Amorphous-FeCoCrZrB ferromagnets for use as high-temperature magnetic refrigerants

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Magnetic metallic glasses, having large magnetic moments and high Curie temperatures ($T_C$), have not been widely studied as magnetic refrigerants. In this study, we report on the magnetocaloric effects of five FeCoCrZrB amorphous alloys [(Fe,Co, Cr)$_{x}$Zr$_2$B$_2$, with Fe:Co:Cr ratios of 100:0:0, 90:15:5, 85:5:10, and 75:15:10] chosen for efficiently surveying the high $T_C$ metallic glass composition surface. Magnetic isotherms were measured at 25 K intervals from 25 to 525 K. The entropy change ($\Delta S$) due to the magnetocaloric effect was computed by integrating the magnetic isotherms. The refrigeration capacity (RC) was computed by Wood-Potter method. At 3979 kA/m (50 kOe) the FeCoCrZrB alloys have RC values of 240–320 J/kg; at 796 kA/m (10 kOe) the alloys have values of 32–54 J/kg. The RC values favorably compare with values reported for other refrigerant materials. The peak $\Delta S$ temperature depends strongly on composition, varying from 200 to 450 K. The wide flexibility in choosing amorphous alloy compositions allows them to be fine tuned for multistage high temperature refrigerators. The saturation magnetization at 25 and 300 K and Curie temperatures are also reported for the five alloys. © 2006 American Institute of Physics. [DOI: 10.1063/1.2172234]

Increased efficiency achieved by reduced system complexity and power consumption is an important design goal in refrigeration technology. Recent advances\textsuperscript{1} have made magnetic refrigerators, already widely used\textsuperscript{2} for achieving ultralow (<100 mK) temperatures, competitive for near-room-temperature applications. Advancing this technology requires understanding and enhancing the magnetocaloric effect (MCE) at elevated temperatures in magnetic materials used as refrigerants.

Low-temperature magnetic refrigerators may employ an Ericsson cycle to transport heat from a cold reservoir to a hot reservoir. In this cycle, adiabatic demagnetization is used to cool the refrigerant material. During demagnetization, the refrigerant must be out of thermal contact with either reservoir. While in contact with the reservoirs, the refrigerant experiences nonisothermal heat transfer causing a change in entropy.

In addition to the chosen thermodynamic cycle, the system performance depends on the properties of the refrigerant material. The selected refrigerant must display a significant magnetocaloric effect, i.e., change in temperature with magnetic field. At low temperatures paramagnetic or superparamagnetic materials are used as refrigerants. These materials obey the Curie law, which states that their susceptibility is inversely proportional to the absolute temperature. As such, the magnetic response of a paramagnet becomes larger as absolute zero is approached. The magnetocaloric effect also becomes larger as the temperature approaches zero. Since the temperature difference over which a low-temperature refrigerator is used is quite small, (1–2 K); the selection of refrigerant materials is driven by the need to maximize the value of the magnetocaloric effect near absolute zero.

At higher temperatures, paramagnets and superparamagnets no longer display usable magnetocaloric effects. Ferromagnets, which transform into paramagnets at their Curie temperatures, are used instead. Above the Curie temperature, the susceptibility of a ferromagnet obeys the Curie-Weiss law. The magnetocaloric effect is maximized at the Curie temperature as this is the point of maximum entropy change between the ordered ferromagnetic and disordered paramagnetic states.

