**Observation of a Broadened Magnetocaloric Effect in Partially Crystallized Gd_{60}Co_{40} Amorphous Alloy**

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**Abstract:** To investigate the effect of crystallization treatment on the structure and magnetocaloric effect of Gd_{60}Co_{40} amorphous alloy, the melt-spun ribbons were annealed at 513 K isothermally for 20, 40 and 60 min. The results indicate that, with increasing annealing time, the Gd_{4}Co_{3} (space group P6/m) and Gd_{12}Co_{7} (space group P2_1/c) phases precipitated from the amorphous precursor in sequence. In particular, in the samples annealed for 40 and 60 min, three successive magnetic transitions corresponding to the phases of Gd_{4}Co_{3}, Gd_{12}Co_{7} and remaining amorphous matrix were detected, which induced an overlapped broadened profile of magnetic entropy change (|ΔSM|) versus temperature. Under magnetic field changing from 0 to 5 T, |ΔSM| values of 6.65 ± 0.1 kg K^{-1} K^{-1} and 6.44 ± 0.1 J kg^{-1} K^{-1} in the temperature spans of 180–196 K and 177–196 K were obtained in ribbons annealed for 40 and 60 min, respectively. Compared with the fully amorphous alloy, the enhanced relative cooling power and flattened magnetocaloric effect of partially crystallized composites making them more suitable for the Ericsson thermodynamic cycle.

**Keywords:** partially crystallized; amorphous matrix; multi-phase; broadened magnetocaloric effect

**1. Introduction**

As a potential alternate of conventional vapor compression refrigeration, magnetic refrigeration on the basis of magnetocaloric effect (MCE), has attracted a great deal of attention with the advantages of compactness, higher energy efficiency, environmental friendliness and less noise [1,2]. At constant pressure, the total entropy S of a magnetic material is composed of magnetic entropy SM, lattice entropy SL and electronic entropy SE, among which the SM depends on both temperature and applied magnetic field strongly, while the SL and SE usually can be considered temperature dependent only [3].

When a ferromagnetic substance is magnetized isothermally, the alignment of magnetic moment causes enhanced magnetic order and lower SM, and then the system releases heat to the surrounding environment since both SL and SE remain constant. If the magnetizing process is adiabatic, to maintain the total entropy unchanged, the SL and SE increase and the temperature becomes higher [4]. The above mentioned is the principle of MCE, and it is reversible for the demagnetization process. Furthermore, the isothermal magnetic entropy change ΔSM and adiabatic temperature change ΔT_{ad} are important parameters to characterize the MCE of magnetic refrigerants [4].

Compared with the reference Carnot cycle, the Ericsson cycle consists of two iso-thermal and two iso-field processes and was proposed to be utilized for temperature ranges higher than 20 K. The influence of SL and SE can be neglected in the two iso-field processes by adding a regenerator to the magnetic refrigeration system [3]. As an ideal material for the Ericsson cycle, its magnetic entropy change |ΔSM| should be a constant value in the...
refigeration temperature range, named “table-like” MCE, which is usually achieved by designing multi(bi)-phase magnetocaloric material or monolithic material with multiple successive magnetic phase transitions [1,15].

The typical material for the latter group is heat-treated Gd₆₅₄Er₀₄₆NiAl compounds with hexagonal ZrNiAl-type crystal structure, which exhibit a nearly temperature independent |ΔSₜ| of 13 J·kg⁻¹·K⁻¹ over the temperature region of 15–45 K for a field change of 0–5.32 T [6]. While for the former group, there are two common strategies to combine multiple phases undergoing neighboring phase transitions, one is manufacturing the composites by artificially mixing, bonding, pressing or sintering [7–10], and the other is preparing the multi-phase materials by traditional producing techniques, like casting and heat-treatment [11–15].

Multilayer hybrid fabricated by gluing 70 wt% Gd₅₀Co₄₀Fe₂ and 30 wt% Gd₅₀Co₄₀Mn₂ amorphous ribbons, displays |ΔSₜ| of ~4.32 J·kg⁻¹·K⁻¹ in the temperature interval of 255 K–275 K under 5 T field [7]. The two |ΔSₜ| peaks of amorphous Gd₆₅Mn₅₀Si₁₀ and crystalline Gd are partly overlapping for the Gd₆₅Mn₅₀Si₁₀-Gd/Sn composites synthesized by hop-pressing with the nearly constant value 2.9 J·kg⁻¹·K⁻¹ in a wide temperature span of 220 K–293 K under field change of 0–5 T [8]. Three kinds of REAL₂ (RE = Er, Ho, Dy) compounds with appropriate molar ratio were pressed and sintered as a layer structural complex, which presents almost constant of |ΔSₜ| (~3 J·mol⁻¹·K⁻¹) induced by 5 T magnetic field in the temperature range from ~15 to ~35 K [10].

