Enhancing the magnetocaloric response of high-entropy metallic-glass by microstructural control

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ABSTRACT Non-equiatomic high-entropy alloys (HEAs), the second-generation multi-phase HEAs, have been recently reported with outstanding properties that surpass the typical limits of conventional alloys and/or the first-generation equiatomic single-phase HEAs. For magnetocaloric HEAs, non-equiatomic \((\text{Gd}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24})_{100-x}\text{Fe}_x\) microwires, with Curie temperatures up to 108 K, overcome the typical low temperature limit of rare-earth-containing HEAs (which typically concentrate lower than around 60 K). For alloys with \(x = 2\) and \(3\), they possess some nanocrystals, though very minor, which offers a widening in the Curie temperature distribution. In this work, we further optimize the magnetocaloric responses of \(x = 3\) microwires by microstructural control using the current annealing technique. With this processing method, the precipitation of nanocrystals within the amorphous matrix leads to a phase compositional difference in the microwires. The multi-phase character leads to challenges in rescaling the magnetocaloric curves, which is overcome by using two reference temperatures during the scaling procedure. The phase composition difference increases with increasing current density, whereby within a certain range, the working temperature span broadens and simultaneously offers relative cooling power values that are at least 2-fold larger than many reported conventional magnetocaloric alloys, both single amorphous phase or multi-phase character (amorphous and nanocrystalline). Among the amorphous rare-earth-containing HEAs, our work increases the working temperature beyond the typical <60 K limit while maintaining a comparable magnetocaloric effect. This demonstrates that microstructural control is a feasible way, in addition to appropriate compositional design selection, to optimize the magnetocaloric effect of HEAs.

Keywords: high-entropy metallic-glass, magnetocaloric effect, universal curve, current annealing, dual-phase

INTRODUCTION

Solid-state magnetic cooling based on the magnetocaloric effect (MCE) has been considered as the next-generation refrigeration technology, and thus attracted intense research interest [1]. This technique offers higher efficiency, environmental amity, compactness, noiselessness, and extended service life as compared with the conventional gas compression-expansion refrigeration technology [2–6]. In the point of view on the energy transfer between the MCE materials and their external environment under varying magnetic fields \((H)\), there is a practical need for the solid refrigerant materials to exhibit high heat-exchange efficiency. This can be well satisfied by processing the MCE materials into microwire form, which has high surface-to-volume ratio [7–9]. Since the first reports in 2004 [10,11], high-entropy alloys (HEAs) are still considered as a new type of materials due to their multi-principal elements design concept (traditional alloys are typically based on one or two principal elements) [12]. The HEAs have evolved into two generations: the first-generation single-phase with quinary equiatomic compositions and the second-generation with non-equiatomic compositions, and/or multiple phases [13–15]. The latter comprising of more than four elements has been reported with excellent properties, such as mechanical [16] and magnetic [17–19] properties. In particular, for MCE research field, evolving to non-equiatomic compositions enables rare-earth (RE)-containing HEAs to surpass their low temperature limit [20,21], and to exhibit large MCE enhancement in transition-metal HEAs due to the first-order magnetostructural phase transitions [22,23]. Above all, RE-containing HEAs, especially Gd-containing high-entropy metallic glasses (HE-MGs), have received the most attention due to their excellent MCE properties [24–29]. However, their Curie temperatures \((T_C)\) are typically below 60 K, which further indicates that their working temperature is limited to that range as their MCE peaks around \(T_C\). In previous work [20], we have found that minor Fe doping to \((\text{Gd}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24})_{100-x}\text{Fe}_x\) \((x = 0–3\ at\%)\) HE-MGs could tune the \(T_C\) from 80 to 108 K, which equates to more than 60% increase than the typical limit. Furthermore, the appearance of some nanocrystals leads to minor compositional difference between the amorphous matrix and nanocrystalline phase, leading to the widening of the \(T_C\) distribution and improving the relative cooling power (RCP) by 7%. MCE enhancement is found for conventional alloys exhibiting amorphous/nanocrystalline dual-phase structures [6,30–35], whereby those Gd-based compositions show an improve-
ment of up to ~84% and ~21% in the values of maximum magnetic entropy change ($\Delta S_M^{\text{max}}$) and refrigeration capacity (RC) (for 5 T), respectively. In particular, a very recent report by Feng et al. [6] highlighted their MCE enhancement obtained by optimizing the Gd content and fabrication method of Gd-based amorphous/nanocrystalline fibers. It should be noted that the small RCP increase for (Gd$_{36}$Tb$_{20}$Co$_{20}$Al$_{24}$)$_{97}$Fe$_3$ (x = 0–3 at%) HE-MGs is due to the limited fraction of the nanocrystalline phase, so only the broadening of the global MCE response is observed. In order to further explore the specific influence of the nanocrystalline phase on the MCE properties and critical behavior of HE-MGs, it is essential to increase the content of the nanocrystals. This can be effectively achieved in amorphous alloys through heat-treatment [36] in a protective atmosphere [34,35], magnetic field [37], stress condition [38], and by using current annealing [33,39]. Among these techniques, direct current (DC) Joule current annealing is more suitable for annealing metallic-glass microwires [33], as its characteristics, such as precisely tunable and controllable processing parameters, could prevent the microwires from becoming brittle.

