



Enhanced Curie temperature and cooling efficiency in melt-extracted $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires



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ARTICLE INFO

Article history:

Received 5 December 2016

Received in revised form

5 March 2017

Accepted 7 March 2017

Available online 9 March 2017

Keywords:

Melt-extraction

Microwire

Magnetocaloric effect

Magnetic refrigeration

ABSTRACT

We report enhancements of both Curie temperature and magnetic refrigerant capacity in $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires, which were fabricated by the melt-extraction method. For a field change of 5 T, the maximum magnetic entropy change ($-\Delta S_M^{\text{max}}$), the refrigerant capacity (RC) and relative cooling power (RCP) reached high values of $6.56 \text{ J kg}^{-1} \text{ K}^{-1}$, 625 J kg^{-1} and 826 J kg^{-1} , respectively. While the RC is similar to those of our previously reported GdAlCo microwires, a much broader working temperature range of $\sim 126 \text{ K}$ and a higher Curie temperature of 170 K make the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires more attractive for active magnetic refrigeration.

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1. Introduction

Magnetocaloric effect (MCE) is an intrinsic characteristic of magnetic materials, which refers to a change of magnetic entropy in the material subjected to an external magnetic field [1]. The material that shows a decrease of magnetic entropy will release heat upon the application of an external magnetic field [2]. Conversely, the material that shows an increase of magnetic entropy will absorb heat when the external magnetic field is removed. As compared with traditional gas compression and expansion technique, magnetic refrigeration (MR) based on the MCE employs a solid magnetic substance as the refrigerant, leading to a higher efficiency and causing no damage to the atmospheric ozone layer. Therefore, MR is considered as an environmental friendly cooling technology [3]. In addition, MR only requires a magnetic field provided by a permanent magnet or an electromagnet or a superconductor instead of a compressor, which enabling an excellent mechanical reliability and resolving the issues of abrasion and mechanical noise in gas compression refrigerators [4].

Magnetic materials with rare-earth components showing normal [5,6] or inverse MCEs [7] are widely explored in the MR technology due to their large magnetic moments, such as $\text{La}_{0.7-x}\text{Pr}_x\text{Ca}_{0.3}\text{MnO}_3$ [8], Er-Ho-Co [9,10], and Ho-Er-Ni [11]. In particular, rare-earth based amorphous alloys such as Ho-, Dy-, Er-, Gd-based alloys exhibit large magnetic entropy changes ($-\Delta S_M$) over wide temperature ranges, resulting in the large refrigerant capacities (RC) [5]. As compared with polycrystals [6], amorphous materials usually possess higher RC values owing to the broadened magnetic phase transitions as a result of structural disorder effect. Rapid solidification technology is a common method for fabrication of earth-based bulk metallic glasses [12] and ribbon-like [13] compounds with excellent magnetocaloric properties. Moreover, the theoretical calculations of Kuz'min [14] have shown that the closely packed cylindrical wires as refrigerants with high mechanical stability and low porosity possess a higher operation frequency as compared to laminar-shaped or chequer-board arranged refrigerants. Vuarroz et al. [15] have also theoretically demonstrated that the energy transfer efficiency can be enhanced in magnetic refrigerators using microscale wire-shaped materials. However, producing amorphous magnetic wires with diameters less than 1 mm using traditional fabrication techniques has remained a challenging task. Applying a precision homemade melt-extraction technique with greater quenching rates, we have been

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successful in preparing a new class of high quality Gd-based microwires such as GdCoAl that possess enhanced MCE and RC [16–21]. In these GdCoAl microwires, Al was used to enhance amorphous structure and hence MCE, but decreased the Curie temperature of the initial alloy. Our current efforts are to increase the Curie temperature and the operation temperature range of such microwires for active magnetic refrigeration.