Magnetic refrigeration at higher temperatures must, by necessity, operate over a wider range of temperatures than low-temperature cycles. Rather than searching for a material with the largest magnetocaloric effect at a single temperature, it becomes desirable to find a material with an enhanced effect over a wide temperature range. An alternative metric, the refrigeration capacity (RC) was described by Wood and Potter\textsuperscript{2} to enable comparisons among ferromagnetic refrigerants used in isothermal demagnetization refrigerators. The scheme of the RC metric begins by selecting a temperature for the hot reservoir $T_h$, and finding the entropy change exhibited for this temperature for a given material and applied magnetic field. By the second law of thermodynamics, the entropy change of the cold reservoir must be less than or equal to the entropy change at the hot reservoir. The optimum temperature of the cold reservoir $T_c$ is then found by transcribing the largest rectangle that can be fit beneath a plot of $\Delta S$ versus temperature. The RC is defined as the area of this rectangle or $\Delta S\Delta T$. For this work, values for $T_h$ and $T_c$ are defined by the full width at half maximum of the $\Delta S$ vs $T$ curve for a given field. The RC is then half the maximum entropy change multiplied by the difference between $T_h$ and $T_c$. Hysteresis losses experienced by the material during the refrigeration cycle must be subtracted from the calculated RC value.\textsuperscript{4}

Maximization of the RC requires selecting ferromagnetic materials with high magnetizations, low hysteretic losses, and Curie temperatures that can be tuned over a wide range

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of temperatures.\textsuperscript{5} Amorphous ferromagnets can satisfy all of these requirements. In particular, systems based on the Fe–Co–Cr–Zr–B system have Curie temperatures that can be tuned from 200 to 800 K and have magnetic moments on the order of 100 A m\textsuperscript{2}/kg(emu/g). These properties can be tuned by adjusting the relative ratios of the Fe, Co, and Cr in the metallic glass. The lack of magnetocrystalline anisotropy in the amorphous state minimizes hysteretic power losses.

In this paper we report the study of a range of amorphous materials whose composition has varied over a range of Fe, Co, and Cr. The magnetocaloric effect is reported as a function of temperature and optimum values of the RC are found. The possibility of using composite or compositionally graded amorphous materials to extend the useful temperature range for multistage refrigerators is discussed.

Amorphous magnetic materials of a range of compositions were prepared by single roller melt spinning. The absence of crystallinity was verified by x-ray diffraction. The alloys were produced with the general composition (in at. \%) of (Fe\textsubscript{100–x−y}Co\textsubscript{x}Cr\textsubscript{y})\textsubscript{9}Zr\textsubscript{7}B\textsubscript{2}. The specific compositions chosen were \(x=y=0\) for alloy 1, \(x=y=5\) for alloy 2, \(x=15, y=5\) for alloy 3, \(x=5, y=10\) for alloy 4, and \(x=15, y=10\) for alloy 5. In these alloys, the proportions of the glass forming elements Zr and B were kept constant while the relative proportions of the transition metal elements Fe, Co, and Cr were adjusted. Magnetic measurements were made with a Quantum Design MPMS-5 superconducting quantum interference device (SQUID) magnetometer and an ADE VSM-10 vibrating-sample magnetometer,\textsuperscript{5} calibrated using NIST SRM’s 772a (Ni sphere) and 2853 (YIG sphere).

To measure the magnetocaloric effect, measurements of magnetization versus field at constant temperature were made for temperatures from 25 to 375 K. The magnetocaloric effect can be expressed from a Maxwell relation as

\[
\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H.
\]

The change in entropy due to the magnetocaloric effect can be calculated by numerically integrating this Maxwell relation over discrete temperature intervals,

\[
\Delta S = \frac{1}{\Delta T} \int_{T_{i+1}}^{T_i} \left[ M(T, H) - M(T', H) \right] dH,
\]

\[
\Delta T = T_{i+1} - T_i.
\]

The change in entropy is proportional to the area between two isotherms on a plot of magnetization versus temperature.\textsuperscript{7} The RC of a material is computed from the method developed by Wood and Potter\textsuperscript{3} in which the entropy change \(\Delta S\) is half the peak \(\Delta S\) due to the MCE, and the \(\Delta T\) is the full width at half maximum of the \(\Delta S\) versus \(T\) curve. The RC is then the product \(\Delta S\Delta T\).