Therefore, with the aim to investigate the role of nanocrystalline phase in the MCE optimization and the critical behavior of the Gd-containing HE-MG composite microwires, we select (Gd$_{36}$Tb$_{20}$Co$_{20}$Al$_{24}$)$_{97}$Fe$_3$ with the highest nanocrystalline phase fraction in the as-cast state from Ref. [20] to subject to various current density values ($5 \times 10^6$, $7.5 \times 10^6$ and $100 \times 10^6$ A m$^{-2}$) to further enhance the precipitation of nanocrystals in the microwires. The fraction of nanocrystals increases with the increase of current density magnitude, leading to a compositional difference between the amorphous matrix and the nanocrystalline phase. This difference, within a certain range, leads to a large expansion in the working temperature span of the annealed HE-MG microwires. As a result, they yield magnetocaloric responses that are at least 2-fold larger than those of conventional second-order magnetic transition (SOMT) amorphous magnetocaloric alloys and cooling efficiency which is comparable to that of the notable Gd$_3$Y$_5$Er$_2$Ho$_4$Tb$_6$ HEA [40]. We further show, using the scaling laws [41], a good collapse of the rescaled magnetocaloric curves onto a universal curve by using two reference temperatures in the construction procedure to avoid the influence of multiphase character of the samples.

**METHODS**

The (Gd$_{36}$Tb$_{20}$Co$_{20}$Al$_{24}$)$_{97}$Fe$_3$ ingot was prepared by arc melting a mixture of pure metals with purities higher than 99.9 wt% in a Ti-gettered high-purity Ar atmosphere. The ingot was re-melted five times and then suction-casted to form a cylindrical rod of 10 mm in diameter and 50 mm in length. The alloy microwires were prepared by a precision home-made melt-extraction equipment with a high-speed spinning molybdenum wheel. The wheel is 320 mm in diameter and 60° in knife-edge. Using 30 m s$^{-1}$ wheel-rim-line-speed and 30 μm s$^{-1}$ melt-feeding-rate, the microwires were formed through rapid solidification when the liquid pool adhered to the wheel rim. Further details of the melt-extracted microwire preparation process can be found in Ref. [42].

For DC current annealing, the microwires were annealed at three current density values, i.e., $5 \times 10^6$, $7.5 \times 10^6$ and $100 \times 10^6$ A m$^{-2}$, for 480 s in air. The maximum temperature reached by the microwires depends on the current density as well as on the microwire diameter, length, resistivity, duration of the treatment, and sample environment. We kept constant all those magnitudes except for the current density. Therefore, there is a direct correlation between temperature and current. However, due to the very small diameter of the microwires, the actual temperature cannot be measured but only estimated. The reader is referred to Ref. [33] for further details. Although both conventional annealing and Joule heating produce crystallization due to the temperature rise, current annealing is more versatile for keeping the emerging crystals within the nanometer range [43].

The surface morphology of the annealed microwires were determined by a scanning electron microscope (SEM, FEI Quanta 200FEG), as shown in Fig. S1 (Supplementary information). The SEM images show that the annealed microwires possess smooth surfaces. Thermal analysis was conducted at a heating rate of 10 K min$^{-1}$ by a differential scanning calorimeter (DSC, Netzsch STA449F3 Jupiter), which was calibrated with pure In, Sn, Zn, Al, and Au before the experiments.

The microstructures of the as-cast and annealed microwires were characterized by transmission electron microscope (TEM, FEI Talos F200X) equipped with energy-dispersive X-ray spectroscopy (EDS). Isothermal magnetization (M) of the microwires was tested using a magnetic property measurement system (PPMS, Quantum Design Dynacool-14T). For the MCE determination, isothermal magnetization curves as a function of field following a discontinuous protocol have been measured [44].