In this context, we propose to combine the excellent magnetic properties of Gd and $\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5}$ to design and fabricate $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires using our melt-extraction method. It is generally accepted that Gd with a large magnetic moment is a benchmark magnetocaloric material for near-room temperature magnetic refrigeration [3], while $\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5}$ amorphous microwires possess excellent glass forming

ability and soft ferromagnetic characteristic at ambient temperature for a wide range of advanced magnetic sensing applications [22–24]. We show that as compared to the GdCoAl microwires, the designed $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires possess large enhancements of both the Curie temperature and the operation temperature range, which are desirable for active magnetic refrigeration.

2. Experimental details

The raw materials used in this study were highly pure Gd (99.5% purity), Co (99.99% purity), Fe (99.99% purity), Si (99.99% purity) and B (99.99% purity). Firstly, the alloy rod with a nominal composition of $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ and a diameter of

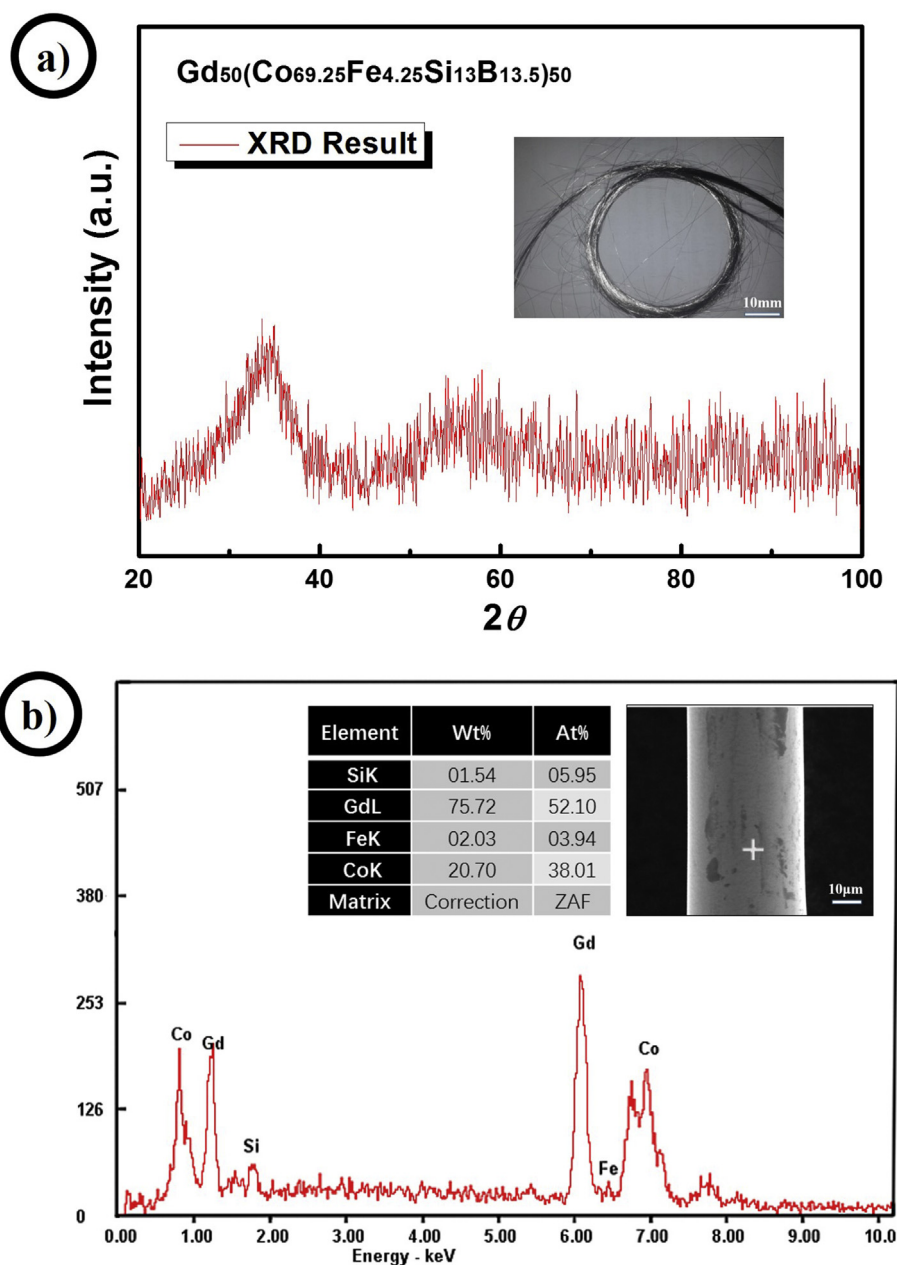


Fig. 1. a) the XRD pattern of melt-extracted $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires and its inset shows an image of these microwires; b) an EDS spectrum (main panel) and an SEM image of the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires (inset).

10 mm was obtained by a vacuum arc melting equipment under argon atmosphere. Subsequently, $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires were prepared by the precision homemade melt-drawing apparatus. The melt extraction process was carried out using a copper wheel with a diameter of 320 mm and an edge of 60° . The linear velocity of the rim was fixed at 30 m/s and the feeding rate of the molten alloy was 10–15 $\mu\text{m/s}$. The details of the preparation process can be found in previous paper of our group [25]. Inset of Fig. 1a shows an optical image of the fabricated $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires.

The micro morphology of $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires was observed using a field emission scanning electron microscope (SEM-Helios Nanolab 600i) operating at 20 kV, and the EDS was used to confirm the composition of the microwire. The microstructure of the microwire was identified by X-ray diffraction (XRD) using a D/MAX- γB X-ray diffractometer ($\text{Cu/K}\alpha$). Magnetic measurements were performed using a Quantum Design Magnetic Property Measurement System (SQUID-VSM).

