by melt spinning. The Curie temperature can be tuned from 213 to 198 K with increasing Si content, while the maximum value of magnetic entropy change for a magnetic field change of 0–5 T can reach 7.3, 7.2 and 6.4 J kg\(^{-1}\) K\(^{-1}\) for \(x=0, 0.05\) and 0.10 respectively. Large values of the refrigerant capacity are obtained in these alloys. The saturation magnetization at 5 K equals 26.5, 24.2, and 22.4 μB per \((\text{Gd}_4\text{Co}_3)_{1-x}\text{Si}_x\) formula with \(x=0, 0.05\) and 0.10, respectively. All samples undergo a second order ferri-paramagnetic phase transition. The critical behavior around the transition temperature is investigated by means of the modified Arrott plots technique and the Widom scaling relation. The results indicate that for \(x=0\) and 0.05, the critical exponents are close to those of the 3D Ising model, while the critical exponents for \(x=0.1\) are between those of the 3D Ising model and mean-field model.

1. Introduction

The magnetic materials with large magnetocaloric effect (MCE) have attracted considerable attention for magnetic refrigeration applications. In recent years, MCE has been found in various intermetallic alloys, such as \(\text{Gd}_6\text{Si}_2\text{Ge}_2\) \([1]\), \(\text{La}[\text{FeSi}]_{13}\) \([2,3]\), \(\text{MnAs}_{1-x}\text{Sb}_x\) \([4]\), \(\text{MnFe}_1-x\text{S}_x\) \([5]\), \(\text{Ni}-\text{Mn-In} \) \([6]\) and amorphous alloy \(\text{Fe}_{88-x}\text{Co}_{x}\text{Ni}_{22}\text{Zr}_{7}\text{B}_{1.7} \) \([7]\). However, a material with a large \(\Delta S_m\) does not mean that it has a large refrigeration efficiency. The refrigerant capacity (RC) can provide an estimate of the performance of a magnetocaloric material \([8]\). To improve the efficiency of magnetic refrigeration, it is important to enhance the RC and to reduce the thermal and magnetic hysteresis of the magnetocaloric materials, which is usually associated to magnetocaloric materials with first-order phase transition.

Extensive investigations indicated that many compounds based on Gd also show large MCE, such as \(\text{Gd-Ge-Si} \) \([1]\), \(\text{Gd-Co-Mn} \) \([9]\), \(\text{Gd-Fe-Al} \) \([10]\), \(\text{Gd-Co-Ni} \) \([11]\), etc. Recently, Zhang et al. \([12]\) found that two successive magnetic-entropy changes occur in the \(\text{Gd}_4\text{Co}_3\) compounds due to a spin-reorientation transition at \(T_{SR}=163\) K and a ferromagnetic (F) magnetic ordering transition at \(T_C=220\) K. Tencé et al. \([13]\) reported that in the Gd–Co system, \(\text{Gd}_4\text{Co}_3\) does not exist and that the phase to be considered is \(\text{Gd}_5\text{Co}_{4.85}\) without an intrinsic spin reorientation transition, with \(T_C=219\) K and \(-\Delta S_m=4.8\) J kg\(^{-1}\) K\(^{-1}\) for a magnetic field change of 0–4.5 T. It can be seen that Gd–Co compounds are those that have the highest Curie temperatures due to the fact that the 4f–3d exchange coupling depends directly on the spins of the 4f and 3d elements and Gd has the highest spin among the rare earths \([14]\).

Having a low \((3/4)\) Co:Gd concentration ratio, \(\text{Gd}_4\text{Co}_3\) is a special system \([15]\). As the Co:Gd concentration ratio increases, the itinerant character of the magnetism is reinforced and both the Curie temperature and the Co-induced magnetic moment increase.