The magnetic entropy change ($\Delta S_M$) was calculated using the integral method based on Maxwell relation [1]:

$$\Delta S_M(T, \mu_0 \Delta H) = S(T, \mu_0 H) - S(T, 0)$$

$$= \mu_0 \left[ \int_0^{\mu_0 \Delta H} \left( \frac{\partial M}{\partial T} \right) \, dH \right]$$

$$= \sum_{j=1}^{n} \left( \frac{(M_{i+1,j} - M_{i,1}) + (M_{i+1,j+1} - M_{i,j+1})}{T_{i+1} - T_{i}} \right) \times \frac{\mu_0 (H_{i+1} - H_i)}{2},$$

where $S_M$ represents the magnetic entropy, $\mu_0 H_{\text{max}}$ represents the maximum external magnetic field, and $M_{ij}$, $M_{i+1,j}$, $M_{i,j+1}$ and $M_{i+1,j+1}$ are magnetization under the fields of $H_i$ and $H_{i+1}$, and at temperatures of $T_i$ and $T_{i+1}$, respectively.

The universal scaling analysis has been reported to study the nature of the phase transitions of the materials [23,45] and also confirm the presence of the additional phase [41–46,48]. The procedure included normalizing the $\Delta S_M$ by their maxima and temperatures to a dimensionless axis ($\theta$) using either one or two reference temperatures ($T_r$) [41]:

$$\theta(1 \text{ ref}) = (T - T_{\text{max}}) / (T_r - T_{\text{max}}),$$

$$\theta(2 \text{ refs}) = \frac{-(T - T_{\text{max}})}{(T_r - T_{\text{max}})},$$

where $T_r$, $T_{i+1}$, and $T_{i}$ were selected corresponding to $\Delta S(M) = 0.7 \Delta S_M^{\text{max}}$ curve while $T_{i+1}$ was chosen above $T_{\text{max}}$.

Besides $\Delta S_M^{\text{max}}$, cooling efficiencies, i.e., RCP and RC, are also used as the figures of merit for magnetocaloric materials. RCP
and RC can be calculated by using the following formulas with full-width at half maximum (FWHM, i.e., working temperature span) of the $\Delta S_M(T)$ curve \[49\]:

\[
RCP = -\Delta S_M^{\text{max}} \times \text{FWHM} = -\Delta S_M^{\text{max}} (T_2 - T_1),
\]

(4)

\[
RC = \int_{T_1}^{T_2} -\Delta S_M(T) dT,
\]

(5)

where $T_1$ and $T_2$ represent the start and end temperatures of FWHM.

The magnetic field dependences of $\Delta S_M^{\text{max}}$, RCP and RC have been reported to follow a power law expression according to \[50\]:

\[
y = ax^b,
\]

(6)

where $y = -\Delta S_M^{\text{max}}$, RCP or RC and they exhibit their respective power law exponents, $a$ and $b$ are constants.

For the magnetic field dependence of $\Delta S_M$, which also follows a power law expression as $\Delta S_M \propto H^n$ \[41\], its exponent $n$ has been recently reported to (i) quantitatively evaluate the order of the phase transition \[51\]; (ii) quantitatively evaluate the critical point when the first order crossovers to second order phase transition \[52\]; (iii) analyze the critical behavior (close to $T_C$, $n$ is correlated to the critical exponents) \[45,53\]; (iv) reveal additional magnetic phases in magnetocaloric alloys due to its sensitivity for the second phase \[47,54\]; and (v) thus deconvolute overlapping phase transitions \[47,48\]. Exponent $n$, dependent on both temperature and magnetic field, can be locally determined as

\[
n = \frac{\text{dln} |\Delta S_M^{\text{max}}|}{\text{dln} [H_0 \Delta H]}.
\]

(7)

RESULTS AND DISCUSSION

Structural characterization

Fig. 1a shows the DSC results of the as-cast and annealed microwires. The results show the obvious exothermic peaks, i.e., crystallization peaks, indicating the presence of amorphous phase in all studied samples. The arrows in the figure indicate the onset temperatures ($T_o$) for the first exothermic peaks. No significant changes of $T_o$ can be found for the microwires annealed at different current density values. The enthalpy of the first crystallization peak ($\Delta H_{x1}$) of the studied microwires was calculated by integrating the area of the first crystallization peaks after $T_o$, for deducing volume fraction evolution of the amorphous phase \[55–57\]. The current density dependence of $\Delta H_{x1}$ is plotted in Fig. 1b. The image illustrates that with the increase of current density, the $\Delta H_{x1}$ consistently decreases from 2.94 kJ mol$^{-1}$ for the as-cast microwires to 1.68 kJ mol$^{-1}$ for $100 \times 10^6$ A m$^{-2}$ annealed microwires. This indicates that the increase of current density decreases the fraction of amorphous phase, implying the increased fraction of additional phase.