However, the potential problems of pressing and sintering, including the low density and the resulting intermediate layer formed during solid-state reactions between constituent materials, as well as the differences in the coefficient of thermal expansion, may reduce the efficiency of the thermodynamic cycle and limit the working life of the refrigerant [16]. Compared with the above-mentioned composites, biphasic Gd + GdZn as-melted composite possesses improved thermal contact between phases and shows table-like |ΔSₜ| - T curves by tuning Gd:Zn ratio (|ΔSₜ| of ~3.2 J·kg⁻¹·K⁻¹ in temperature range of 266–290 K under 2 T field for the material with nominal composition of Gd₇₅Zn₂₅) [12].

Gd-TM (TM = Co, Fe, Ni, and Mn) amorphous alloys with near-room temperature MCE have attracted more attention in recent years. Generally, the broadened |ΔSₜ| - T profile can be observed in these materials, owing to the highly disordered structure of amorphous systems, which smears out the magnetic transition [1,11,15,17–26]. In-situ crystallization treatment of the amorphous ribbons is also utilized to obtain multi-phase magnetic refrigerant, such as crystallized Gd₅₅Co₃₅Ni₁₀ ribbon containing Gd₄(Co, Ni)₃ and Gd₁₂(Co, Ni)₇ phases, and partially crystallized Gd₅₅Co₃₅Mn₁₀ with precipitation of the Gd₃Co-type and Gd₁₂Co₇-type phases in the amorphous matrix, both of them possess broadened table-like MCE [14,15].

We found that the maximum magnetic entropy change of Gd₆₀Co₄₀ amorphous alloy (8.3 J·kg⁻¹·K⁻¹ [17]) was higher than that of Gd₅₅Co₃₅Ni₁₀ (6.5 J·kg⁻¹·K⁻¹ [15]) and Gd₅₅Co₃₅Mn₁₀ (6.47 J·kg⁻¹·K⁻¹ [14]) amorphous counterparts with analogous Curie temperature (T_C). Additionally, according to the Gd-Co binary phase diagram [27], the constituent phases of Gd₆₀Co₄₀ alloy after equilibrium solidification are Gd₄Co₃ and Gd₁₂Co₇ types. The T_C of crystalline Gd₄Co₃, Gd₁₂Co₇ and amorphous Gd₆₀Co₄₀ are 220 K [21], 179 K [22] and 193 K [17], respectively, and the intervals between different T_C are suitable for achieving the table-like MCE [28,29]. To reveal whether the partially crystallized Gd₆₀Co₄₀ alloy ribbon will exhibit enhanced table-like or broadened MCE, in this study, the influence of crystallization treatment on the structure, magnetic and magnetocaloric properties of Gd₆₀Co₄₀ melt-spun ribbons was investigated.

2. Materials and Methods

Amorphous ribbons with a nominal composition of Gd₆₀Co₄₀ were prepared in two steps. First, the master alloy was fabricated by arc melting the mixtures of high purity metals Gd (99.9 wt%), Co (99.9 wt%), Fe (99.9 wt%) and prealloy B-Fe with a mass ratio
of 17.62/81.46 under a Ti gettered argon atmosphere. The alloy ingots were turned over and remelted four times to ensure the homogeneity. Secondly, the ingots were broken into small pieces of 3–4 g, and then the ribbon samples were manufactured by a single-roller melt spinning technique with a surface linear speed of 50 m/s under high-purity argon atmosphere.

The width and thickness of the ribbons were 2–3 mm and 20–50 µm, respectively. In this work, the partially crystallized samples were obtained by annealing the as-spun ribbons at 513 K for 20, 40 and 60 min, and the fully crystallized counterpart was produced through thermal treating at 653 K (the termination temperature of crystallizing exothermic peak on the heat flow curve) for 20 min.