3. Results and discussion

3.1. Structural characterization

As can be seen in inset of Fig. 1b, the fabricated $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires possess a smooth surface, a high circular cross section, and no apparent Rayleigh wave with a uniform diameter of $\sim 30 \mu\text{m}$. The XRD pattern of the microwires measured from 20° to 100° (2θ) with a scanning speed of $2^\circ/\text{min}$ is shown in Fig. 1a. There is only a broad diffuse peak detected at the position of $\sim 34^\circ$ without any obvious crystal sharp peaks, indicating that the microwires possess a typical amorphous microstructure. The compositional analysis confirms the presence of Gd, Co, Fe and Si in the sample. However, the atomic percent of the sample differs from the nominal composition because the element B cannot be detected using EDS.

The amorphous structure of the microwires can also be predicted based on Inoue's three rules of thumb [26]: (1) Multi-component (e.g. five components) system; (2) significant atomic size mismatch: the atomic radii of Gd, Co, Fe, Si and B are about 0.178 nm, 0.126 nm, 0.125 nm, 0.111 and 0.082 nm, respectively; (3) negative mixing heat: the mixing enthalpy is -22 kJ/mol for the Gd-Co pair, -1 kJ/mol for the Gd-Fe pair, -73 kJ/mol for the Gd-Si pair, -50 kJ/mol for the Gd-B pair [27]. The analysis indicates that the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires possess a good glass-forming ability (GFA).

3.2. Magnetic properties

Fig. 2 (left hand) shows the temperature dependence of magnetization (M - T) for the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires measured from 20 to 260 K under a constant external field of 200 Oe. It can be seen that the ferromagnetic to paramagnetic transition takes place with the increase of temperature. The derivation of the M - T curve was analyzed to determine the Curie temperature of the microwires, as shown in inset of Fig. 2. The lowest point of the dM/dT curve corresponds to the Curie temperature of $\sim 170 \text{ K}$. It is interesting that the T_C of the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires is $\sim 70 \text{ K}$ higher than those of our previously reported Gd-Al-Co amorphous microwires ($T_C \sim 100 \text{ K}$) [16–21]. It has been reported that relative to GdCo binary alloys [28], the Al addition enhanced the MCE but reduced the Curie temperature in GdCoAl ternary alloys [29]. In our present study, the combination of

Gd with $\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5}$ that possesses an excellent glass forming ability and an excellent soft ferromagnetic characteristic above room temperature is expected to retain high values of the Curie temperature.