Table I presents the saturation magnetization values and Curie temperatures measured for the five amorphous alloys studied in this paper. Figures 1 and 2 are plots of the entropy change due to the magnetocaloric effect as a function of temperature for a change in an applied field from 3979 kA/m (50 kOe) to 0 field and from 796 kA/m (10 kOe) to 0 field, respectively. Alloys 3 and 5 are not included in Fig. 1 as their Curie temperatures are above the maximum temperature achievable by the MPMS-5. Figure 2 is calculated from the measurements performed on both the MPMS-5 and VSM-10 instruments for applied fields up to 796 kA/m (10 kOe). Tables II and III summarize the peak \(\Delta S\) value due to the magnetocaloric effect, the temperatures of the hot \((T_h)\) and cold \((T_c)\) reservoirs taken from the full width at half maximum of the curve, and the calculated RC values.

The RCs for the FeCoCrZrB alloys are competitive with other materials being considered as magnetic refrigerants. For a maximum applied field change from 3979 kA/m (50 kOe) to 0 field the FeCoCrZrB alloys have RCs in the range of 200–300 J/kg. This compares favorably to elemen-

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Peak (\Delta S) (J/K kg)</th>
<th>(T_h) (K)</th>
<th>(T_c) (K)</th>
<th>RC (J/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.9</td>
<td>320</td>
<td>100</td>
<td>320</td>
</tr>
<tr>
<td>4</td>
<td>2.8</td>
<td>375</td>
<td>205</td>
<td>240</td>
</tr>
</tbody>
</table>

FIG. 1. Entropy change as a function of temperature for a change in applied field from 3979 kA/m (50 kOe) to 0 field. Numbers refer to alloy designations.

FIG. 2. Entropy change as a function of temperature for a change in applied field from 796 kA/m (10 kOe) to 0 field. Numbers refer to alloy designations.
tal Gd which, measured in our laboratory, has an RC of 273 J/kg. The peak entropy change for Gd is 5.8 J/K kg at 300 K, which is larger than the 2.8 J/K kg observed for alloy 4 \([\text{Fe}_{65}\text{Co}_{25}\text{Cr}_{10}]_{10} \text{Zr}_{2}\text{B}_{2}\)]. However, the full width at half maximum of the \(\Delta S\) vs \(T\) curve of Gd is only 95 K while it is 170 K for alloy 4, thereby explaining the similarity in RC values. The presently studied amorphous alloys also compare favorably to \(\text{Gd}_{2}\text{Ge}_{2}\text{Si}_{2}\) (200 J/kg), \(\text{Gd}_{2}\text{Ge}_{1}\text{Si}_{2}\text{Fe}_{0.1}\) (235 J/kg), and \(\text{MnFeP}_{0.45}\text{As}_{0.55}\) (225 J/kg, computed from the graph in Ref. 8).

It is observed that the temperature dependent magnetic properties of these alloys are strong functions of their compositions. Previous work has shown that Co increases the Curie temperature and saturation magnetization of amorphous and nanocrystalline alloys, whereas Cr is observed to decrease both quantities.\(^{10,11}\) The combinations of these elements in alloys 2–5 give rise to countervailing trends when compared to the base FeZrB alloy. Alloy 4 \([\text{Fe}_{65}\text{Co}_{25}\text{Cr}_{10}]_{10} \text{Zr}_{2}\text{B}_{2}\] which has the lowest Co but highest Cr content, has the lowest Curie temperature, whereas alloy 3 \([\text{Fe}_{60}\text{Co}_{15}\text{Cr}_{5}]_{10} \text{Zr}_{2}\text{B}_{2}\] which has the highest Co but the lowest Cr content, has the highest Curie temperature. The trend of Co and Cr contents on the saturation magnetization \((M_s)\) at 25 K is less clear. Alloy 3 \([\text{Fe}_{60}\text{Co}_{15}\text{Cr}_{5}]_{10} \text{Zr}_{2}\text{B}_{2}\] has the highest \(M_s\). However, the \(M_s\) of the alloys with high Cr [alloys 4 \((\text{Fe}_{65}\text{Co}_{25}\text{Cr}_{10})_{10} \text{Zr}_{2}\text{B}_{2}\) and 5 \((\text{Fe}_{60}\text{Co}_{15}\text{Cr}_{5})_{10} \text{Zr}_{2}\text{B}_{2}\)] are not sensitive to the Co content. This may be due to the Cr, which is antiferromagnetic in the bulk state, strongly interrupting the ferromagnetic exchange interactions in these alloys.