X-ray diffraction (XRD, Bruker D8 Advance, Karlsruhe, Germany) measurements were performed at room temperature using Cu Kα radiation (λ = 0.154178 nm) and a 2θ range of 20–90° with operation conditions of 40 keV and 150 mA. The thermal properties of the ribbons were characterized using differential scanning calorimetry (DSC, Netzsch STA 449F3, Selb, Germany) under the protection of an argon atmosphere with a heating rate of 0.33 K/s. The magnetic properties of the ribbons were detected by a physical property measurement system (PPMS, Quantum Design PPMS-9 T system, San Diego, CA, USA).

In this study, the temperature dependence of the zero-field cooling magnetization (M-T) curve was collected under an applied field of 0.02 T during the heating process from 50 to 350 K. The isothermal initial magnetization (M-H) curves were collected under the applied magnetic field change from 0 to 5 T at selected temperatures from 108 to 248 K. The temperature interval of 4 and 10 K were chosen for the region in vicinity of and far away from TC, respectively, and the scanning speed of the magnetic field was slow enough to ensure accurate recording of the data in the isothermal process. Then, the magnetic entropy change |∆SM| can be calculated by the M-H curves based on the Maxwell relation [2]:

$$\Delta S_M(T, H) = S_M(T, H) - S_M(T, 0) = \int_0^H \left( \frac{\partial M(T, H)}{\partial T} \right) dH$$ (1)

where $S_M$, $T$, $H$ and $M$ indicate the magnetic entropy, temperature, applied magnetic field and magnetization of the material, respectively. To derive the temperature dependence of |∆SM|, the numerical approximation of the integral is usually utilized as follows [30,31]:

$$\Delta S_M \left( \frac{T_{i+1} + T_i}{2} \right) = \sum_i \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i$$ (2)

where $M_i$ and $M_{i+1}$ are experimental values of magnetization at temperatures $T_i$ and $T_{i+1}$ under external magnetic field $H_i$.

3. Results and Discussion

3.1. Structural and Thermal Characterization

From the XRD pattern of the as-spun Gd₆₀Co₄₀ alloy shown in Figure 1a, there is only one typical diffuse broaden peak without any detectable crystalline peaks, indicating its amorphous structure. This feature was verified by the two exothermal crystallization peaks on DSC curve of the Gd₆₀Co₄₀ as-spun ribbon exhibited in Figure 1b. Additionally, the onset crystallization temperature $T_x$ and the end temperature of crystallization peak with values of 523 and 653 K can be obtained, respectively. Based on these, the annealing temperatures of 513 K (10 K lower than $T_x$) and 653 K were chosen. As displayed in Figure 1b, the absence of an exothermal peak on the DSC curve of the sample annealed at 653 K for 20 min demonstrates that it is fully devitrified. Then, according to the XRD result (in Figure 1a), two types of crystalline phases Gd₄Co₃ (space group P6₃/m) and Gd₁₂Co₇ (space group P2₁/c) were identified.
From Figure 1a, the sharp peaks in XRD patterns of the samples annealed at 513 K for 20, 40 and 60 min indicate the existence of crystals. Combined with the exothermic crystallization process on DSC curves illustrated in Figure 1b, we deduced the microstructure of the alloys as crystals embedded in an amorphous matrix. In the 513 K/20 min annealed ribbon, a broad hump overlapped by one obvious crystalline peak was detected, demonstrating that the precipitation amount is slight, and the crystallites can be identified as Gd$_4$Co$_3$ phase in comparison with the fully crystallized sample. In the 513 K/40 min and 513 K/60 min counterparts, complicated diffraction peaks reveal that the Gd$_4$Co$_3$ and Gd$_{12}$Co$_7$ phases in-situ crystallized from the amorphous precursor.

Although the annealing temperature is lower than the $T_x$, the precipitation of Gd$_4$Co$_3$ and Gd$_{12}$Co$_7$ crystalline phases likely corresponds to the first and second crystallization peaks, respectively, due to heat fluctuation or thermal inertia during crystallization treatment [11]. The DSC curves of the annealed ribbons confirm this assumption, since the primary crystallization peak becomes broader (513 K for 20 min) and then disappears (513 K/40 min and 513 K/60 min) [32,33]. Moreover, with increasing annealing time, the area under the peak gradually decreases, indicating a reduction of the relative content of the amorphous phase in the whole composite material [33].

