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Gd+GdZn biphasic magnetic composites synthesized in a single preparation step: Increasing refrigerant capacity without decreasing magnetic entropy change

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ABSTRACT

Biphasic Gd + GdZn composites ($Gd_{(50+x)}Zn_{(50-x)}$; x = 0, 5, 15 and 25 at.%) were successfully obtained in a single fabrication step by induction melting. X-ray microdiffraction results reveal the homogeneity of all the prepared samples and indicate a combination of GdZn and Gd phases with different proportions. With this method, the main drawbacks of preparing composites have been avoided, providing the additional advantage of enhanced thermal conductivity between phases. The biphasic Gd + GdZn composite shows an enhanced refrigerant capacity in comparison to Gd (11%) as well as to single phase GdZn (45%). Heat capacity measurements provide an adiabatic temperature change of around 3.5 K for 20 kOe for the optimal composite.

1. Introduction

Magnetic refrigeration, based on the magnetocaloric effect (MCE), has been widely classified as an emergent cooling technology with environment amity and good energy efficiency [1]. In general, single phase magnetocaloric materials exhibit a peak in the entropy change close to the transition temperature, which can be particularly abrupt for first order phase transitions. However, in some thermodynamic refrigeration cycles, such as Ericsson-cycle, it would be beneficial to reduce the variation of the magnetic entropy values ($\Delta S_M(T)$) in a range of about 30 K to approach a table-like MCE (a constant ΔS_M in the refrigeration temperature range). This can be indirectly characterized using the refrigerant capacity (*RC*). Basically, the enhancement of *RC* requires a broad $\Delta S_M(T)$ with a large peak value of magnetic entropy change (ΔS_M^{pk}). However, it is challenging to find these two features for a single-phased magnetocaloric material. Care has to be taken when claiming of a large *RC* but corresponding to very low ΔS_M values, as it would be impossible to exploit these values in experimental devices. Thus, a realistic approach to optimize *RC* is the development of a two- or multi-phase magnetocaloric material with the appropriate selection of magnetic phase transition temperatures [2]. Magnetocaloric composites have been both theoretically and experimentally shown to exhibit enhanced *RC* in comparison to pure phases [2]. However, multiphase magnetocaloric materials are typically reported with relatively small ΔS_M^{pk} values [3–6]. Nevertheless, to be realistically applicable in devices, it is essential that each of the existing phases in the composite presents a large magnetocaloric response. Moreover, the typical approach to combine different phases in MCE composites, to date, involves the preparation of multilayers, mixing powders etc. However, these methods entail drawbacks, such as poor thermal conductivity between surfaces, additional time-consuming preparation steps during the synthesis, etc.

The binary GdZn intermetallic, whose Curie temperature (T_C) lies near room temperature, could co-exist with Gd phase in a composite alloy by varying the Gd:Zn ratio, according to its phase diagram [7]. As Gd is the reference magnetocaloric material near room temperature, it is of keen interest to study the MCE of the two-phase (Gd and GdZn) composite material. Theoretical predictions of the two-phase alloy showed that magnetocaloric properties are tuned by compositional variation of Gd:Zn ratio, which could enable flexibility in the choice of thermodynamic cycle and highly effective MCE composite regenerator materials [8]. Despite the promising results from the theoretical MCE

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predictions of Gd + GdZn composite, no systematic studies of the composite were reported but the MCE of pure GdZn phase alloy instead [8]. Other relevant literature reports the MCE of several Gd eutectic compositions, which included Gd–GdZn but receiving the least focus [9,10]. In addition, the synthesis routes of fabricating these composites were challenging, implying several steps and sophisticated manipulation [8–10].

Hence, in this work, we aim to use an alternative approach to develop, in a single fabrication step, a material with mixed constituent phases within the composite (Gd + GdZn) with large magnetocaloric response.

2. Experimental

The GdZn alloy series, with nominal composition of $Gd_{(50+x)}Zn_{(50-x)}$ (with x = 0, 5, 15 and 25 at.%), was prepared by induction melting in argon a stoichiometric mixture of pure Gd and Zn in a quartz crucible. Both commercial Gd and Zn are 99.9 and 99.98 wt.% pure, respectively. Besides pure Gd, the alloys are denoted by their Zn content as Zn50, Zn45, Zn35 and Zn25. A vacuum of 10^{-5} mbar was obtained in the induction-melting furnace prior to filling the furnace with Ar gas to 700 mbar. The alloy (total weight of ~5 g) was melted 2 times to ensure homogeneity. Their microstructure and phases were characterized by X-ray microdiffraction (XRMD) on the very samples used for magnetic and heat capacity measurements. Phase fractions were measured using Rietveld fitting of the patterns. The experimental broadening prevents further discussion on the crystal size or the microstrains of the samples. The magnetic and heat capacity properties were measured using a commercial Physical Property Measurement System from Quantum Design in the temperature range of 220–380 K for magnetic fields up to 20 kOe. The ΔS_M of the alloys was determined from the M–H isotherms using the Maxwell relation $\Delta S_M = \mu_o \int_0^H (\partial M/\partial T)_H dH$, where μ_o is the magnetic permeability of vacuum, H is the applied magnetic field, M is the magnetization and T is the temperature. RC is calculated using two methods: (a) RC_{FWHM}: the product of ΔS_M^{pk} and the full temperature width at half maximum of the peak ($RC_{FWHM} = \Delta S_M^{pk} \cdot \delta T_{FWHM}$), and (b) RC_{AREA}: numerical integration of the area under the $\Delta S_M(T)$ curves, using the full temperature width at half maximum of the peak as the integration limits. The adiabatic temperature change (ΔT_{ad}) has been calculated as:

