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Citation: Journal of Applied Physics 100, 064307 (2006); doi: 10.1063/1.2337871
View online: http://dx.doi.org/10.1063/1.2337871
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The magnetocaloric effect in soft magnetic amorphous alloys
The influence of Co addition on the magnetocaloric effect of Nanoperm-type amorphous alloys

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(Received 3 March 2006; accepted 21 June 2006; published online 22 September 2006)

The effect of Co addition on the magnetocaloric effect of amorphous alloys with Nanoperm-type composition has been studied for temperatures above room temperature. Co addition produces an increase in the maximum magnetic entropy change and a shift of its associated temperature to higher temperatures. The maximum refrigerant capacity (RC) value obtained in this study is 82 J kg⁻¹ for a maximum applied field H=15 kOe. This value is ~30% larger than that of a Mo-containing Finemet-type alloy measured under the same experimental conditions. However, the RC of the alloys, when calculated from temperatures corresponding to the half-maximum entropy change value, deteriorates with the presence of Co in the alloy. The field dependence of the magnetic entropy change has also been analyzed, showing a power dependence for all the magnetic regimes of the samples. This field dependence at the Curie temperature deviates from mean field predictions. © 2006 American Institute of Physics. [DOI: 10.1063/1.2337871]

INTRODUCTION

The magnetocaloric effect (MCE), reported by Warburg in 1881,¹ consists in the temperature change of a magnetic material upon the application of a magnetic field. When magnetized, the entropy of the spin subsystem is decreased and, under adiabatic conditions, the transfer of energy to the lattice provokes the heating of the material. Conversely, the adiabatic demagnetization of the material causes its cooling, an effect that has been employed for reaching temperatures below 1 K since 1933.²

MCE phenomenon is not new, and there were proposals for employing it at temperatures close to room temperature since 1976.³ In 1998 a prototype was efficiently tested for room-temperature magnetic refrigeration.³ This long delay in the application of the MCE at high temperatures was not due to conceptual difficulties, but to technological ones, the selection of adequate materials being among them.

To display a significant MCE response, a material needs to exhibit an appreciable temperature dependence of magnetization in the application temperature range. Therefore, for cooling at temperatures around 1 K, paramagnetic materials can be used as their magnetic response increases when approaching 0 K. However, their response is negligible at temperatures close to room temperature. In order to obtain materials with a noticeable temperature dependence of magnetization at higher temperatures, ferromagnetic materials can be used. When the Curie temperature of the material is approached, the ferromagnetic-paramagnetic transition causes a peak in the magnetic entropy change associated with the magnetization/demagnetization of the material. As the Curie temperature of Gd is close to room temperature (294 K) and its magnetic moment is large, this element was the material of choice for developing the initial room-temperature prototypes.³⁴ The efforts for finding materials which can be employed as high temperature magnetic refrigerants are not futile, because refrigeration based on MCE is energetically more efficient than that of conventional gas compression-expansion refrigerators and more environmentally friendly as neither ozone-depleting nor global-warming volatile refrigerants are required. Therefore, currently there is an intensive research in this field,⁵⁻⁷ with two main objectives: the maximization of material properties and the reduction of material cost. In this respect, the peak entropy change (ΔSM) has been maximized with the so-called giant MCE (Ref. 8) and giant inverse MCE,⁹ while cost reduction is being investigated by using transition metal based alloys instead of rare earth based materials.¹⁰ In particular, there is a growing interest in studying the applicability of soft magnetic amorphous alloys as magnetic refrigerants¹¹⁻¹⁵ due to their reduced magnetic hysteresis (virtually negligible), enhanced electrical resistivity, and tunable Curie temperature. In the case of bulk amorphous alloys,¹⁶,¹⁷ outstanding mechanical properties are also exhibited. All these characteristics are beneficial for a successful application of the material.

The aim of this work is to analyze MCE of soft magnetic amorphous alloys of the Nanoperm family, taking into consideration the influence of Co addition on the refrigerant capacity of the material, and to study the field dependence of the magnetic entropy change. As the magnetic moment and Curie temperature of Fe based amorphous alloys depend on Co addition, it could be expected that it will also have an influence on MCE.

