Influence of La and Ce additions on the magnetocaloric effect of Fe–B–Cr-based amorphous alloys

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The magnetic entropy change (ΔS\textsubscript{M}), temperature of peak ΔS\textsubscript{M} (T\textsubscript{pk}), and refrigerant capacity (RC) in Fe(RE)\textsubscript{0.8}B\textsubscript{12}Cr\textsubscript{8} (RE=La, Ce, or Gd) alloys were studied. Increasing La, Ce, and Gd content led to relatively constant, decrease, and increase in T\textsubscript{pk}, respectively. Both the phenomenologically constructed universal curve for ΔS\textsubscript{M} and field dependence power laws demonstrated that these alloys exhibited similar critical exponents at Curie temperature. With 5% Ce added to Fe\textsubscript{80}B\textsubscript{12}Cr\textsubscript{8}, T\textsubscript{pk} could be tuned near room temperature with relatively constant peak ΔS\textsubscript{M}. Fe\textsubscript{79}B\textsubscript{12}Cr\textsubscript{8}La\textsubscript{1} exhibited enhanced RC compared to Gd\textsubscript{5}Si\textsubscript{2}Ge\textsubscript{1.9}Fe\textsubscript{0.1}. The tunable T\textsubscript{pk} and enhanced RC are needed in active magnetic regenerators. © 2011 American Institute of Physics. [doi:10.1063/1.3589353]

Magnetic refrigeration (MR) offers a competitive alternative to conventional vapor compression refrigeration systems due to its high energy efficiency and environmental friendliness.1–4 It employs the magnetocaloric effect (MCE), which is related to the reversible temperature change in a magnetocaloric material (MCM) subjected to varying magnetic field under adiabatic conditions.1 The Curie temperature (T\textsubscript{C}) of MCM plays a significant role in magnetocaloric studies because MCE peaks near T\textsubscript{C}. Gadolinium, a well-known MCM, exhibits large MCE with a second order magnetic transition (SOMT) at T\textsubscript{C} near room temperature (RT). However, its high cost, poor corrosion resistance, and restricted availability necessitate the development of MCM for near RT MR. An ideal MCM should be low cost and exhibit good refrigerant capacity (RC) and peak magnetic entropy change (|ΔS\textsubscript{M}^\text{pk}|) with little hysteresis. Iron-based amorphous alloys fulfill such requirements. They offer low magnetic hysteresis, high electrical resistivity, enhanced corrosion resistance, good mechanical properties, and tunable T\textsubscript{C} by composition variation.4–6 In addition, the elements involved are abundant and fabrication costs are reasonable, making them highly competitive. Fe\textsubscript{80}Cr\textsubscript{12}amorphous alloys exhibit promising MCE near RT, Cr additions enhance the corrosion resistance of the alloy.7 Gd additions to this alloy have been studied previously8 with the aim of tuning the T\textsubscript{C} of the alloy. Fe\textsubscript{79}B\textsubscript{12}Cr\textsubscript{8}Gd\textsubscript{1} alloy displayed enhanced |ΔS\textsubscript{M}^\text{pk}| (~33% larger than Fe\textsubscript{80}B\textsubscript{12}Cr\textsubscript{8}) and RC values (~29% larger than Gd\textsubscript{5}Si\textsubscript{2}Ge\textsubscript{1.9}Fe\textsubscript{0.1} (Ref. 9)). These findings suggest that studies of the effect of rare earths (REs) additions on the MCE of Fe-based amorphous alloys would be useful. The type of RE additions to transition metals (TMs), such as Fe, influences the net magnetic moment of the alloys significantly: Gd and heavy RE contribute to ferromagnetism while light RE contribute to ferromagnetism, which generally results in a larger net magnetic moment than the former.10 The magnetism in such alloys depends on the nature of coupling between the RE and TM moments. As the 4f-5d electron exchange interaction at the RE site is ferromagnetic, the antiferromagnetic 5d(RE)-3d(TM) electron interactions result in ferromagnetic coupling of light RE to TM moments and vice versa for heavy RE.11 This present work shows that La, Ce, and our previously studied Gd additions to Fe–B–Cr amorphous alloys influence the temperature of ΔS\textsubscript{M} (T\textsubscript{pk}) differently.