Fig. 2 shows the bright-field TEM results for the as-cast and annealed microwires. The nanocrystals observed within the amorphous matrix grow in amounts (see Fig. 2a–d) as the current density used for annealing increases. The measured compositions (tabulated in Table S1) taken from various regions as numbered in Fig. 2 show that the composition of the amorphous phase is similar for the as-cast microwires and $50 \times 10^6$ and $75 \times 10^6$ A m$^{-2}$ annealed microwires. This indicates that up to $75 \times 10^6$ A m$^{-2}$ of current annealing, it has little effect on the amorphous phase composition. On the other hand, further annealing to $100 \times 10^6$ A m$^{-2}$, the amorphous matrix shows a larger deviation in composition as compared with those of as-cast and $50 \times 10^6$ and $75 \times 10^6$ A m$^{-2}$ annealed microwires. EDS

Figure 1 (a) DSC results for the as-cast, $50 \times 10^6$, $75 \times 10^6$ and $100 \times 10^6$ A m$^{-2}$ annealed microwires. (b) The corresponding enthalpies of the first peaks after $T_o$ as a function of current density.

Figure 2 Bright-field TEM images for (a) the as-cast, (b) $50 \times 10^6$, (c) $75 \times 10^6$, and (d) $100 \times 10^6$ A m$^{-2}$ annealed microwires, respectively. The symbols and numbers in the images are the regions corresponding to the EDS analysis.
mapping results presented in Figs S2 and S3 show some compositional differences between the amorphous matrix and the nanocrystalline phase as observed from some of the bright regions for Co precipitates.

Face-centered cubic (FCC) structure is observed from the selected area electron diffraction (SAED) patterns of the single nanocrystal of \(50 \times 10^6\) A m\(^{-2}\) annealed microwires, as shown in Fig. 3a. For \(75 \times 10^6\) A m\(^{-2}\) annealed microwires, their high-resolution TEM (HRTEM) images are shown in top panel of Fig. 3b while the fast Fourier transform (FFT) results corresponding to the red dashed squares in the HRTEM images are displayed at the bottom of Fig. 3b. These results in combination with the diffraction rings in the SAED pattern (right side of Fig. 3b) confirm the FCC structure of the nanocrystalline phase of \(75 \times 10^6\) A m\(^{-2}\) annealed microwires. The FCC structure of nanocrystalline phase of \(100 \times 10^6\) A m\(^{-2}\) annealed microwire is confirmed by their FFT results (where the red dashed squares in the HRTEM images at the top of Fig. 3c correspond to the FFT images in the bottom panel of Fig. 3c) and the observed diffraction rings in the SAED pattern (on the right side of Fig. 3c). In addition, the influence of the current density magnitude on the nanocrystalline phase fraction is further studied as plotted in Fig. 4. It shows that the nanocrystal content monotonously increases with the increase of current density, agreeing well with the DSC analysis in Fig. 1b.

**Magnetocaloric properties**

Fig. 5a–c show the temperature dependence of \(\Delta S_M\) for the as-cast and annealed microwires at magnetic field changes (\(\mu_0\Delta H\)) of 0.5, 2, and 5 T, respectively. At low \(\mu_0\Delta H\) (Fig. 5a, b), the \(\Delta S_M(T)\) curves of the annealed microwires show shoulders at 15–55 K in addition to the main \(\Delta S_M\) peaks at \(T > 90\) K (not observed for the as-cast state). This indicates the presence of additional phase upon annealing. This observation is not found for 5 T. Furthermore, it is observed that the \(\Delta S_M\) peaks of the microwires are maintained when annealed to \(75 \times 10^6\) A m\(^{-2}\) but for \(100 \times 10^6\) A m\(^{-2}\) of annealing, it shows a 22% reduction, compared with that of the as-cast state. This can be ascribed to the decreased magnetic moment of amorphous phase, arising from the reduction of Co content [35,53], which is observed from the EDS results (Table S2 and Fig. S3). A further analysis on the temperatures corresponding to the \(\Delta S_M\) peaks shows that they are relatively magnetic-field-independent and only decrease from 102.3 to 97.4 K for \(100 \times 10^6\) A m\(^{-2}\) annealed microwires. This can be attributed to the largest compositional deviation observed in the amorphous matrix for \(100 \times 10^6\) A m\(^{-2}\) annealed microwires as compared with the other studied samples in this work.

