Influence of Co and Ni addition on the magnetocaloric effect in Fe 88 − 2 x Co x Ni x Zr 7 B 4 Cu 1 soft magnetic amorphous alloys

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Influence of Co and Ni addition on the magnetocaloric effect in $Fe_{88-2x}Co_xNi_xZr_7B_4Cu_1$ soft magnetic amorphous alloys

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We have studied the magnetocaloric effect in a series of $Fe_{88-2x}Co_xNi_xZr_7B_4Cu_1$ alloys. The partial substitution of Fe by Co and Ni leads to a monotonic increase in the Curie temperature (T_C) of the alloys from 287 K for $x=0$ to 626 K for $x=11$. The maximum magnetic entropy change (ΔS_M^{pk}) at an applied field of 1.5 T, shows a value of 1.98 J K^{-1} kg^{-1} for $x=8.25$. The refrigerant capacity (RC) has maximum values near 166 J kg^{-1} (for $x=0$ and 2.75). These values place the present series of alloys among the best magnetic refrigerant materials, with an RC ~40% larger than $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ and ~15% larger than Fe-based amorphous alloys. © *2010 American Institute of Physics*. [doi:10.1063/1.3427439]

Ambient-temperature solid-state magnetic refrigeration employing the magnetocaloric effect (MCE) is a field of active research.[1–3] Compared with conventional gas compression-expansion refrigeration, magnetic refrigeration based on MCE offers improved energy efficiency and reduced environmental impact.[4] In magnetic materials, the MCE arises from the reversible temperature change that occurs during the application or removal of an external magnetic field H under adiabatic conditions. This temperature change is accompanied by a change in magnetic entropy (ΔS_M), leading to a refrigerant capacity (RC), which is defined as the heat transferred between the hot and cold reservoirs used in the ideal thermodynamic cycle. The RC depends both on the magnitude of ΔS_M (i.e., its peak value, ΔS_M^{pk}) as well as its temperature dependence (i.e., the width of the peak). An optimal refrigerant material maximizes both ΔS_M^{pk} and RC.

The largest ΔS_M^{pk} values generally occur in materials with a first order magnetostructural phase transition [e.g., $Gd_5(Si,Ge)_4$, $La(Fe,Si)_{13}$, FeMnPAs, etc].[5,6] There are, however, several complications arising from the nature of the phase transition.[7,8] These include the following: (i) the effects of thermal- and field-hysteresis,[9] (ii) a large volume change and the concomitant stresses between the coexisting phases,[10,11] (iii) magnetic degrees of freedom coupling with vibrational ones[12] producing additional contributions to MCE, and (iv) the slow kinetics of the first order transitions which can limit the performance of a refrigerator employing these materials.

Amorphous magnetic materials offer significant potential as magnetic refrigerant materials[13–15] because they (i) undergo a second order magnetic phase transition which exhibits a broad ΔS_M peak around the Curie temperature T_C (Ref. 13) (in contrast with the usually narrow ΔS_M peak present in materials with first order phase transitions), (ii) provide tunable magnetic transition temperatures by alloying,[16] (iii) present neither volume nor structural changes, and (iv) produce large RC,[17] significantly reduced magnetic and thermal hysteresis, high electrical resistivity, good mechanical properties, and an improved corrosion resistance. Rare earth based amorphous alloys have large values of ΔS_M^{pk} and RC, but their T_C is well below room temperature, making them unsuitable for ambient-temperature applications.[18–20] Iron-based (e.g., nanoperm-type Fe–Zr–B–Cu) alloys have a T_C close to room temperature (which can be further modified by alloying)[21] and are much more affordable than rare earth based alloys, but their magnetocaloric response is comparatively much smaller.[17] In this work it will be shown that the combined addition of Co and Ni to Fe–Zr–B–Cu type alloys leads to amorphous materials with large magnetocaloric response, surpassing the RC of the well known crystalline magnetic refrigerant $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ by ~40% and a leading amorphous alloy, $Fe_{83}Zr_6B_{10}Cu_1$, by ~15%.