Alloys with nominal composition Fe\textsubscript{80−x}RE\textsubscript{x}B\textsubscript{12}Cr\textsubscript{8} (x=0, 1, 5, 10, and 15) and Fe\textsubscript{80−y}RE\textsubscript{y}B\textsubscript{12}Cr\textsubscript{8}Ce\textsubscript{y} (y=2, 5, 10, and 15) were melt spun into ribbons. The ribbons are denoted by their (a) La content as La\textsubscript{1}, La\textsubscript{5}, La\textsubscript{10}, and La\textsubscript{15}, and (b) Ce content as Ce\textsubscript{2}, Ce\textsubscript{5}, Ce\textsubscript{10}, and Ce\textsubscript{15}. The amorphicity of the ribbons was confirmed by x-ray diffraction. Magnetic properties were measured by Lakeshore 7407 vibrating sample magnetometer for magnetic fields up to 15 kOe. The magnetic entropy change (ΔS\textsubscript{M}) due to the variation in applied magnetic field (H) was determined from ΔS\textsubscript{M}=\int_0^H (dM/dT)\text{d}H. RC is calculated in two ways in this study: (a) RC\textsubscript{FWHM}: the product of ΔS\textsubscript{M}^\text{pk} times the full temperature width at half maximum of the peak (RC\textsubscript{FWHM}=ΔS\textsubscript{M}^\text{pk} × ΔT\textsubscript{FWHM}), and (b) RC\textsubscript{AREA}: numerical integration of the area under the ΔS\textsubscript{M}(T) curves, using the full temperature width at half maximum of the peak as the integration limits.

The compositional dependence of |ΔS\textsubscript{M}^\text{pk}|, T\textsubscript{pk}, and RC\textsubscript{FWHM} are shown in the main panel of Fig. 1. For both La and Ce series, |ΔS\textsubscript{M}^\text{pk}| values remain relatively constant for RC content up to 5 at. % and progressively decreases for higher concentrations. The |ΔS\textsubscript{M}^\text{pk}| for Fe\textsubscript{80−x}RE\textsubscript{x}B\textsubscript{12}Cr\textsubscript{8} (RE=La or Ce; x=1–5 at. %) alloys compare favorably with the base Fe\textsubscript{80}B\textsubscript{12}Cr\textsubscript{8} amorphous alloy.7 For higher Gd content, the decrease in |ΔS\textsubscript{M}^\text{pk}| for the Gd alloy series was larger than those of the La and Ce series (Gd content ≥3 at. %). ΔS\textsubscript{M} has been shown to be correlated with the magnetic moment of the material in other alloy systems.8,12,13 To investigate whether such a relationship holds between |ΔS\textsubscript{M}^\text{pk}| and the magnetic moment of Fe\textsubscript{80−x}B\textsubscript{12}Cr\textsubscript{8}La\textsubscript{x} and Fe\textsubscript{80−y}B\textsubscript{12}Cr\textsubscript{8}Ce\textsubscript{y} amorphous alloys, the temperature dependence of magnetization was measured below T\textsubscript{C}. The low temperature spontaneous magnetization (M\textsubscript{0}) was obtained by the linear extrapolation of M(T)\textsuperscript{1/2} plots. The experimental |ΔS\textsubscript{M}^\text{pk}| values were plotted as a function of M\textsubscript{0} in the inset.
of Fe–Ce alloys was reported to exhibit tetravalent state in Ce–Fe alloys, which can lead to reduction in the Fe–Fe distance, which in turn reduces $T_C$, and thus these alloys exhibit lowest $T_C$ compared to other light RE alloys. Gd has been reported to display the largest $T_C$ among all RE,\textsuperscript{22,23} which led de Gennes to correlate this maximum with the maximal value of $4f$ spin in Gd.\textsuperscript{24} In addition, $T_{pk}$ in the La series showed little variation with La content compared to those of Ce and Gd containing alloys. In contrast, Ce alloys show a monotonic decrease in $T_{pk}$ with increasing Ce content. Unlike the La and Ce series, $T_{pk}$ was observed to increase with higher Gd additions.\textsuperscript{25,26} $RC_{FWHM}$ reduced with increasing RE content, with the Gd alloy series displaying the largest decrease compared to the La and Ce alloy systems. For Ce15, the decreasing trend of $RC$ shows a larger negative slope compared to that of the La15 alloy. To study this reduction in $RC_{FWHM}$, the compositional dependence of full temperature width at half maximum ($\delta T_{FWHM}$) of $|\Delta S_M^{pk}|$ was plotted [inset of Fig. 1(c)]. For RE=15 at. %, $\delta T_{FWHM}$ increased for the La15 alloy while the Ce15 alloy showed a large reduced $\delta T_{FWHM}$ among the Ce alloy series. For La alloy series, $\delta T_{FWHM}$ did not significantly change with La concentration. On the other hand, $\delta T_{FWHM}$ decreased with increasing Ce concentration. The decrease in $RC$ for the La alloy series could be attributed to the reduction in $|\Delta S_M^{pk}|$ ($RC$ being proportional to $|\Delta S_M^{pk}|$ and $\delta T_{FWHM}$ since $|\Delta S_M^{pk}|$ generally plays a dominant role in $RC$ maximization for SOMT materials.\textsuperscript{27} For the Ce alloy series, the reduced $|\Delta S_M^{pk}|$ and $\delta T_{FWHM}$ contributes to a much lower $RC$ value, e.g., in the Ce15 alloy. For the Gd series, the large decreasing trend of $RC$ could be attributed to the large reduction in $|\Delta S_M^{pk}|$ with Gd addition.