To further understand the magnetic behavior of a multi-component system like $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$, a H/M vs. T conversion curve based on the M - T curve was constructed and the result is shown in Fig. 2 (right hand). It can be seen that the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwire follows the Curie-Weiss law above the T_C [30]. The paramagnetic Curie point is positive which indicating that the exchange ferromagnetic interaction dominates below the T_C temperature. Based on the Curie-Weiss law, the Curie constant (C) and Curie-Weiss temperature (θ_p) can be calculated by fitting the line parts as indicated in Fig. 2 (right hand). The fitted result yields C of $4.19 \text{ emu}\cdot\text{K/mol}$ and θ_p of 186.5 K , respectively. Furthermore, the Curie constant can be expressed as:

$$C = \frac{nN_A g^2 J(J+1) \mu_B^2}{3k_B} \quad (1)$$

and the effective magnetic moment (μ_{eff}) is calculated by:

$$\mu_{\text{eff}} = g \sqrt{J(J+1)} \mu_B, \quad (2)$$

where n is the amount of substance for the fiber composition, N_A is the Avogadro constant, g is the Lande factor, J is the total angular momentum, k_B is Boltzmann constant and μ_B is Bohr magneton. From these relationships we obtained the μ_{eff} of $\sim 5.8 \mu_B$ for the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwire. The obtained effective magnetic moment is mainly induced by the interaction of magnetic moments between transition metal (TM) elements with 3d-electrons and rare-earth (RE) element with 4f-electrons [30]. This value is lower than that of theoretical value ($\sim 6.3 \mu_B$) and the $\text{Gd}_{60}\text{Co}_{15}\text{Al}_{25}$ microwire ($\sim 6.9 \mu_B$) [19]; this is expected that the Gd amount is larger in the latter case. It is worth noting that the Curie temperature of the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwire ($\sim 170 \text{ K}$) is greater than that of the $\text{Gd}_{60}\text{Co}_{15}\text{Al}_{25}$ microwire ($\sim 100 \text{ K}$), which indicating enhanced ferromagnetic interaction in case of the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwire due to the multi-component alloying effect.

In order to determine the nature of the ferromagnetic-paramagnetic phase transition and also the MCE for the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires, we measured the isothermal M - H curves around the Curie temperature (Fig. 3a). The M - H isotherms are converted into the modified Arrott plots (H/M vs. M^2), as shown in Fig. 3b. It can be observed that the tangent slopes of all the curves are positive, indicating a second-order phase transition of the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwire and in accordance with the Banerjee criterion [31]. In second-order phase transition materials, the thermal and magnetic hysteresis are often negligible, which are beneficial for the operation of active magnetic refrigerators [17].

3.3. Magnetocaloric properties

The magnetic entropy changes of $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires were calculated from the isothermal magnetization curves (Fig. 3a) using Maxwell relationship [32]:

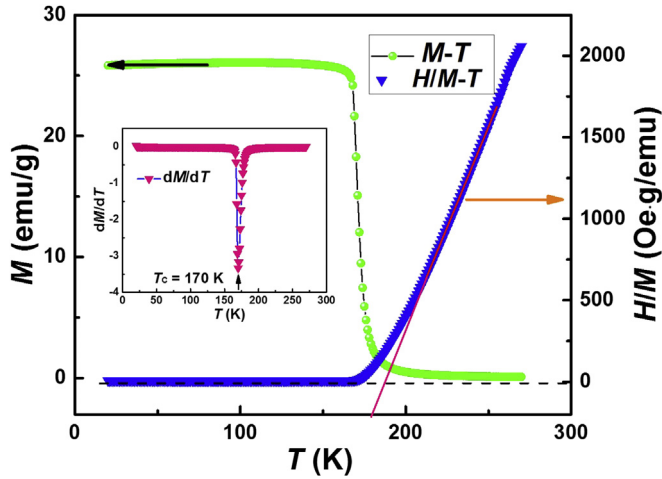


Fig. 2. The temperature dependence of magnetization at a field of 200 Oe (left hand) and the curve constructed by the Curie-Weiss law (right hand). Inset shows the dM/dT vs. T curve.