EXPERIMENT

Amorphous ribbons (~5 mm wide and 20–30 μm thick) of Fe₈₃Zr₁₀B₁₀Cu₁ and Fe₇₈Co₅Zr₁₀B₁₀Cu₁ were obtained by melt spinning. The amorphous character of the as-quenched alloys was checked by x-ray diffraction. The field dependence of magnetization was measured in a LakeShore 7407 vibrating sample magnetometer using a ma-
mum applied field $H = 15$ kOe with field steps of 50 Oe, for constant temperatures in the range of 300–625 K with increments of 10 K. Prior to the measurements, the stress of the samples was relaxed by preannealing them at 700 K.

The MCE can be characterized by the magnetic entropy change due to the application of a magnetic field $H$, which can be evaluated from the processing of the temperature and field dependent magnetization curves using a numerical approximation to the equation

$$\Delta S_M = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH,$$

where the partial derivative is replaced by finite differences and the integration is performed numerically.

In order to compare the performance of different materials, either the peak entropy change $|\Delta S_M^{pk}|$ or the refrigerant capacity (RC) is used. The refrigeration at low temperatures requires a narrow temperature span of the refrigeration cycle, making $|\Delta S_M^{pk}|$ the parameter of choice for comparing low temperature materials, while high temperature refrigeration implies a wider temperature range and, consequently, RC is employed for comparison. According to Wood and Potter, the RC of a reversible refrigeration cycle operating between $T_h$ and $T_c$ (the temperatures of the hot and cold reservoirs, respectively) is defined as $\text{RC} = \Delta S_M \Delta T$, where $\Delta S_M$ is the magnetic entropy change at the hot and cold ends of the cycle and $\Delta T = T_h - T_c$. Moreover, hysteresis losses can be taken into account when evaluating the refrigerant material by subtracting them from the computed RC, making the comparison between materials with different coercivities more straightforward. The optimal refrigeration cycle is that which maximizes the RC.

RESULTS AND DISCUSSION

Temperature dependence of the magnetic entropy change

Figure 1 shows the temperature dependence of the magnetic entropy change corresponding to an applied field $H = 15$ kOe for the two studied samples. Co addition produces an enhancement in the temperature at which the maximum entropy change takes place, in agreement with the influence of Co content on the Curie temperature of the amorphous phase ($T_{Cm}^{am}$) for these alloys. 20 It is worth mentioning that, in contrast to this behavior, amorphous alloys with larger metalloid concentration exhibit a monotonous decrease of $T_{Cm}^{am}$ with increasing Co content. 21-23 In the case of the studied alloys, Co addition leads to an increase of the $|\Delta S_M^{pk}|$ value, unlike the observed behavior for the FeCoSiAlGaPCB alloy series, with larger metalloid content. 17 It has to be noted that an estimate of the error in $|\Delta S_M^{pk}|$ is below 3%, which is below the differences observed for both samples. The explanation of this influence of the metalloid content on $T_{Cm}^{am}$ and $|\Delta S_M^{pk}|$ should be ascribed to the change in the local environment of Fe and Co atoms and its effect on the exchange interaction between atoms. 23 The $|\Delta S_M^{pk}|$ value of the Co-containing Nanoperm-type alloy is ~50% larger than that of a Mo-containing Finemet-type alloy, with a comparable $T_{Cm}^{am}$, measured under the same experimental conditions, 14 while the Co-free Nanoperm-type alloy increases the peak entropy change by ~31% with respect to the same Finemet-type alloy. Comparing with the Fe70B5Si5Al5Ga10P10 amorphous alloy, 17 the Co-containing alloy presents a comparable value of $|\Delta S_M^{pk}|$, with the advantage of a peak temperature $T_{pk}$ which is 100 K closer to room temperature for the alloy studied in the present work.