Increasing the ratio of Co relative to Fe by 10 at. % is seen to increase the peak \(\Delta S\) temperature by 100 K for alloys 2 \([\text{Fe}_{60}\text{Co}_{15}\text{Cr}_{5}]_{10} \text{Zr}_{2}\text{B}_{2}\) and 3 \([\text{Fe}_{60}\text{Co}_{15}\text{Cr}_{5}]_{10} \text{Zr}_{2}\text{B}_{2}\), and 75 K for alloys 4 \([\text{Fe}_{65}\text{Co}_{25}\text{Cr}_{10}]_{10} \text{Zr}_{2}\text{B}_{2}\) and 5 \([\text{Fe}_{75}\text{Co}_{15}\text{Cr}_{5}]_{10} \text{Zr}_{2}\text{B}_{2}\). In contrast, increasing the ratio of Cr relative to Fe by 5 at. % is seen to decrease the peak \(\Delta S\) temperature by 25 K for alloys 2 and 4 and 50 K for alloys 3 \([\text{Fe}_{60}\text{Co}_{15}\text{Cr}_{5}]_{10} \text{Zr}_{2}\text{B}_{2}\) and 5 \([\text{Fe}_{75}\text{Co}_{15}\text{Cr}_{5}]_{10} \text{Zr}_{2}\text{B}_{2}\). These results further illustrate the opposite effects that minority Co and Cr additions have on the exchange interactions in Fe-based alloys.\(^{1,12}\)

The choice of an amorphous material as a magnetic refrigerant offers some advantages. As shown in Fig. 2, the peak magnetocaloric effect can be shifted by approximately 250 K by Co and Cr substitutions for Fe of less than 25 at. %. Since there are no solubility limits for transition metals in this type of amorphous alloy, even larger substitutions for Fe may be contemplated. The upper range for the peak temperature will be limited by the crystallization temperatures, which range from 600 to 800 K for FeCoZrB alloys.\(^{13}\) Future research may consider using other magnetic transition elements, such as Ni and Mn, or the rare-earth elements such as Gd to further tune the magnetic properties of these amorphous alloys. Ni is known to reduce the Curie temperature and \(M_s\) of amorphous alloys systems.\(^{14}\) The influence of Mn is less well explored but its antiferromagnetic nature may be expected to decrease the \(M_s\) of the amorphous alloy. Gd will increase the average atomic magnetic moment but decrease the Curie temperature, and is likely to be a more expensive alloying element than the transition metals. Amorphous alloys are typically produced by rapid solidification processes that yield flexible ribbonlike materials with high surface area to volume ratio that is ideal for heat transport. Alloying compositions are easily varied raising the possibility of composite structures usable in staged refrigerators operating over a very wide temperature range.

The FeCoCrZrB amorphous alloys yield refrigeration capacities that are comparable to other materials being considered as near-room-temperature magnetic refrigerants. At an applied field change of 3979 kA/m (50 kOe) the presently studied materials show refrigeration capacities in the range of 200–300 J/kg. Magnetic properties such as \(M_s\) and Curie temperature of the FeCoCrZrB alloys vary sensitively with the relative proportions of Fe, Co, and Cr within the alloy. As a consequence, the peak in the \(\Delta S\) vs \(T\) curve can be precisely tuned over a wide temperature range. The wide choice of alloy compositions available in amorphous alloys makes them an attractive choice for refrigerants in multistage, near-room-temperature magnetic refrigerators.

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\(^{6}\) Certain commercial equipment, instruments, or materials are identified in this paper to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.