$$\Delta S_M(T, H) = S(T, H) - S(T, 0) = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T} \right)_H dH, \quad (3)$$

where S represents the magnetic entropy and $H_{\max}$ represents the maximum external magnetic field. The temperature dependence of magnetic entropy change ($-\Delta S_M(T, H)$) at different applied field changes is shown in Fig. 4. The maximum magnetic entropy change, ($-\Delta S_M^{\max}$), reaches a large value of $\sim 6.56 \text{ J kg}^{-1} \text{ K}^{-1}$ at $\sim 170 \text{ K}$ for a magnetic field change of 50 kOe. This value is lower than that of $\sim 10.3 \text{ J kg}^{-1} \text{ K}^{-1}$ reported previously by us for the $\text{Gd}_{53}\text{Al}_{24}\text{Co}_{20}\text{Zr}_3$ microwires [17]. This decrease in $\Delta S_M^{\max}$ for the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires can be related to the decrease of the effective magnetic moment as discussed above. However, the full width at half maximum of the $-\Delta S_M(T, H)$ curves ($\sim 126 \text{ K}$) for the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires is much greater as compared to that ($\sim 83 \text{ K}$) of the $\text{Gd}_{55}\text{Al}_{20}\text{Co}_{25}$ microwires. This feature makes the former more desirable for practical cooling applications.

To explore the relationship between the maximum magnetic entropy change and the applied magnetic field near the magnetic phase transition temperature for the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires, the $\Delta S_M^{\max}(H)$ at $T = 170 \text{ K}$ is plotted and fitted to the following expression [33]:

$$-\Delta S_M^{\max} \propto H^n, \quad (4)$$

where n is a local exponent. The fitted result is shown in Fig. 5a, which yields $n = 0.77$, in good agreement with those reported previously for the Gd-Al-Co microwires [16–21]. This value of n is also close to that reported previously for typical Fe-based amorphous alloys ($n = 0.75$) [34], but deviates from the mean-field theoretical value ($n = 0.67$) [33]. This deviation may arise from the structural and magnetic disorders caused by the multi-component alloying effect.

It is worth noting that ($-\Delta S_M^{\max}$) is just one of parameters for evaluating the magnetocaloric property of a material. Some of the first-order phase transition materials show $\Delta S_M^{\max}$ of more than $10 \text{ J kg}^{-1} \text{ K}^{-1}$ but their working temperature ranges are limited to