Recently, Gd based soft magnetic amorphous alloys have been proposed as promising candidates for magnetic refrigeration. Owing to the amorphous nature, they exhibit some special advantages such as negligible magnetic hysteresis losses and tunable Curie temperature \(T_C\). It was reported that Gd–Co metallic glasses around eutectic composition showed large refrigerant capacity but a relatively low transition temperature \([16]\). Despite the fact that metallic glasses are generally obtained over a range of composition around the eutectic point, alloys far from eutectic composition or even at a compound composition are expected to be formed into metallic glasses at a high enough cooling rate. There is no related reference reporting the magnetic properties of \(\text{Gd}_4\text{Co}_3\) amorphous alloy. In this work, the magnetic properties and magnetocaloric effect of amorphous \(\text{Gd}_4\text{Co}_3\) and \((\text{Gd}_4\text{Co}_3)_{0.95}\text{Si}_{0.05}\) alloys are investigated. The nature of the ferrimagnetic (F) to paramagnetic (PM) phase transition was investigated with the study of the critical exponents of the transition.

2. Experiment

Ingots with nominal compositions of \((\text{Gd}_4\text{Co}_3)_{1-x}\text{Si}_x\) \((x=0, 0.05\) and 0.10) were prepared by arc-melting a mixture of pure Gd (99.95 wt%),

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3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of all ribbon samples. Only one broad peak appears between 2θ of 30° and 40° in all alloys, and no obvious diffraction peak corresponding to crystalline phases is observed, indicating the mainly amorphous nature of (Gd4Co3)1−xSi x (x = 0, 0.05, and 0.10) alloys.

Fig. 2 presents the magnetization as a function of temperature for (Gd4Co3)1−xSi x (x = 0, 0.05, and 0.10) amorphous alloys from 30 to 360 K under an applied field of 500 Oe. With the increase of temperature, magnetization decreases due to the magnetic transition from FI ordered state to PM state. The Curie temperatures, Tc, determined as the temperature at the maximum of dM/dT vs T plot, are 208, 198 and 213 K for x = 0, 0.05 and 0.15, respectively. These values are smaller than the reported result of 220 K for the crystalline compound Gd4Co3 [17,18].

The effective magnetic moment is calculated by \( \mu_{\text{eff}} = \sqrt{C/T - \Theta_p} \), in which C is the Curie constant and \( \Theta_p \) is the paramagnetic Curie temperature. The determined values of paramagnetic Curie temperature, \( \Theta_p \), are 202, 204 and 208 K for x = 0, 0.05, and 0.10, respectively. The paramagnetic Curie temperature increases with increasing Si contents and the positive value of \( \Theta_p \) may indicate the ferromagnetically ordered structure of (Gd4Co3)1−xSi x. The paramagnetic Curie temperature is close to Tc, indicating the presence of ferromagnetic spin interaction near Tc. By using the least-square fitting to obtain the value of C, the experimentally determined effective magnetic moment is calculated by \( \mu_{\text{eff}} = 2.83\sqrt{C/\mu_B} \). Assuming that only Gd atoms contribute to the total effective magnetic moment, we obtain effective moments of 9.12, 8.25 and 7.3 J kg\(^{-1}\) per Gd atom for x = 0, 0.05 and 0.10, respectively, which exceed those of Gd\(^{2+}\) free ion (7.94 μB). Thus, it is more reasonable to assume that Co atoms also contribute to the total effective moment, although the effective moment of (Gd4Co3)1−xSi x decreases with increasing Si content [14].

Fig. 3 shows the hysteresis loops of (Gd4Co3)1−xSi x (x = 0, 0.05, and 0.10) amorphous alloys measured at 5 K. The samples are magnetically saturated at 5 K in an applied field of 0.5 T and the saturation magnetization (M\(_s\)) equals to 26.3μB, 24.2μB and 22.4μB per (Gd4Co3)1−xSi x formula with x = 0, 0.05 and 0.10, respectively, in accord with the result in Refs. [11,17]. There is an antiparallel alignment between the magnetic moments of Gd and Co sublattice that reduces the total magnetic moment per unit cell. As seen in the inset of Fig. 3, all alloys show negligible hysteresis and coercivity, and the coercivity decreases from 81 Oe to 22 Oe with increasing Si content.