$$\Delta T_{ad}(H) = [T_H(S) - T_0(S)]_S \tag{1}$$

where $T_H(S)$ curves were obtained from heat capacity measurements at constant pressure and magnetic field ($C_{P,H}$) using that $S(T,H) \cong \int_0^T \frac{C_{P,H}(T)}{T} dT$ (where the entropy at zero temperature is neglected) [11]. Results are compared with the widely used method that neglects the field dependence of $C_{P,H}$, thus ΔT_{ad} can be approximated as [12]:

$$\Delta T_{ad}(H) \cong \frac{T}{C_{P,H}} \Delta S_M \tag{2}$$

To check the validity of the approximation, $C_{P,H}$ has been considered for the extreme cases $H = 0$ and $H = 20$ kOe.

3. Results and discussion

The experimental XRMD patterns of the alloys are presented in Fig. 1 along with the corresponding theoretical ones and the individual contribution of each phase used in the fitting. Rietveld refinement analysis reveals 100% GdZn (CsCl-type) phase for Zn50 alloy, indicating the successful synthesis preparation method. For the rest of alloys, an amount of ~ 4–8 wt.% Gd_2O_3 impurity phase in addition to Gd and GdZn phases were detected, which suggests surface oxidation of the alloy as a likely scenario since Gd is easily susceptible to oxidation. The refinement results also showed increasing GdZn phase content with Zn concentration, which is in good agreement with the nominal composition.

The $\Delta S_M(T)$ curves of the alloys under an applied magnetic field of 20 kOe is presented in Fig. 2. It is observed that only one ΔS_M^{pk} value was observed for single-phase alloys (Gd and Zn50 alloy) while a more table-like behavior (two ΔS_M^{pk} values at 265 ± 1 K and 290 ± 1 K) was obtained for biphasic alloys. In addition, all the ΔS_M^{pk} values occur at temperatures near room temperature and show very similar values (3.2 ± 0.2 J kg^{-1} K^{-1}). In the case of GdZn, the ΔS_M^{pk} (3.22 J kg^{-1} K^{-1}) of the alloy displays ~70% of that observed for pure Gd piece.

The compositional dependence of RC of the Gd–Zn alloys ($\Delta H = 20$ kOe) is presented in inset of Fig. 2. An enhancement of RC of 11% and 45% was attained by the composites when compared to pure Gd and GdZn alloy, respectively, which could be attributed to the relatively small separation of the magnetic entropy change peaks of the two phases (266 and 290 K), giving rise to the table-like shape of $\Delta S_M(T)$ curves. The large temperature range of the maximum MCE properties, 266–290 K, facilitated these composites with good flexibility in adjusting the temperature dependencies of ΔS_M, which is accessible from the tuning of Gd:Zn ratio. This enables the composites as potential candidate materials for different magnetic refrigeration cycles and thus different cooling applications. It is worth noting that the separation between peaks cannot be arbitrarily chosen in a composite, as too large distance will decrease RC, while too close peaks would cause no improvement [2]. The improvement of the table-like character of $\Delta S_M(T)$ curves can be estimated as the dispersion, $\sigma(\Delta S_M)$, of these values around the average one, $\langle\Delta S_M\rangle$, in a certain temperature span, ΔT. Using $\Delta T = 30$ K, the flatness, defined as $f = 100\frac{\sigma(\Delta S_M)}{\Delta S_M}$ with lower f values corresponding to a more table-like behavior, reduces from 16% and 13% for pure Gd and GdZn phases, respectively, to less than 6% for Zn25 alloy.

Assuming a non-interacting phases model for Gd + GdZn biphasic alloy, the total magnetic entropy change of a sample with a fraction y of pure Gd phase is $\Delta S_M = y\Delta S_M(\mathrm{Gd})+(1-y)\Delta S_M(\mathrm{GdZn})$. Therefore, the quantitative mass fractions of each phase could be deconvoluted from the experimental $\Delta S_M(T)$ curves [13], as shown in Fig. 3. The results show that the composites are well represented by this model. The phase analysis calculated from the XRMD and MCE data show good agreement with the nominal composition of the Gd–Zn alloys, as seen in Fig. 3(d). This indicates that this single step synthesis method is capable of producing samples with Gd + GdZn phases, allowing full integration of Zn in GdZn phase.

The C_p curves ($H = 0$, 10 and 20 kOe) for the studied composites are presented in Fig. 4(a). For zero applied field, abrupt transition peaks are observed. These distinct peaks become smoother and eventually merge with higher magnetic fields. Moreover, $C_{P,H}$ curves show the largest field dependence for relatively small applied fields and temperatures around the transition temperatures. Based on eq. (1), ΔT_{ad} curves calculated from $C_{P,H}$ data, reveal maximum values of 3.5 K ($H = 20$ kOe) for the optimal composite (as shown in Fig. 4(b)). The calculated ΔT_{ad} curves ($H = 0$ and 20 kOe) using eq. (2) are shown in the inset of Fig. 4, showing a good agreement of the different calculation methods (difference of ~8%).