Amorphous ribbons of $Fe_{88-2x}Co_xNi_xZr_7B_4Cu_1$ (typically 2–3 mm wide and ~20 μm thick) with compositions corresponding to $x=0$, 2.75, 5.5, 8.25, and 11, were obtained by a melt-spinning technique. Further details about sample preparation, microstructural, and magnetic characterization are given elsewhere.[22]

The change in magnetic entropy caused by a variation in applied magnetic field has been obtained by numerical approximation of

$$\Delta S_M(T,\Delta H) = \mu_0 \int_{H_0}^{H_f} \left[\frac{\partial M(T,H)}{\partial T}\right]_H dH, \qquad (1)$$

where $\Delta H=H_f-H_0$ is the magnetic field change, μ_0 is the magnetic permeability of vacuum, and $M(T,H)$ is the magnetization of the material. The field and temperature dependence of $M(T,H)$ was measured (up to $\mu_0 H_{max}=1.5$ T in 10 mT increments and from 100 to 713 K in 10 K increments) by vibrating sample magnetometry. Figure 1 shows the corresponding temperature dependence of ΔS_M at a maximum applied field of 1.5 T for the alloys studied. The curves have a caret-like shape, characteristic of a second order phase transition, which becomes sharper with increasing Co/Ni content.

RC may be calculated from ΔS_M according to

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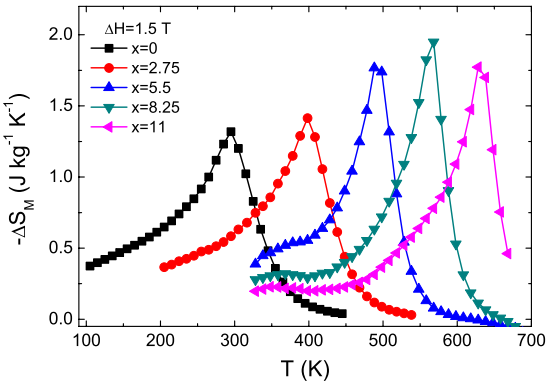

FIG. 1. (Color online) Temperature dependence of the magnetic entropy change corresponding to a magnetic field change $\Delta H=1.5$ T in the amorphous $Fe_{88-2x}Co_xNi_xZr_7B_4Cu_1$ ($x=0$, 2.75, 5.5, 8.25, and 11) alloy series.

$$\mathrm{RC}(\Delta H)=\int_{T_{\mathrm{cold}}}^{T_{\mathrm{hot}}}\Delta S_{\mathrm{M}}(T,\Delta H)dT. \tag{2}$$

From the experimental data, this integral may be evaluated by a number of methods. $\mathrm{RC_{AREA}}$ is calculated by integrating ΔS_{M} across the temperature range spanning the half-maximum of the entropy change. $\mathrm{RC_{FWHM}}$ approximates the integral as the product of $\Delta S_{\mathrm{M}}^{\mathrm{pk}}$ with the same full width at half maximum (FWHM) temperature range. According to Wood and Potter,[23] $\mathrm{RC_{WP}}$ is taken as the area of the largest rectangle which can be inscribed inside the $\Delta S_{\mathrm{M}}(T)$ curve. In this work all three definitions are used, to facilitate comparison with prior studies.

The compositional dependence of RC, $\Delta S_{\mathrm{M}}^{\mathrm{pk}}$, and T_{C} is shown in Fig. 2 for the alloys studied. The values of T_{C} have been obtained from the inflection point of the experimental magnetization data at low field ($\mu_{\mathrm{o}}H_{\mathrm{max}}=10$ mT). There is a monotonic increase in T_{C} from 287 K for $x=0$ to 626 K for $x=11$, which follows a power law defined as $T_{\mathrm{C}}(x)\propto x^{0.81}(r^2=0.999)$. This empirically obtained power law can be used to fine tune the composition of the alloy for a desired T_{C}. The temperature at which $\Delta S_{\mathrm{M}}^{\mathrm{pk}}$ occurs (Fig. 1) correlates well to the value of T_{C} for each alloy. The compositional evolution of $\Delta S_{\mathrm{M}}^{\mathrm{pk}}$, however does not show a power law behavior. For the extreme compositions of the series, $\Delta S_{\mathrm{M}}^{\mathrm{pk}}$ passes from 1.32 J $\mathrm{K^{-1}}$ $\mathrm{kg^{-1}}$ for $x=0$ to 1.81 J $\mathrm{K^{-1}}$ $\mathrm{kg^{-1}}$ for $x=11$, and is maximized for $x=8.25$ with a value of 1.98 J $\mathrm{K^{-1}}$ $\mathrm{kg^{-1}}$.