The magnetocaloric effects of the (Gd4Co3)1−xSi x (x = 0, 0.05, and 0.10) amorphous ribbons are estimated in terms of isothermal magnetic entropy change using Maxwell’s relation. Fig. 4 shows the temperature dependence of ΔS\(_{\text{M}}\) for magnetic field change from 0 to 2 T and 5 T. The peak values of ΔS\(_{\text{M}}\) of (Gd4Co3)1−xSi x are found to be 7.3, 7.2 and 6.4 J kg\(^{-1}\) K\(^{-1}\) for x = 0, 0.05 and 0.10, respectively. These values are higher than those of Gd4Co2 compounds (5.7 J kg\(^{-1}\) K\(^{-1}\) at 5 T) [12] and Gd4Co1.85 compounds (4.8 J kg\(^{-1}\) K\(^{-1}\) at 4.5 T) [13]. From Table 1, it can be seen that Gd4Co3 metallic
glasses show a lower Curie temperature than that of the crystalline compound. Previous studies on RE–Co metallic glasses had indicated that the variation of Curie temperature showed RKKY-like behaviors [19]. Although RKKY interaction did not work well in improving the Curie temperature. It is well known that metallic glasses are ordered in short range, while the crystalline ones are long-range ordered. In general, this disordered state may decrease the exchange interaction, resulting in the decrease of the Curie temperature.

The value of $-\Delta S_M$ is not the only parameter in characterizing the magnetocaloric properties. Another important parameter is RC, which is connected to the heat absorbed in a reversible cycle by the refrigerant at the cold end of the cycle. It offers a comprehensive evaluation between the peak value of $-\Delta S_M$ and the width of the peak. In this work, the RC values of these amorphous ribbons were calculated by numerically integrating the area under the $(\Delta S_M)$ vs $T$ curves, using the temperatures at half maximum of the peak as the integration limits [21,22]. When the applied field change from 0 to 5 T, RC values of $x=0$, 0.05 and 0.10 amorphous ribbons are 547, 524 and 511 J kg$^{-1}$, respectively, as shown in Table 1. These values are comparable to or even higher than those of Gd (556 J kg$^{-1}$, $\mu_0H=5.0$ T) [23], Gd$_2$Co$_7$ (478 J kg$^{-1}$, $\mu_0H=4.0$ T) [24] and Gd$_5$Si$_2$Ge$_2$ (305 J kg$^{-1}$, $\mu_0H=5.0$ T) [20] compounds.

The Arrott plots of the (Gd$_4$Co$_3$)$_{x5}$Si$_{0.1x}$ amorphous ribbons are displayed in Fig. 5. The isothermal magnetization $M$–$H$ curves are presented in the inset of Fig. 5. A typical FI–PM transition is evident in the vicinity of $T_C$. No inflection or negative slope is observed as an indication that FI–PM transition is of second order.

To analyze the nature of the magnetic phase transition in detail, we have carried out the study of the critical behavior near the Curie temperature $T_C$ for the alloys. For the second-order magnetic phase transition, in the vicinity of Curie temperature $T_C$, the existence of a diverging correlation length $\xi = \phi_0(1-T/T_C)^{-\nu}$ leads to universal scaling laws for the spontaneous magnetization $M_s(T)$ and initial susceptibility $\chi(T)$. According to the scaling hypothesis, the spontaneous magnetization $M_s(T)$ below $T_C$, the inverse initial susceptibility $\chi_0^{-1}(T)$ above $T_C$ and the measured magnetization $M$ at $T_C$ are characterized by a set of critical exponents $\beta$, $\gamma$ and $\delta$, respectively. They are defined as

$$M_s(0, T) = m_0|t|^{\beta}, \quad t \leq 0$$

$$\chi_0^{-1}(0, T) = \frac{h_0}{m_0} |t|^{\gamma}$$(1)

$$H = DM^\delta, \quad t = 0$$

where $t$ is the reduced temperature ($t=|t/T_C-1|$), and $m_0$, $h_0$ and $D$ are the critical amplitudes. Although the different critical exponents can be determined independently from experimental measurements, they are related to each other, which is taken in most cases to be of the form $\beta+\gamma = \beta_0$. In order to properly determine the $T_C$ as well as the critical exponents $\beta$, $\gamma$, and $\delta$, several methods can be used, including the modified Arrott plots technique (MAPs), the Kouvel–Fishcr (KF) method and the Widom scaling relation.