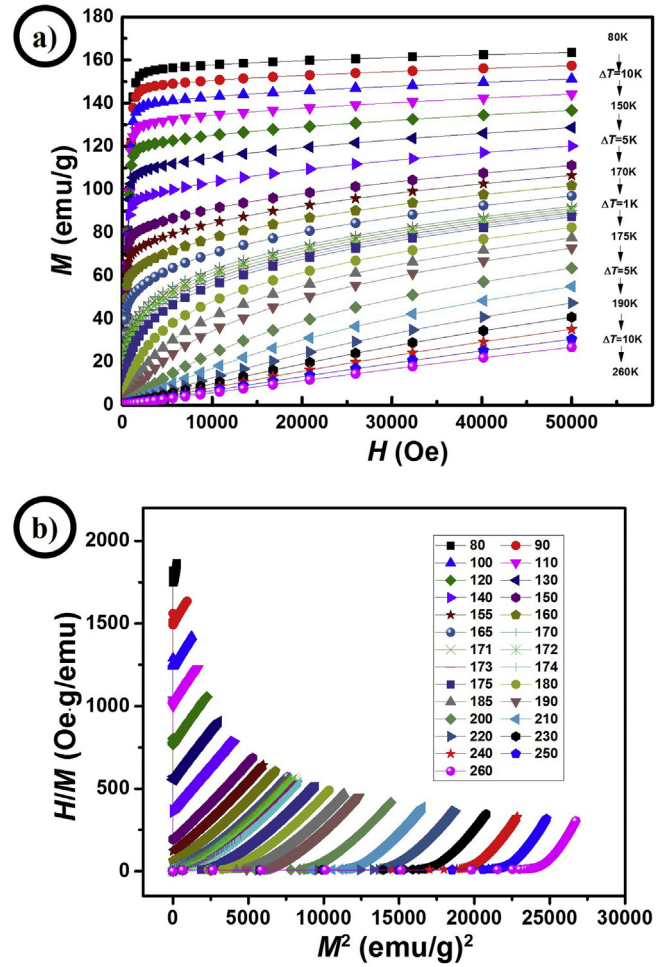


Fig. 3. a) The isothermal magnetization (M - H) curves of the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires at different temperatures and b) is the corresponding Arrott conversion H/M vs. M^2 curves.

only a few Kelvins and the ΔS_M decreases sharply when the temperature deviates from the phase transition point [35,36]. However, both the first-order and the second-order phase transition materials show the peak-shaped curves of $\Delta S_M(T)$. Therefore, the full width at half maximum of the magnetic entropy change vs. temperature curve (δT_{FWHM}) is defined as the operating temperature range of a material. Obviously, the $\text{Gd}_{50}(\text{Co}_{69.25}\text{Fe}_{4.25}\text{Si}_{13}\text{B}_{13.5})_{50}$ microwires show broad triangle $-\Delta S_M(T, H)$ curves especially at high applied fields as exhibited in Fig. 4 and an extremely large working temperature range of $\sim 126 \text{ K}$ is obtained at $\mu_0 \Delta H = 5 \text{ T}$. This δT_{FWHM} value is larger than those of GdAlCo microwires and Gd-based bulk metallic glasses [37]. The excellent working temperature range of the microwires is regarded as a result of both the size effect and the good glass forming ability. Moreover, Liu et al. have proposed a model that the magnetic phase transitions in amorphous materials would be broadened due to the fluctuation of exchange integrals as a result of structural disorder that is always present in amorphous alloys [38].

For a cooling application, it is essential for a magnetocaloric material possessing a large magnetic entropy change over a wide working temperature range. In reality, however, one must consider balancing these two factors. In this regard, the refrigerant capacity

