Magnetocaloric effect in Gd$_{5}$Si$_{1.85}$Ge$_{2.15}$ prepared by Gd metal with lower purity

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Abstract The magnetic phase transition and magnetocaloric effect of Gd$_{5}$Si$_{1.85}$Ge$_{2.15}$ alloy are studied. The alloy was prepared from distilled commercial gadolinium. The major impurities (in wt.% in the distilled commercial Gd are 0.016 O, 0.0054 C, and 0.0016 N. The impurities are higher than those in the high pure Gd but lower than those in commercial Gd. The results of X-ray diffraction and magnetic susceptibility show that there exists the first-order magnetic phase transition in the Gd$_{5}$Si$_{1.85}$Ge$_{2.15}$ alloy at 253 K. The maximum of magnetic entropy change $\Delta S_{\text{max}}$ is 12.5 J/kg K near the temperature of magnetic phase transition in the alloy.

Keywords: magnetocaloric effect, first-order magnetic transition, magnetic refrigeration.

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Recently, Pecharsky et al. have discovered that Gd$_{5}$(Si$_{1-x}$Ge$_x$)$_4$ (0 < $x$ < 0.5) has a significantly large magnetocaloric effect (MCE), which is 50% to 200% larger than any known materials$^{[1-4]}$. This behavior is called as ‘giant magnetocaloric effect’. The giant MCE is caused by simultaneous magnetic and crystallographic transition in these alloys. The first order magnetic ordering temperature of Gd$_{5}$(Si$_{1-x}$Ge$_x$)$_4$ can be tuned from 20 to 280 K by changing the ratio of Si : Ge$^{[5]}$. The temperature can also be increased to 290 K by the substitution of element Ga for Si+Ge$^{[5]}$. These results are very useful for developing the technology of magnetic refrigeration near room temperature.

However, the giant MCE is critically dependent on an impurity concentration in the Gd$_{5}$(Si$_{1-x}$Ge$_x$)$_4$ (0 < $x$ < 0.5) alloys. Gd$_{5}$(Si$_{1-x}$Ge$_x$)$_4$ (0 < $x$ < 0.5) alloys with giant MCE are commonly prepared by using high purity Gd metal. The purity of high Gd is 99.9 at.% Gd$_{5}$(Si$_{1-x}$Ge$_x$)$_4$ (0 < $x$ < 0.5) alloys could not exhibit any giant MCE if commercial Gd (93 at.% pure) was used for preparing these alloys$^{[4]}$. It is reported that higher impurity concentration of C, O, N in commercial Gd causes the loss of the first-order nature of magnetic phase transition and the disappearance of giant MCE$^{[4-7]}$. But the cost of high purity Gd metal is ten times higher than that of commercial Gd. So it is very important how to prepare the giant MCE Gd$_{5}$(Si$_{1-x}$Ge$_x$)$_4$ alloys at low cost. Gschneidner et al. reported a manufacture process to get Gd$_{5}$(Si$_{1-x}$Ge$_x$)$_4$ alloys with giant MCE at low cost$^{[8]}$. The starting materials Si, Ge and commercial Gd are melted and kept at 2073 K for 1 h in the dynamic vacuum during the process. So the C and O in commercial Gd can react fully enough to form CO or CO$_2$, which are pumped off in the dynamic vacuum. Ta or W crucible must be used in the process because Ta and W crucibles do not react with the melting Gd.

In this paper, we present another manufacture process to get Gd$_{5}$(Si$_{1-x}$Ge$_x$)$_4$ alloys at low cost. The Gd$_{5}$Si$_{1.85}$Ge$_{2.15}$ alloy was prepared by using commercial distilling Gd by arc-melting. The commercial distilling Gd was obtained by distilling commercial Gd by the manufacturer. The results of magnetic susceptibility and magnetization show that there exists the first-order magnetic phase transition and the giant magnetic entropy changes in the Gd$_{5}$Si$_{1.85}$Ge$_{2.15}$ alloy prepared from distilled commercial Gd. The impurity concentration in distilled commercial Gd is higher than that in high pure Gd but lower than that in commercial Gd. It should be noted that the cost of the distilled commercial Gd is only three times higher than that of commercial Gd.