To obtain the best fitting, a self-consistent method was considered. As shown in Fig. 5, the Arrott plot isotherms are slightly curved at low field, because those parts correspond to multi-domain configurations. Starting from an initial estimation of the values of the critical exponents, modified Arrott plots are constructed. $M_2(0)$ is determined from the intersection of the linear extrapolation of the straight line in the modified Arrott plots with the $M^{1/\beta}$ axis, while $\chi_0^{-1}$ corresponds to the intersection of these lines with the $(H/M)^{1/\delta}$ axis. An initial value of $T_C$ is determined from the isotherm that passes through the origin. Only the high field linear region is used for the analysis. These data are fitted to the exponential behavior using Eqs. (1)–(3) to obtain new values of $\beta$ and $\gamma$. The new values of $\beta$ and $\gamma$ are then used to obtain new Arrott plots. This procedure is repeated until they converge to a stable value.

**Table 1**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Structure</th>
<th>$T_C$ (K)</th>
<th>$-\Delta S_M$ (J kg$^{-1}$ K$^{-1}$)</th>
<th>RC (J kg$^{-1}$)</th>
<th>$\Delta H$ (T)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x=0$</td>
<td>GR</td>
<td>208</td>
<td>7.3</td>
<td>547</td>
<td>5</td>
<td>This work</td>
</tr>
<tr>
<td>$x=0.05$</td>
<td>GR</td>
<td>198</td>
<td>7.2</td>
<td>524</td>
<td>5</td>
<td>This work</td>
</tr>
<tr>
<td>$x=0.10$</td>
<td>GR</td>
<td>213</td>
<td>6.4</td>
<td>511</td>
<td>5</td>
<td>This work</td>
</tr>
<tr>
<td>Gd$_5$Co$_2$Si$<em>2$N$</em>{0.05}$</td>
<td>GR</td>
<td>192</td>
<td>6.5</td>
<td>502</td>
<td>5</td>
<td>[11]</td>
</tr>
<tr>
<td>Gd$_5$Co$_2$Si$_2$N$_5$</td>
<td>GR</td>
<td>202</td>
<td>7.1</td>
<td>–</td>
<td>5</td>
<td>[9]</td>
</tr>
<tr>
<td>Gd$_5$Co$_2$Si$_2$</td>
<td>C</td>
<td>220</td>
<td>4.8</td>
<td>–</td>
<td>5</td>
<td>[17]</td>
</tr>
<tr>
<td>Gd$_5$Co$_2$Mn$_5$</td>
<td>C</td>
<td>220</td>
<td>5.7</td>
<td>573</td>
<td>5</td>
<td>[12]</td>
</tr>
<tr>
<td>Gd$_5$Co$<em>2$A$</em>{10}$</td>
<td>C</td>
<td>219</td>
<td>4.8</td>
<td>–</td>
<td>4.5</td>
<td>[13]</td>
</tr>
<tr>
<td>Gd$_5$Co$<em>2$Co$</em>{10}$</td>
<td>C</td>
<td>160</td>
<td>8.8</td>
<td>478</td>
<td>5</td>
<td>[20]</td>
</tr>
</tbody>
</table>
The critical exponents of experimental data fall on two curves, one above is an important criterion for critical regime. As shown in Fig. 7, the on two universal curves: one above $\beta$ critical exponents may be caused by the formation of some magnetic clusters; in other words, ferromagnetic (FM) spin interaction does increase. The critical exponents are close to those of the 3D Ising model but $\delta$ is mean-field-like. We believe that the above mentioned differences are possibly due to the inhomogeneous nature of samples in the microscopic scale. For sample $x=0.10$, the critical exponents are between those of the 3D Ising model and the three-dimensional (3D) Ising theory. It should be noted that the 3D Heisenberg model or 3D Ising model is based on the short-range magnetic coupling, and the mean-field theory is based on the long-range magnetic coupling. The magnetic interactions in the present alloys exhibit local magnetic interactions. As seen from Table 2, it is obvious that the values of critical exponent $\beta$ decrease firstly and then increase whereas those of $\gamma$ decrease continuously with increasing Si content. Physically, $\beta$ describes how the ordered moment grows below $T_C$ while $\gamma$ describes the divergence of the magnetic susceptibility at $T_C$. The smaller the value of $\beta$, the faster the growth of the ordered moment. The $\beta$ value decreases with increasing Si content, reflecting a faster growth of the ordered moment with decreasing temperature. Compared with $\beta=0.359$ for $x=0.05$, $\beta$ value quickly increases to 0.465 for $x=0.10$, which results in slower growth of the ordered moment below $T_C$. This change of tendency is in agreement with magnetization intensity at low temperatures around 180 K, which decreases firstly and then increases with increasing Si content, as shown in Fig. 2. Also, the change in the values of critical exponents may be caused by the formation of some magnetic clusters; in other words, ferromagnetic (FM) spin interaction does increase. The critical exponents $\beta$ and $\gamma$ for $x=0$ are close to those of 3D Ising model but $\delta$ is mean-field-like. We believe that the above mentioned differences are possibly due to the inhomogeneous nature of samples in the microscopic scale. For sample $x=0.10$, the critical exponents are between those of the 3D Ising model and the mean-field one, which is based on the long-range magnetic coupling. The results show that the critical exponents are close to those of the 3D Ising model. This Ising-like behavior suggests that samples have high magnetic anisotropy, which comes from internal stress in samples generated in the preparation process and inhomogeneous contents in the microscopic scale.