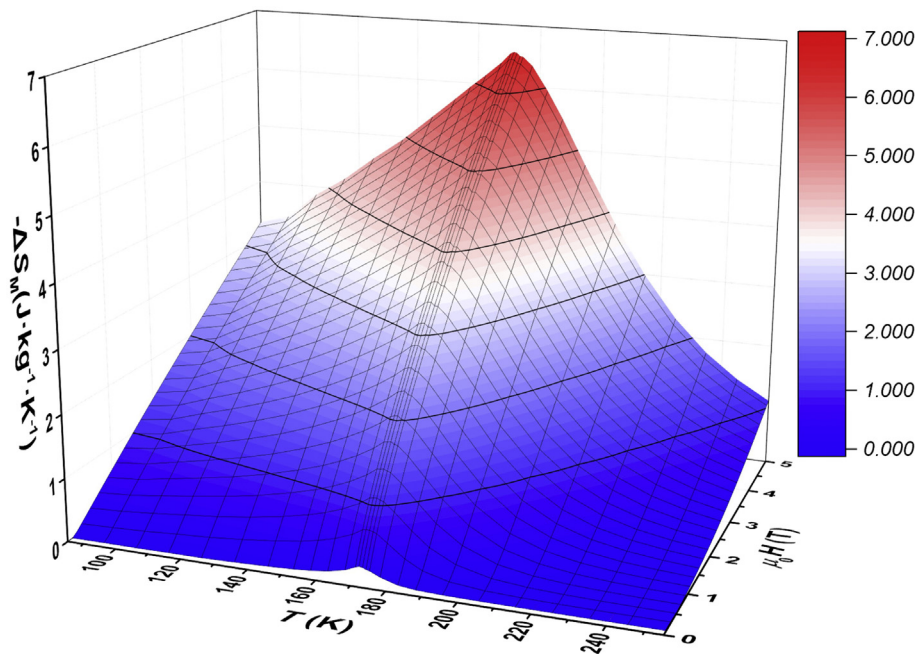


Fig. 4. The temperature dependence of magnetic entropy change ($-\Delta S_M$) for different applied field changes.

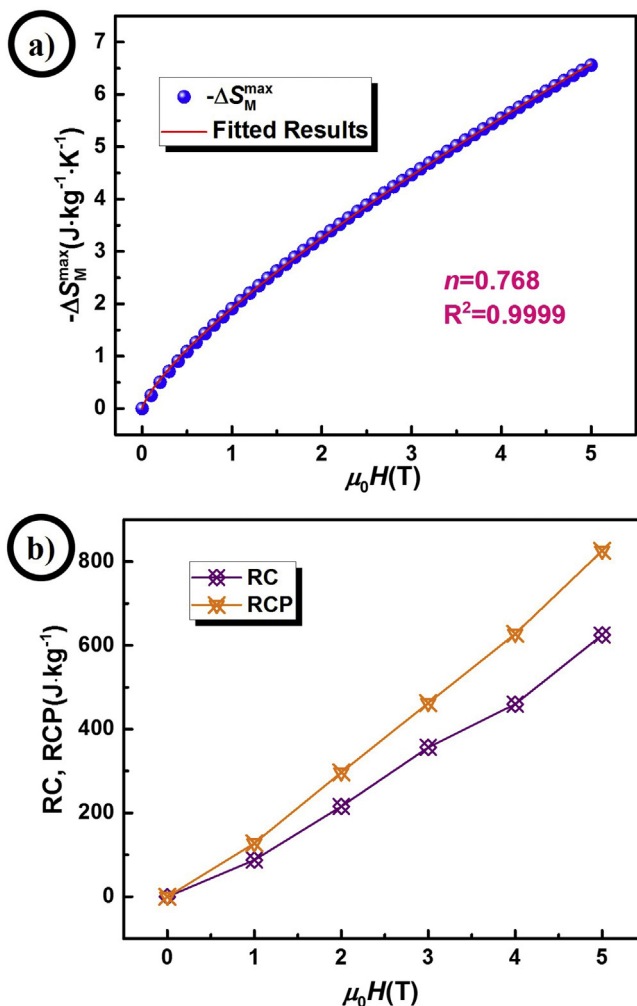


Fig. 5. a) the fitted result of the maximum magnetic entropy change ($-\Delta S_M^{\max}$) vs. magnetic field; b) the calculated RC and RCP values at different applied fields.

(RC) defined by integrating the area of the $-\Delta S_M$ curves enclosed within FWHM temperatures and/or the relative cooling power (RCP) defined as the product of $-\Delta S_M$ and δT_{FWHM} are often employed for characterizing the cooling efficiency of a material. RC and RCP can be expressed as follows [17]:

$$RC = \int_{T_1}^{T_2} -\Delta S_M(T) dT, \quad (5)$$

$$RCP = -\Delta S_M^{\max} \cdot \delta T_{FWHM} = -\Delta S_M^{\max} (T_2 - T_1), \quad (6)$$