The $\mathrm{RC_{FWHM}}$ and $\mathrm{RC_{AREA}}$ have a stepwise behavior due to the much narrower peak widths of the alloys with $x\geq 5.5$. $\mathrm{RC_{FWHM}}$ varies abruptly from ~166 J $\mathrm{kg^{-1}}$ ($x=0$ and 2.75) to 130 J $\mathrm{kg^{-1}}$ ($x=5.5$, 8.25, and 11). This is due to the different shapes of the low temperature tails of the $\Delta S_{\mathrm{M}}(T)$ curves presented in Fig. 1. $\mathrm{RC_{WP}}$, however, decreases monotonically from ~95 J $\mathrm{kg^{-1}}$ for $x=0$ to ~73 J $\mathrm{kg^{-1}}$ for $x=11$.

In order to compare these experimental values with those reported in the literature for other alloys, it would be necessary in most cases to formulate an expression to convert the values to an applied field of 5 T. It has been shown theoretically and experimentally that the field dependence of ΔS_{M} can be represented as[24,25] $\Delta S_{\mathrm{M}}(T,H)=c(T)H^n$. At $T=T_{\mathrm{C}}$ and $T=T_{\mathrm{pk}}$, the exponent n is field independent. At any other temperature, n is a function of the applied magnetic field.[26]

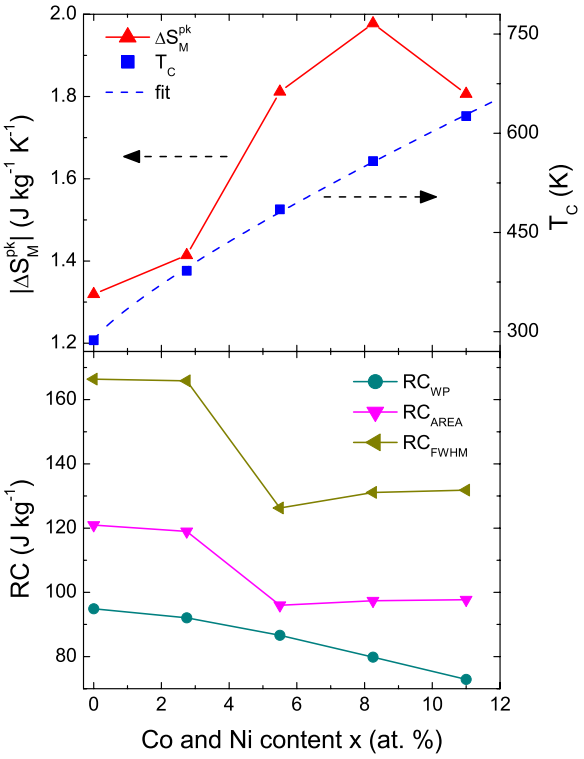

FIG. 2. (Color online) Dependence of the T_{C}, $\Delta S_{\mathrm{M}}^{\mathrm{pk}}$, and the different RCs, $\mathrm{RC_{WP}}$, $\mathrm{RC_{AREA}}$, and $\mathrm{RC_{FWHM}}$ on the Co and Ni content of the amorphous $Fe_{88-2x}Co_xNi_xZr_7B_4Cu_1$ ($x=0$, 2.75, 5.5, 8.25, and 11) alloy series. A magnetic field of $\mu_0H_{\mathrm{max}}=1.5$ T was employed to measure the $\Delta S_{\mathrm{M}}^{\mathrm{pk}}$ and RC values. Dashed line indicates the fitted data of T_{C} according to a power law $T_{\mathrm{C}}(x)\propto x^{0.81}(r^2=0.999)$.

RC can also be expressed as a power law of the field: $\mathrm{RC}(H)=bH^{n'}$.