Utilizing the Scherrer formula [34], grain sizes of ~23 ± 3 nm were estimated for the crystallites in these amorphous-nanocrystalline composites, which were almost unaffected by the annealing time. Furthermore, the similar XRD patterns and DSC curves of the 513 K/40 min and 513 K/60 min annealed ribbons imply their analogous microstructure. In another word, the grain size and transformation volume tend to saturate after certain annealing time, which is attributed to the metastable equilibrium between the remaining amorphous matrix and the crystallites [35].

### 3.2. Multi-Magnetic Phase Transition

Figure 2a represents the temperature dependence of magnetization ($M$-$T$ curves) of the annealed Gd$_{60}$Co$_{40}$ alloy ribbons under an applied field of 0.02 T. Subsequently, the Curie temperature $T_C$ was defined as the temperature corresponding to the minimum of
the derivative $dM/dT$-$T$ curves shown in the Figure 2b. It is evident that all the composite materials experienced two or more magnetic phase transitions during heating.

From the magnified image of the 210–230 K part on $dM/dT$-$T$ curves (displayed in the inset of Figure 2b), there is a weak peak for 513 K/20 min annealed ribbon, which reveals first magnetic phase transition at 219 K correlated to the magnetic transition of the Gd$_4$Co$_3$ phase ($T_C = 220$ K) [21]. Its second magnetic transition obtained at 196 K is sharp and associated with the amorphous ferrimagnetic phase ($T_C = 193$ K) [17], which is in good agreement with the microstructure consisted by slight amount of crystallites and predominant amorphous matrix, as discussed in Section 3.1.

![Figure 2](image.png)

**Figure 2.** (a) Temperature dependence of magnetization and (b) $dM/dT$-$T$ curves of the Gd$_{60}$Co$_{40}$ alloys after annealing treatment. The inset of (b) is the magnified image of the part between 210 K and 230 K.

Owing to the analogous microstructure of the 513 K/40 min and 513 K/60 min annealed samples, their multi-magnetic transition behaviors are similar to each other and three transitions can be observed at temperatures 174 K/194 K/219 K and 176 K/195 K/219 K. Compared with the magnetic transition behavior in the 513 K/20 min annealed sample, an extra transition related to the Gd$_{12}$Co$_7$ crystalline ($T_C = 160.8$ K) appeared [36]. The deviation of the $T_C$ is possibly ascribed to the different microstructure (e.g., crystal size and surrounding phase structure) between the bulk crystalline material and the in-situ precipitated crystallites, in addition, similar phenomena and values of $T_C$ were reported in Gd$_{12}$Co$_7$ melt-spun ribbon ($T_C = 179$ K) [22].

For the fully devitrified ribbon annealed at 653 K for 20 min, the $dM/dT$-$T$ curve manifested three magnetic phase transitions at 162 K and 218 K associated with Gd$_{12}$Co$_7$ and Gd$_4$Co$_3$, respectively, which is consistent with the XRD results.

### 3.3. Magnetocaloric Properties

The isothermal initial magnetization $M$-$H$ curves under the magnetic field change $\Delta H = 5$ T of partially crystallized Gd$_{60}$Co$_{40}$ ribbons with different annealing time are displayed in Figure 3. With raising temperature, the magnetization of all the samples exhibits apparent transition from easy-saturated to linear-field-dependent. The type of the magnetic phase transition was estimated through Arrott plots ($M^2$ vs. $H/M$) according to Banerjee criteria [37], which is based on the mean-field theory and derived from the $M$-$H$ isotherms [38]. As shown in Figure 4, the positive slope of all the curves indicates every magnetic transition in the multi-phase alloys is second order magnetic phase transition (SOMT). In comparison with the materials of first order magnetic phase transition (FOMT), such as Gd$_3$(Si$_2$Ge$_2$) and LaFe$_{13-x}$Si$_x$ compounds [30,39], the magnetic refrigerants with
SOMT possess advantages of negligible thermal and magnetic hysteresis, which make them more suitable for practical application, although their magnetic entropy change is lower [40].

Figure 3. $M$-$H$ isotherms of Gd$_{60}$Co$_{40}$ amorphous ribbon after annealing at 513 K for (a) 20, (b) 40 and (c) 60 min under the $\Delta H$ of 0–5 T.

Figure 4. Arrott plots of the multi-phase Gd$_{60}$Co$_{40}$ alloy annealed at 513 K for (a) 20, (b) 40 and (c) 60 min.

