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Enhancement of the magnetocaloric effect in composites: Experimental validation

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ABSTRACT

Recent calculations have shown that the refrigerant capacity (*RC*) of magnetic refrigerants can be enhanced using multiphase materials or composites, which expand the temperature range over which a significant magnetic entropy change can be obtained. This work is a systematic experimental validation of the improvement of *RC* (*RCI*) using layered composites comprised of two $Fe_{88-2y}Co_yNi_yZr_7B_4Cu_1$ amorphous alloy constituents, with $y=8.25$ and $y=11$ compositions. *RCI* has a nonmonotonic dependence on the applied magnetic field H and the fraction x of the two constituent phases. In contrast to common assumptions, the composite has a smaller *RCI* than its constituent phases for small values of H and x, and there are critical values of each for which *RCI* is maximized. This work demonstrates the outstanding agreement between the experimental results and the continuous curves predicted by numerical calculations, indicating that this approach can be used to design magnetic refrigerant materials with enhanced magnetocaloric response for moderate magnetic fields.

1. Introduction

Solid-state magnetic refrigeration (MR) based on the magnetocaloric effect (MCE) is an active area of research, due in part to the recent discovery of materials exhibiting appreciable magnetocaloric response near room temperature [1–3,17]. Improved energy efficiency and reduced environmental impact are the primary advantages of MR as compared with conventional gas compression–expansion refrigeration technology [4].

The MCE consists in a reversible temperature change of the material that occurs during application of a changing external magnetic field (ΔH) under adiabatic conditions. Related to this process, there is a reversible isothermal magnetic entropy change (ΔS_M), given by

$$\Delta S_M(T,\Delta H) = \int_{H_0}^{H_f} \mu_0 \frac{\partial M(T,H)}{\partial T}\bigg|_H dH, \quad (1)$$

where $\Delta H = H_f - H_0$ is the change in applied field, μ_0 is the magnetic permeability of vacuum, and $M(T,H)$ is the specific magnetization of the material. In this work $\mu_0 H_0 = 0$ T. According to Eq. (1), ΔS_M depends on the variation of $M(T,H)$ with temperature and attains a peak value (ΔS_M^{pk}) around the Curie temperature (T_C), the temperature at which a magnetic phase transition occurs and $M(T,H)$ varies most rapidly. The MCE can also be characterized by the refrigerant capacity (*RC*) [5] defined as the heat transferred per unit mass of the refrigerant material from the hot (at temperature T_{hot}) to the cold (at temperature T_{cold}) reservoirs in the thermodynamic cycle:

$$RC(\delta T,H) = \int_{T_{cold}}^{T_{hot}} \Delta S_M(T,H)dT, \quad (2)$$

where $\delta T = T_{hot} - T_{cold}$. This temperature span must be specified *a priori* when comparing different refrigerant materials. It is common to define δT as the temperature range spanning the half-maximum of the $\Delta S_M(T)$ curve (δT_{FWHM}), with the resulting integral denoted as RC_{AREA}. While the hysteretic losses (primarily associated with first order magnetic phase transitions) should be subtracted from Eq. (2) [6], these losses are negligible for the specimens studied.

The MCE can be maximized by increasing the value of maximum entropy change ΔS_M^{pk} and/or broadening the temperature span δT, thereby increasing the integrated value of the $\Delta S_M(T)$ curve. To date, magnetic refrigeration at room temperature has been limited by three challenges: (*i*) for most materials, T_C is not near room temperature; (*ii*) the materials that exhibit the largest MCE have a first order magnetic phase transition and are based on rare earth elements, with large thermal and magnetic hysteretic losses and high cost; and (*iii*) the large fields required for

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appreciable MCE preclude the use of this technology in domestic appliances.

Fe-based amorphous alloys offer significant promise as magnetocaloric materials. The T_C of these alloys can be easily modified by alloying [7]. While the second order magnetic phase transition in these materials results in a moderate value of ΔS_M^{pk}, the transition is relatively broad with a wide temperature span δT around T_C [8,9], resulting in a significant *RC*. The remaining problem of the high field requirements needed in the MR process is still an unsolved issue, although there have been approaches to enhance the magnetic field responsiveness of MCE materials by altering their microstructure (e.g., by multilayering [10]).

Recent calculations have shown [11] that the use of multiphase materials could help enhance the *RC* values of magnetic refrigerants. In this work we present a systematic experimental validation of the improvement of *RC* (*RCI*) via the study of bi-layered composites using $Fe_{88-2y}Co_yNi_yZr_7B_4Cu_1$ amorphous alloys, with $y=8.25$ (phase A) and $y=11$ (phase B) compositions, changing the fraction x of phase B. We will show that *RC* can be enhanced 34% with respect to that of the constituent phase with the largest value. The response of the composite for 1.5 T is comparable to that of single phase for 2 T, which demonstrates that the use of composites could be a good strategy to reduce the high field requirements needed in the MR process.