By normalizing these expressions with the values corresponding to the maximum applied field, dimensionless relationships can be written for the different studied compositions

$$\delta s=\frac{\Delta S_{\mathrm{M}}^{\mathrm{pk}}(H,x)}{\Delta S_{\mathrm{M}}^{\mathrm{pk}}(H_{\mathrm{max}},x)}=\frac{a(x)H^n}{a(x)H_{\mathrm{max}}^n}=h^n,$$

$$\mathrm{rc}=\frac{\mathrm{RC_{FWHM}}(H,x)}{\mathrm{RC_{FWHM}}(H_{\mathrm{max}},x)}=\frac{b(x)H^{n'}}{b(x)H_{\mathrm{max}}^{n'}}=h^{n'}, \tag{3}$$

where $h=H/H_{\mathrm{max}}$. In principle, the exponents n and n' could be composition dependent (i.e., dependent on x). However, when these power laws are plotted for the different alloys (Fig. 3) both power law exponents have very similar values for the full series of alloys.

The present alloys compare favorably with other magnetocaloric materials. Among crystalline compounds, $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ is one of the most prominent materials due to its reduced hysteresis. For an applied field of 5 T its $\mathrm{RC_{AREA}}$ is 355 J $\mathrm{kg^{-1}}$; when the values of the studied alloys are calculated at 5 T based on the power law relationship in Fig. 3, the two alloys with the transition temperatures closest to room temperature ($x=0$ and 2.75) have $\mathrm{RC_{AREA}}$ =496 J $\mathrm{kg^{-1}}$, which is a ~40% increase. The values of $\Delta S_{\mathrm{M}}^{\mathrm{pk}}$ for the present alloys, which extrapolate to 5.3 J $\mathrm{kg^{-1}}$ $\mathrm{K^{-1}}$ for an applied field of 5 T, is smaller than that of $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ (7 J $\mathrm{kg^{-1}}$ $\mathrm{K^{-1}}$). The comparison with the

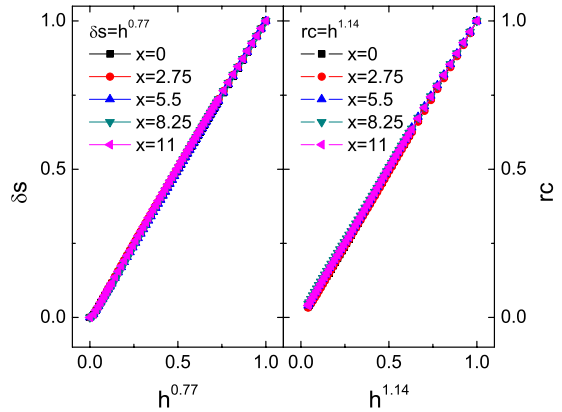

FIG. 3. (Color online) Dimensionless field dependence of the dimensionless peak entropy change, δs, and rc of the amorphous $Fe_{88-2x}Co_xNi_xZr_7B_4Cu_1$ (x=0, 2.75, 5.5, 8.25, and 11) alloy series. The collapse into a single master curve indicates that exponents n and n' are composition independent. For x=8.25, rc has been calculated from the width at 60% of the peak (instead of width at half maximum) to avoid mixing experimental data from the cryostat and the furnace.

$Fe_{83}Zr_6B_{10}Cu_1$ amorphous alloy (the Fe-based amorphous alloy with largest RC reported to date) is also favorable.[17] In that case, for an applied field of 1.5 T, RC_{AREA} = 104 J kg^{-1}, indicating that the series of alloys studied in this work give an increase of ~15%. In addition to this enhancement, with the present alloy series we have been able to tune the Curie temperature down to room temperature, while $Fe_{83}Zr_6B_{10}Cu_1$ had a T_C=398 K. The values of the peak entropy change for $Fe_{83}Zr_6B_{10}Cu_1$ and for the present series are similar.

In summary, it has been shown that by the simultaneous addition of Co and Ni to Fe–Zr–B–Cu alloys, the Curie temperature of the alloys can be tuned in a range which includes room temperature. The RC of this family of alloys is enhanced in ~40% with respect to the crystalline $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ and ~15% with respect to the best Fe-based amorphous alloy reported so far. This makes these alloys promising candidates to be used as room temperature magnetic refrigerants.

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