The correlation between magnetic entropy change $|\Delta S_M|$ and temperature was determined by using Equation (2) to calculate the data of $M$-$H$ isotherms, and the $|\Delta S_M|$ vs. $T$ curves of the annealed Gd$_{60}$Co$_{40}$ ribbons under the field change from 0 to 5 T are illustrated in Figure 5. The achieved values of maximum magnetic entropy change ($|\Delta S_M|_{\text{pk}}$) were 7.73, 6.75 and 6.54 J·kg$^{-1}$·K$^{-1}$ at temperatures $T_{\text{pk}}$ of 194, 190 and 190 K for samples annealed at 513 K for 20, 40 and 60 min, respectively, which are smaller than those of as-spun Gd$_{60}$Co$_{40}$ amorphous alloy (8.3 J·kg$^{-1}$·K$^{-1}$) [17].

The $T_{\text{pk}}$ is near to the $T_C$ of the amorphous matrix in each partially crystallized alloy, meaning that the amorphous phase makes the predominant contribution to magnetocaloric effect. With increase of the annealing time, the Gd$_3$Co$_3$ and Gd$_{12}$Co$_7$ phases successively...
precipitated from the amorphous matrix and resulted in a reduction of the amorphous phase content; therefore, the $|\Delta S_M|_p$ of the multi-phase alloys decreases.

However, due to the synergistic effects of multi-magnetic phase transition, the $|\Delta S_M| - T$ curves of the annealed Gd$_{60}$Co$_{40}$ alloys in this study were broadened, usually accompanied by wide full temperature width at half maximum ($\Delta T_{FWHM}$) and large relative cooling power ($RCP$, another parameter to evaluate the MCE as heat transferred between the hot and cold reservoirs in an ideal refrigeration cycle) with expression of $RCP = |\Delta S_M|_p \times \Delta T_{FWHM}$ [1]. The $RCP$ of the 513 K/20 min, 513 K/40 min and 513 K/60 min annealed samples were 726.6, 789.8 and 797.9 J·kg$^{-1}$, respectively. In comparison with that of as-spun Gd$_{60}$Co$_{40}$ amorphous alloy (713.8 J·kg$^{-1}$) [17], the results reveal that the $RCP$ increases with elongation of the annealing time.

Figure 5. The relation of $|\Delta S_M|$ to temperature for the different annealed Gd$_{60}$Co$_{40}$ alloy ribbons.

As discussed in [23,36], the $\Delta T_{FWHM}$ values of the materials in this study are much larger than the temperature span of any real magnetocaloric refrigerator so that the $RCP$ may overestimate their performance in practical applications. In comparison with $RCP$, the temperature averaged entropy change ($TEC$) can properly reflect the merit of materials with a broad magnetocaloric response but small magnetic entropy change [41]. This is calculated over a range of temperatures $\Delta T_{lift}$ that a material can reasonably support in response to a given field change $\Delta H$, as follows:

$$TEC(\Delta T_{lift}) = \frac{1}{\Delta T_{lift}} \max_{T_{mid}} \left\{ \int_{T_{mid}}^{T_{mid}+\Delta T_{lift}} \Delta S(T)\Delta T \right\}$$

(3)

The value of the temperature at the center of the average, $T_{mid}$, is chosen by sweeping over the available $\Delta S(T)\Delta T$ data and selecting the value that maximizes $TEC(\Delta T_{lift})$ for the given $\Delta T_{lift}$, similar to the evaluation of the maximum energy product of a permanent magnet. In this study, the $\Delta T_{lift}$ of 10 K and $\Delta H$ of 1 T were chosen, and the $TEC(10 K)$ of the 513 K/20 min, 513 K/40 min and 513 K/60 min annealed samples were 2.34, 1.69 and 1.71 J·kg$^{-1}$·K$^{-1}$, respectively, at $T_{mid}$ of 192, 178 and 188 K. The values are lower than that of Gd and higher than that of La$_{0.815}$K$_{0.16}$Mn$_{0.987}$O$_{3}$, indicating their magnetocaloric performance is not very good.
Table 1. Magnetocaloric properties of present alloys and some representative materials under applied field change of 0–5 T (A and C stand for amorphous and crystalline, respectively). The $\Delta T$ plateau denotes the temperature range of the plateau part of the $|\Delta S_M| - T$ curves.