The starting materials Si and Ge are 99.9999 wt.% in purity. The Gd metal was purchased from the General Research Institute for Nonferrous Metals of China. The metal Gd was purified by distilling a commercial Gd by the manufacturer. The major impurities in distilled Gd metal are shown in Table 1. The data of distilled Gd are supplied by the manufacturer. To compare with the distilled Gd, the major impurities in highly pure Gd and commercial Gd$^{[5,6]}$ are also shown in Table 1. It is seen that the distilled Gd metal is inferior to highly pure Gd metal and superior to commercial Gd metal in purity. The Gd$_{5}$Si$_{1.85}$Ge$_{2.15}$ alloy was prepared by the arc melting method. The alloy was remelted 5 times to make it homogeneous. The chemical analysis shows that the Gd$_{5}$Si$_{1.85}$Ge$_{2.15}$ alloy contained 0.025 wt.% C, 0.063 wt.% O and 0.0127 wt.% N. The impurities in the Gd$_{5}$Si$_{1.85}$Ge$_{2.15}$ alloy increase with the distilled commercial Gd decreasing. The structure of the alloy was examined by X-ray diffraction. The ac magnetic susceptibility was determined using an ac magnetometer with an excitation field of 10 Oe at a frequency of 10 Hz. Magnetization of this alloy was measured from 200 to 300 K by the superconducting quanta interfere device. The magnetic entropy change ($\Delta S$) was calculated from magnetization curves.

Fig. 1 shows X-ray diffraction patterns of the Gd$_{5}$Si$_{1.85}$Ge$_{2.15}$ at 298 and 200 K, respectively. The dif-
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Table 1: Impurities in different Gd metals

<table>
<thead>
<tr>
<th>Impurity (wt.%)</th>
<th>Distilled commercial Gd</th>
<th>Highly pure Gd</th>
<th>Commercial Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0.0160</td>
<td>0.0045</td>
<td>0.191</td>
</tr>
<tr>
<td>C</td>
<td>0.0054</td>
<td>0.0015</td>
<td>0.034</td>
</tr>
<tr>
<td>N</td>
<td>0.0016</td>
<td>0.0008</td>
<td>0.039</td>
</tr>
<tr>
<td>H</td>
<td>--</td>
<td>0.0001</td>
<td>--</td>
</tr>
</tbody>
</table>

The difference between the two diffraction patterns indicates the occurrence of structural transition. A main orthorhombic phase is confirmed from the X-ray diffraction pattern at 298 K, and a main monoclinic phase is confirmed at 200 K. These diffraction patterns are in good agreement with that of ref. [7]. Fig. 2 shows that the ac magnetic susceptibility is a function of temperature for the Gd₅Si₁₆Ge₂₁₅ alloy. As seen in Fig. 2, an abrupt transition is observed at 253 K when decreasing the temperature with thermal hysteresis around 6 K. It is in good agreement with the first order magnetic transition reported by ref. [7]. A small anomaly at 293 K is considered as the second order paramagnetic-ferromagnetic transition of the orthorhombic Gd₅Si₁₆ phase. Figs. 1 and 2 show that the first order magnetic transition exists in the Gd₅Si₁₆Ge₂₁₅ alloy prepared from distilled commercial Gd.

Fig. 1. X-ray diffraction patterns of Gd₅Si₁₆Ge₂₁₅ alloy at 298 and 200 K.

Fig. 2. ac susceptibility of Gd₅Si₁₆Ge₂₁₅ alloy as a function of increasing (or decreasing) temperature.

Fig. 3. Magnetization curves of Gd₅Si₁₆Ge₂₁₅ alloy.

The magnetization of the Gd₅Si₁₆Ge₂₁₅ alloy was measured near the first-order magnetic transition temperature, as shown in Fig. 3. The change of magnetic entropy $\Delta S$ was calculated from the magnetization curves by the following expression:

$$\Delta S = \int \left[ \frac{\partial M}{\partial T} \right] dH.$$  \hspace{1cm} (1)

The magnetic entropy change ($\Delta S$) as a function of temperature is given in Fig. 4. The maximum $\Delta S_{\text{max}}$ value of the Gd₅Si₁₆Ge₂₁₅ is obtained to be 12.5 J/kg \cdot K. The $\Delta S_{\text{max}}$ is smaller than that (15 J/kg \cdot K) of the Gd₅Si₂Ge₂ alloy prepared from highly pure Gd \cite{1,3-5}. But the $\Delta S_{\text{max}}$