4. Conclusion

The Curie temperature of amorphous $(\text{Gd}_4\text{Co}_3)_x\text{Si}_{1-x}$ ($x=0, 0.05$, and 0.10) alloys can be tuned from 198 to 213 K with increasing Si content. The maximum values of $-\Delta S_M$ are 73, 72 and 64 \text{ J kg}^{-1} \text{ K}^{-1} for $(\text{Gd}_4\text{Co}_3)_x\text{Si}_{1-x}$ with $x=0$, 0.05 and 0.10, respectively, under the applied field change from 0 to 5 T. The saturation magnetization ($M_s$) is 26.5, 24.2 and 22.4 $\text{emu} \text{cm}^{-3}$ per $(\text{Gd}_4\text{Co}_3)_x\text{Si}_{1-x}$ formula with $x=0$, 0.05 and 0.10, respectively. The $(\text{Gd}_4\text{Co}_3)_x\text{Si}_{1-x}$ amorphous alloys exhibit second order magnetic phase transition from the FI to PM state. The critical exponent values obtained for $x=0$ and $x=0.05$ are comparable to the values predicted by the 3D Ising model, and which have also been verified by the scaling equation of state. For sample $x=0.10$, the critical exponents are between 3D Ising model and the

### Table 2

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
<th>Reference</th>
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<tr>
<td>$x=0$</td>
<td>0.389</td>
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<td>3.158</td>
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<tr>
<td>$x=0.05$</td>
<td>0.359</td>
<td>1.223</td>
<td>4.405</td>
<td>This work</td>
</tr>
<tr>
<td>$x=0.10$</td>
<td>0.405</td>
<td>1.134</td>
<td>3.436</td>
<td>This work</td>
</tr>
<tr>
<td>Mean-field theory</td>
<td>0.5</td>
<td>1.0</td>
<td>3.0</td>
<td>[25–28]</td>
</tr>
<tr>
<td>3D Heisenberg theory</td>
<td>0.365</td>
<td>1.336</td>
<td>4.8</td>
<td>[25–28]</td>
</tr>
<tr>
<td>3D Ising theory</td>
<td>0.325</td>
<td>1.24</td>
<td>4.82</td>
<td>[25–28]</td>
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</table>
mean-field ones, which indicates that there is long-range magnetic coupling in the amorphous matrix.

Acknowledgments

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