| Alloys             | Structure | $T_C$ (K) | $\Delta T_{\text{plateau}}$ (K) | $|\Delta S_M|_{40}$ (J kg$^{-1}$ K$^{-1}$) | $\Delta T_{\text{FWHM}}$ (K) | RCP (J kg$^{-1}$) | References |
|--------------------|-----------|-----------|----------------------------------|------------------------------------------|---------------------------|-----------------|------------|
| Gd$_{60}$Co$_{40}$ | A + C     | 196/219   | -                                | 7.73                                     | 94                        | 726.6           | This Work   |
| Gd$_{60}$Co$_{40}$ | A + C     | 174/194/219 | 180–196                         | 6.75                                     | 117                       | 797.9           | This Work   |
| Gd$_{60}$Co$_{40}$ | A + C     | 176/195/219 | 177–196                         | 6.54                                     | 122                       | 797.2           | This Work   |
| Gd$_4$Co$_9$       | C         | 220       | -                                | 6.4                                      | 123                       | -               | [21]        |
| Gd$_6$Co$_{35}$    | A         | 193       | -                                | 8.3                                      | 86                        | 713.8           | [17]        |
| Gd$_{12}$Co$_7$    | A + C     | 179       | -                                | 7.9                                      | -                         | -               | [22]        |
| Gd$_{10}$Co$_{50}$Fe$_{15}$ | A | 217 | 178–228 | 4.1 | 200 | 820 | [17] |
| Gd$_{10}$Co$_{50}$Mn$_{25}$ (600 K/30 min) | A + C | 123/170 | 137–180 | 5.46 | 123 | 671.6 | [14] |
| Gd$_{10}$Co$_{50}$Ni$_{50}$ (620 K/30 min) | C | 158/214 | 154–214 | 5.0 | - | - | [15] |
| Gd$_{10}$Co$_{50}$Fe$_{25}$Si$_{15}$B$_{15.5}$ (600 K/30 min) | A | 194 | - | 5.7 | - | - | [24] |
| Gd$_{10}$Co$_{50}$Fe$_{25}$Si$_{15}$B$_{15.5}$ | A | 170 | - | 6.56 | 126 | 826 | [25] |

On another hand, when compared with single amorphous phase alloys, like Gd$_{75}$ (Fe$_{25}$Co$_{0.75}$)$_2$S$_5$ [24] and Gd$_{50}$ (Co$_{0.925}$Fe$_{0.25}$Si$_{13}$B$_{15.5}$)$_5$ [25], the combined merits of larger or comparative $|\Delta S_M|$ and broader working temperature range can be observed in these Gd$_{60}$Co$_{40}$ annealed samples. The MCE in a temperature range of 160–220 K can be used in the fields of space technology, medicine, biology, life sciences and more [14].

The correlation between $|\Delta S_M|$ and $H$ follows the power law of $|\Delta S_M| \approx H^n$ for the SOMT materials [42], and $n$ is an exponent depending on both applied field and temperature. Particularly, at temperature $T = T_C$ or $T_{pk}$, $n$ is field independent, and $n(T_{pk})$ can be extracted from the slope of the linear fit of the rescaled $\ln|\Delta S_M|_{40}$ vs. $\ln H$ plots [26,43]. Through the fitting results displayed in Figure 6, the values of 0.76 can be obtained for the 513 K/20 min annealed Gd$_{60}$Co$_{40}$ alloy, which is close to ~0.75 derived from the experimental data of other soft magnetic amorphous alloys [42], which indicates the prevailing contribution of amorphous matrix and negligible influence from the slight amount of crystallite in the sample as mentioned above. However, the deviations of 0.90 and 0.91 can be observed in 513 K/40 min and 513 K/60 min annealed counterparts owing to the in-situ precipitated nanocrystalline in the amorphous precursor [44,45].