Literature reports of the properties of MCM are usually published at the maximum available magnetic field in individual laboratories. To compare different literature values, the field dependence studies of $\Delta S_M^{pk}$ and $RC$ should be known. The field dependence of magnetic entropy change can be expressed as $\Delta S_M^{pk} \propto H^2$, validated experimentally in several soft magnetic amorphous alloys and some RE-based crystalline MCM.\textsuperscript{17} The exponent $n$ is field invariant at $T_C$ or $T_{pk}$.\textsuperscript{17} The field dependence of $RC$ can also be represented by a power law expression: $RC_{FWHM} \propto H^n$. Exponents $n$ and $N$ should have similar values for a given alloy series since they are controlled by the critical exponents of the alloy series. As an example, $\Delta S_M^{pk}(H)$ and $RC(H)$ for the La5 and Ce5 alloys are presented in the insets of Fig. 2. The good fits shown aid the determination of the exponents $n$ and $N$. For the La alloys: $n=0.79 \pm 0.01$ and $N=1.20 \pm 0.01$; and Ce alloys: $n=0.77 \pm 0.03$ and $N=1.20 \pm 0.01$. These values are close to those obtained for Gd alloys ($n=0.75 \pm 0.01$ and $N=1.16 \pm 0.01$). Both $RC_{FWHM}$ and $RC_{AREA}$ have been predicted to scale with field with the same value of exponent,\textsuperscript{17} in good agreement with our experimental results. When $|RC_{AREA}|$ for the La1 and La5 alloy are extrapolated to $H=50$ kOe, values of 386 J kg$^{-1}$ and 356 J kg$^{-1}$, respectively, are obtained, which are up to $\sim 9\%$ higher than the well-known MCM—Gd$_{5}$Si$_{2}$Ge$_{1.9}$Fe$_{0.1}$.\textsuperscript{9} For Ce2 alloys, its $|RC_{AREA}|$ yield 367 J kg$^{-1}$ when extrapolated to 50 kOe, compared to the literature.\textsuperscript{18–20} In contrast, $T_{pk}$ reduces as Ce concentration increases. The Ce alloy series displays lower $T_{pk}$ values compared to the La alloy series.\textsuperscript{21}
Fe$_{80}$B$_{12}$Cr$_8$RE$_x$ alloys exhibit enhanced RC compared to the previous results for the Gd alloy series.

1.20, respectively, for the La alloy series and 0.77 and 1.20, of a power law dependence, yielding exponents as 0.79 and 0.87. Both $\Delta S_M$ curves collapse nicely onto a single curve for each alloy series, confirming that they exhibit SOMT, that the universal curve is applicable to these alloys and that their critical exponents should be the same.

In summary, additions of La and Ce to Fe–B–Cr amorphous alloys led to different influences on $T_{\text{pk}}$. With increasing RE content, $T_{\text{pk}}$ decreases for Fe$_{80-x}$B$_{12}$Cr$_8$Gd$_x$, but increases for Fe$_{80-x}$B$_{12}$Cr$_8$La$_x$. La additions have little effect on $T_{\text{pk}}$. For $x=1$ and 5, at % in Fe$_{80-x}$B$_{12}$Cr$_8$La$_x$ and Fe$_{80-x}$B$_{12}$Cr$_8$Ce$_x$ amorphous alloys, $T_{\text{pk}}$ can be tuned near RT with $\Delta S_M$ comparable to the base Fe$_{80}$B$_{12}$Cr$_8$ alloy. Both $\Delta S_M^p$ and RC plots agree with theoretical predictions of a power law dependence, yielding exponents as 0.79 and 1.20, respectively, for the La alloy series and 0.77 and 1.20, respectively, for the Ce alloys. These are in good agreement with the previous results for the Gd alloy series. Fe$_{80-x}$B$_{12}$Cr$_8$La$_x$, alloys exhibit enhanced RC compared to the well-known MCM Gd$_5$Si$_2$Ge$_4$Fe$_{0.1}$. This work was supported by the U.S. AOARD (Grant No. AOARD-08-4018), program manager, Dr. R. Ponnapan, by the Spanish Ministry of Science and Innovation and EU FEDER (Project No. MAT 2010-20537), the PAI of the Regional Government of Andalucía (Project No. FQM-6462), and the United States Office of Naval Research (Project No. N00014-11-1-0311).

FIG. 2. (Color online) Universal curves for Fe$_{80-x}$B$_{12}$Cr$_8$RE$_x$ where RE =La or Ce. Inset: field dependence of $\Delta S_M^p (\bigcirc)$, RC$_{\text{FWHM}} (\bigcirc)$, and RC$_{\text{AREA}} (\triangle)$ for (a) La5 and (b) Ce5 alloys. Lines are fits to the power law expressions.