Field dependence of the magnetic entropy change

The magnetic entropy change not only depends on the measuring temperature but also on the value of the maximum applied field. Figure 2 shows the combined field and temperature dependence of $|\Delta S_M|$ for the two studied alloys. For all temperatures, the magnetic entropy change increases with increasing maximum applied field $H$. The field dependence can be expressed as

FIG. 1. (Color online) Temperature dependence of the magnetic entropy change for a maximum applied field of 15 kOe.

FIG. 2. (Color online) Field and temperature dependences of the magnetic entropy change for Fe70Zr5B10Cu1 (bottom) and Fe70Co5Zr5B10Cu1 (top).
The field dependence of $\Delta S_M$ at $T_{pk}$ for the Co-free alloy is also analyzed in Fig. 4 by representing $\Delta S_M$ versus field and fitting the curve to a power law (equivalent results are obtained for the Co-containing alloy). The value obtained for the exponent (−0.76) is comparable to the minimum in Fig. 3. This value of the exponent, higher than the mean field predictions, could be due to local inhomogeneities in the amorphous alloy, causing a distribution of Curie temperatures, although the amorphous character of the alloy can also have an effect. On the other hand, discrepancies with mean field theories in the vicinity of a transition temperature can be expected.

**Refrigerant capacity**

As previously mentioned, the comparison between different materials for high temperature magnetic refrigeration should be based on the refrigerant capacity. Figure 5 shows the refrigerant capacity of the studied alloys as a function of the temperature of the cold reservoir, $T_c$, ranging from room temperature up to $T_{pk}$ of each alloy. As $T_c$ separates from $T_{pk}$, the refrigerant capacity of the material increases. An optimal refrigeration cycle can be found for the Co-containing alloy in the experimental temperature range, as evidenced by a maximum in RC. The maximum RC values obtained in this study are 77 and 82 J/kg for the Co-free and Co-containing alloys, respectively, indicating a superior performance of the Co-containing alloy for refrigeration cycles with $T_c$ above room temperature. However, the shape of the curve for the Co-free alloy suggests a maximum RC below room temperature for this alloy.

Instead of comparing the maximum obtained RC values, if we compare the RC values of refrigeration cycles with temperatures corresponding to half of $|\Delta S_M^0|$ (i.e., the temperature span of the cycle corresponds to the width at half-maximum in the data), the amorphous alloy, caused by a distribution of Curie temperatures, although the amorphous character of the alloy can also have an effect. On the other hand, discrepancies with mean field theories in the vicinity of a transition temperature can be expected.
maximum), the consideration of the Co-containing alloy as the one with a better performance no longer holds. In this case RC values are 71 and 63 J/kg for the Co-free and Co-containing alloys, respectively. This is in agreement with the previous suggestion of an optimal cycle for the Co-free alloy because the Co-containing alloy, the optimal refrigeration cycle corresponds to the Co-containing alloy, the optimal cycle for the Co-free alloy with a cold end below room temperature. These values are comparable to recent results on the magnetocaloric effect of Co–Cr containing Nanoperm-type alloys.15

Figure 6 presents the relationship between $T_h$ and $T_c$ for cycles which produce the maximum RC for a given $T_c$. For the Co-containing alloy, the optimal refrigeration cycle corresponds to $T_h = 531$ K and $T_c = 325$ K, while for the Co-free alloy the maximum obtained RC corresponds to $T_h = 440$ K and $T_c = 308$ K.

The maximum RC value measured in this work favorably compares to the previously mentioned Finemet-type and Fe$_{70}$B$_5$C$_5$Si$_3$Al$_5$Ga$_2$P$_10$ amorphous alloys, being ~30% larger in the present case.

CONCLUSIONS

The field dependence of the magnetic entropy change has also been analyzed, showing a power dependence for all the magnetic regimes of the samples. In the ferromagnetic range the exponent is 1. In the paramagnetic regime, well above the Curie temperature, the power is 2, in agreement with the Curie-Weiss law. However, the field dependence at the Curie temperature deviates from mean field predictions.

ACKNOWLEDGMENTS

This work was supported by the Spanish Government and EU-FEDER (Project No. MAT 2004-04618) and the PAI of Junta de Andalucía. One of the authors (J.S.B.) is grateful to Junta de Andalucía for a research contract.