Assuming that the different magnetic phases are non-interacting, the total magnetic entropy change of the multiphase composites can be computed using a rule-of-mixtures sum of the entropy change in the constituent materials with expression described as [13]:

$$\Delta S_{\text{com}}^M = a\Delta S_M^1 + \beta\Delta S_M^2 + \gamma\Delta S_M^3$$

(4)

where $\Delta S_M^1$, $\Delta S_M^2$ and $\Delta S_M^3$ imply the magnetic entropy change, as well as $a$, $\beta$ and $\gamma$ denote the relative weight fractions of the phases 1, 2 and 3 respectively, with the relation of $a + \beta + \gamma = 1$. According to the experimental data of the amorphous Gd$_{60}$Co$_{40}$, crystalline Gd$_4$Co$_9$ and Gd$_{12}$Co$_7$ [17,21,22], the fitting results of $|\Delta S_M|$ - $T$ curves under field changing from 0 to 5 T for 513 K/20 min and 513 K/60 min annealed Gd$_{60}$Co$_{40}$ alloys were depicted in Figure 7. For comparison, the experimental results are also shown.
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Figure 6. Ln–Ln plots of the field dependence of the $|\Delta S_{M}^{pk}|$ for calculating $n(T_{pk})$ exponent of the annealed Gd$_{60}$Co$_{40}$ alloys.

It can be seen the calculated results fit the experimental data very well, and the adopted weight fractions of the phases in 513 K/20 min and 513 K/60 min samples are 85 wt% amorphous matrix + 15 wt% Gd$_4$Co$_3$ and 30 wt% amorphous matrix + 36 wt% Gd$_4$Co$_3$ + 34 wt% Gd$_{12}$Co$_7$, respectively. Although the relative content of each phase is roughly estimated [46], the fraction of phases is significant to construct the broadened MCE in this kind of multiphase materials [29,47]. In this work, with increasing annealing time, the evolution of microstructure in Gd$_{60}$Co$_{40}$ amorphous ribbon achieves an appropriate constituent of different phases, resulting in the enhanced magnetocaloric performance.

Figure 7. Temperature dependence of $|\Delta S_{M}|$ for the annealed Gd$_{60}$Co$_{40}$ alloys: (a) 513 K/20 min and (b) 513 K/60 min, fitted by calculating experimental data of constituent materials 1, 2 and 3, which correspond to amorphous Gd$_{60}$Co$_{40}$ [17], crystalline Gd$_4$Co$_3$ [21] and melt-spun Gd$_{12}$Co$_7$ [22], respectively.
On basis of the numerical approach provided by A. Smaïli et al. [48], in this study, when the composite is consisted by 63 wt% Gd$_4$Co$_3$ + 26 wt% Gd$_{12}$Co$_7$ + 11 wt% amorphous Gd$_{60}$Co$_{40}$, a nearly flat-shape $|\Delta S_M|$-$T$ profile can be observed between 180 K and 220 K. As discussed in Section 3.1, the Gd$_4$Co$_3$ is probably the primary precipitate. Therefore, the possible method to achieve this composite is as following: at first, rapid thermal annealing in temperature range of 523 K–563 K (the onset and end temperatures of the first crystallization peak on DSC curve) to induce large amount of Gd$_4$Co$_3$ crystallites; and then, annealing at 513 K for 40–60 min (similar to the treatment in this work) to remain certain of the content of the amorphous phase. Further research will be carried out in the next step.

4. Conclusions

In summary, amorphous-nanocrystalline Gd$_{60}$Co$_{40}$ alloys were synthesized by crystallization treatment of the melt-spun amorphous ribbons. With different annealing times (20, 40 and 60 min) at 513 K, Gd$_4$Co$_3$-type and Gd$_{12}$Co$_7$-type phases precipitated from the amorphous matrix in sequence; however, the grain size and transformation volume tended to saturate after certain annealing times due to the metastable equilibrium between the crystallites and the remaining amorphous phase. In the samples annealed for 40 min and 60 min, the multi-phase structure consisted of the Gd$_4$Co$_3$, Gd$_{12}$Co$_7$ and amorphous phases, which resulted in three successive magnetic phase transitions at temperatures of 174 K/194 K/219 K and 176 K/195 K/219 K, respectively.

Owing to the overlap of multi-peaks in the $|\Delta S_M|$-$T$ curves, broadened MCE with $|\Delta S_M|$ values of 6.65 ± 0.1 J kg$^{-1}$K$^{-1}$ and 6.44 ± 0.1 J kg$^{-1}$K$^{-1}$ in the temperature spans of 180 K–196 K and 177 K–196 K under a field change of 0–5 T were obtained in ribbons annealed for 40 min and 60 min, respectively, and could be modeled by considering non-interacting phases. The enhanced relative cooling power and flattened magnetocaloric properties of partially crystallized composites enable them to be more suitable for the Ericsson thermodynamic cycle, in comparison with the single amorphous phase counterparts.

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