The aim of this paper is to evidence, with extensive experimental data, that the theoretical predictions of an enhanced *RC* for composite materials can be achieved in practice. In addition to the previously indicated characteristics of Fe-based amorphous alloys, which make them promising as magnetic refrigerant materials, there are further reasons which make us choose this kind of materials for the current work: they lack magnetocrystalline anisotropy, they are extremely soft from the magnetic point of view, and the magnetocaloric response of each phase can be modeled with high accuracy in the environment of the transition temperature by using an easy to handle equation of state. This combination of properties make them ideal for correlating the modeled response of a virtually fabricated composite and the experimental results of the material itself. The main results of this paper are to show experimentally that the compositional, thermal and magnetic field dependencies of the magnetocaloric composite agree with the model, and to prove that this can be a good strategy for improving *RC*, which is complementary to the search of new magnetocaloric materials. Depending on the characteristic of the individual phases, the applicability of the material would be different. In the present case, when the choice of materials is made to simplify the modeling, the full width at half maximum of the peak of the composite will be extended for a temperature span which is larger than that which would be used in current refrigerator designs; but the application of the same strategy to other phases will help to improve the performance of materials with potentiality to be used in refrigerators.

2. Experimental

Amorphous $Fe_{88-2y}Co_yNi_yZr_7B_4Cu_1$ alloys, with compositions corresponding to $y=8.25$ (phase A) and $y=11$ (phase B), were produced by a melt-spinning technique resulting in ribbons 2–3 mm wide and ~20 μm thick. Further details about sample preparation, and microstructural and magnetic characterization are provided elsewhere [12]. A series of layered composites were prepared, consisting of two layers of amorphous as-spun ribbons (phases A and B) in intimate contact. The mass fraction x of phase B was systematically increased from $x=0$ (only phase A) to $x=1$ (only phase B) in approximately 10% increments. The magnetization, M, of the composite specimens was measured using a LakeShore 7407 by vibrating sample magnetometer under maximum applied fields ranging from $\mu_0 H_f=0.25$ to 1.50 T (in 10 mT increments), and at temperatures from 423 to 673 K (in 10 K increments).

3. Results and discussion

Fig. 1 displays the temperature and field dependence of the magnetization, $M(T,H)$, of the ten laminated composites (open symbols) and the constituent phases A and B (solid symbols), for applied fields of $\mu_0 H=0.5$ and 1.5 T. These results indicate that the magnetic phases in these composites are non-interacting, as the total magnetization $M(T,H)$, can be expressed as a rule-of-mixtures sum of the magnetization $M_A(T,H)$, and $M_B(T,H)$, of the constituent phases A and B, respectively, according to the expression

$$M(T,H,x)=(1-x)M_A(T,H)+xM_B(T,H) \quad (3)$$

The solid curves in Fig. 1 are calculated using Eq. (3), confirming the excellent agreement between the rule-of-mixture sum and the experimental data. The constituent phases have Curie temperatures $T_{C,A}=558$ K and $T_{C,B}=626$ K, obtained from the inflection points of experimental magnetization data measured at low field ($\mu_0 H=0.01$ T), and are independent of the fraction of the constituent phases, as expected according to Eq. (3). The magnetization of the composites predicted by Eq. (3) is especially accurate between $T_{C,A}$ and $T_{C,B}$, which is also the temperature range where the magnetocaloric response of the samples is greatest.

Fig. 2a displays the temperature dependence of the magnetic entropy change of the ten laminated composites (open symbols, except for the $x_{opt}=0.646$ sample, for which the solid symbol ▲ is used) and the two constituent phases A and B (solid symbols ■ and ●, respectively), measured for a maximum applied magnetic field of $\mu_0 H=1.5$ T. The curves for the two constituent phases exhibit a caret-like shape, characteristic of a second order magnetic

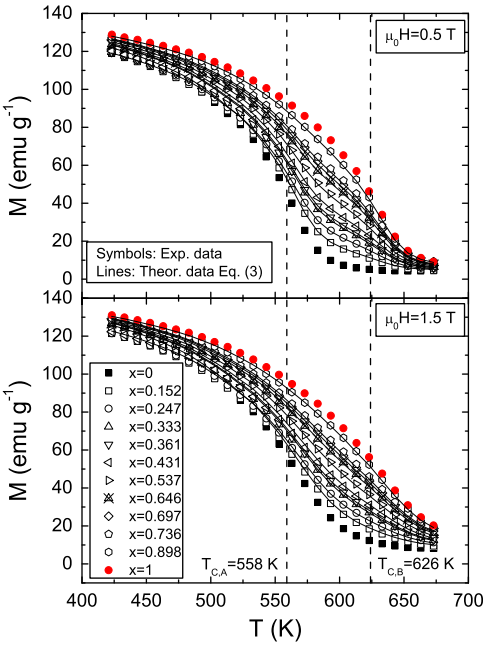

Fig. 1. (Color online) Temperature dependence of the magnetization $M(T,H)$ of the ten laminated composites (open symbols) and that of the constituent phases A and B (solid symbols ■ and ●, respectively) under an applied field of $\mu_0 H=0.5$ T (upper panel) and under an applied field of $\mu_0 H=1.5$ T (lower panel). Solid lines indicates the theoretical M(T,H) values of the composite samples given by Eq. (3), and dashed lines mark the Curie temperatures of the constituent phases.