where T_1 and T_2 are the onset and offset temperatures of δT_{FWHM} , respectively. The value of RC is usually $\sim 3/4$ of the RCP due to the wide triangular peak of $-\Delta S_M(T, H)$ curves [38]. The calculated results of RC and RCP for the $Gd_{50}(Co_{69.25}Fe_{4.25}Si_{13}B_{13.5})_{50}$ microwires are shown in Fig. 5b, and which all are also summarized in Table 1 combined with δT_{FWHM} . The RC and RCP values of the $Gd_{50}(Co_{69.25}Fe_{4.25}Si_{13}B_{13.5})_{50}$ microwires are $\sim 625 \text{ J kg}^{-1}$ and 826 J kg^{-1} at $\mu_0 \Delta H = 5 \text{ T}$, respectively. Compared to GdAlCo microwires [16–21], the present microwires possess smaller $-\Delta S_M^{\max}$ values but equal or even larger RC and RCP values (see Table 1), making them more desirable for active magnetic refrigeration. Some intermetallic compounds such as TdGa and $Gd_{0.8}Er_{0.2}Ga$, in the same temperature range of interest, show similar magnetocaloric properties and even larger RC values than the present microwires; this is due to the presence of two successive transitions which are the spin-reorientation (SR) and second-order ferromagnetic-paramagnetic (FM-PM) that enhanced the δT_{FWHM} and hence the RC values [39,40].

4. Conclusions

In summary, the melt-extracted $Gd_{50}(Co_{69.25}Fe_{4.25}Si_{13}B_{13.5})_{50}$ microwires show amorphous microstructures and good metallic glass forming ability. These microwires possess an improved T_C temperature of $\sim 170 \text{ K}$ as compared to the GdAlCo microwires

Table 1

The magnetocaloric parameters of the present wires, and the wires and some intermetallic compounds reported previously in the literature.

Composition	T_C (K)	$\mu_0\Delta H$ (T)	$-\Delta S_{M}^{\max}$ (J kg ⁻¹ K ⁻¹)	RC (J kg ⁻¹)	RCP (J kg ⁻¹)	δT_{FWHM} (K)	Ref.
Gd ₅₀ (Co _{69.25} Fe _{4.25} Si ₁₃ B _{13.5}) ₅₀	170	5	6.56	625	826	126	Present
Gd ₅₀ Al ₃₀ Co ₂₀	86	5	10.1	672	—	90	[16]
Gd ₅₃ Al ₂₄ Co ₂₀ Zr ₃	96	5	10.3	733	—	—	[17]
Gd ₅₅ Al ₂₅ Co ₂₀	100	5	9.7	652	—	—	[18]
Gd ₆₀ Co ₁₅ Al ₂₅	101	5	9.7	732	973	—	[19]
Gd ₆₀ Al ₂₀ Co ₂₀	109	5	10.1	681	915	91	[20]
Gd ₅₅ Al ₂₀ Co ₂₅	110	5	9.7	580	804	83	[21]
TdGa ^a	154	5	5.9	620.6	—	—	[36]
Gd _{0.8} Er _{0.2} Ga ^a	168	5	5.6	715.3	—	185.5	[37]

^a Intermetallic compounds.

(~100 K), due to the multi-component alloying effect. The Gd₅₀(Co_{69.25}Fe_{4.25}Si₁₃B_{13.5})₅₀ microwires also possess large values of RC ~625 J kg⁻¹ and RCP ~826 J kg⁻¹ at $\mu_0\Delta H = 5$ T, which are equal and even larger as compared to the previously reported GdAlCo microwires. The excellent magnetic and magnetocaloric properties of the Gd₅₀(Co_{69.25}Fe_{4.25}Si₁₃B_{13.5})₅₀ microwires make them very attractive for active magnetic refrigeration in the nitrogen temperature range.

Acknowledgments

The work was partially supported by the National Natural Science Foundation of China (NSFC, Nos. 51671071 and Nos. 51371067). M.H.P acknowledges support from the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-07ER46438 (Magnetic and magnetocaloric analysis).

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