**Analysis on the presence of additional phase and the order of magnetic phase transition**

The temperature dependence of exponent \(n\) has been used in many reports to reveal the presence of multi-phases of magnetocaloric materials [47,54]. For our studied microwires, their \(n(T)\) plots are displayed in Fig. 6. At low temperatures, the exponent \(n\) values are around 1 (ferromagnetic state), and then decrease to minimum \((n_{\text{min}})\) at temperatures near \(T_{\text{max}}\) before increasing towards 2 \((n\text{ at the paramagnetic state is 2})\). The fingerprint for first-order magnetic phase transitions, i.e. overshoot of \(n\) above 2 near transition temperatures [51], is not observed in Fig. 6, which indicates that the studied microwires undergo SOMT. The observed shallow \(n_{\text{min}}\) for all studied microwires can be attributed to the presence of additional phases, in agreement with the shoulders noticed in Fig. 5a (below 60 K). As shown in Figs 2, 3, and Figs S2, S3, the annealed microwires exhibit the amorphous/nanocrystalline...
The temperature dependence of exponent $n$ for $\mu_0\Delta H = 5$ T with the inset showing the enlarged curves at temperatures around $T_{\text{max}}$.

Furthermore, we studied the $\mu_0\Delta H$ dependences of $\Delta S_{\text{max}}$, $RCP$, and $RC$ of the studied microwires, as presented in Fig. 8. It can be observed that they follow a power law dependence (see the fittings presented as dashed lines) as Equation (6), similar to the SOMT reports in the literatures [41,58]. The fitting results further listed in Table 1 show a good fit for all curves.

It should be noted that the exponent $b$ differs the most for the $100 \times 10^6$ A m$^{-2}$ annealed microwires in this work, which is influenced by the critical behavior of amorphous matrix. When annealed with low current density values ($50 \times 10^6$ and $75 \times 10^6$ A m$^{-2}$), the concomitant fraction of nanocrystalline phase has little influence on the composition of the amorphous phase. Thus, the critical exponents of the amorphous phase can be close to those of the as-cast microwires, indicating that the critical behaviors of the main phases of the as-cast, $50 \times 10^6$ and $75 \times 10^6$ A m$^{-2}$ annealed microwires are similar. When increasing the current density to $100 \times 10^6$ A m$^{-2}$, the increased amount of nanocrystalline phase leads to a larger compositional difference between the amorphous and nanocrystalline phases. Such difference, at this moment, is significant enough to result in dual-phase structure with composition difference between the phases. This could lead to the difference between $T_C$ of the amorphous and nanocrystalline phases [20], giving rise to the appearance of a shoulder besides the main $\Delta S_M$ peak. It should be noticed that as the current density increases to $100 \times 10^6$ A m$^{-2}$, the value of $n_{\text{min}}$ increases, as magnified in the inset of Fig. 6.

The collapse of rescaled $\Delta S_M(T)$ curves onto a single universal curve is widely reported for magnetocaloric materials that undergo SOMT. For our studied as-cast and annealed microwires, their rescaled curves constructed using two $T_i$ show that they collapse onto a single universal curve for different magnetic fields (Fig. 7a). This indicates that the samples undergo SOMT, which agrees with the observations from Fig. 6 and the Banerjee’s criterion whereby SOMT shows positive slopes in Arrott plots (as observed in Fig. S4). Furthermore, the rescaling of $\Delta S_M(T)$ curves can be used to reveal the presence of multiphase character in SOMT materials by using one reference temperature [41,46–48] even if the transition temperature of the additional phase is out of the experimental range [41]. Thus, in our case, a poor collapse of the rescaled curves is observed when rescaling the $\Delta S_M(T)$ curves of our studied microwires using one $T_i$ (Fig. 7b) due to the overlap of multiple SOMT phases present in this study. In addition, at $\Delta S_M / \Delta S_{\text{max}} = 0.7$, the deviations ($\delta\theta$) between the rescaled curves become evidently distant for $100 \times 10^6$ A m$^{-2}$ annealed microwires (markedbythe black arrows in Fig. 7b). Hence, the use of two $T_i$ for rescaling $\Delta S_M(T)$ curves helps to remove the influence of the overlapped phases on the universal curve analysis of the multiple SOMT phases for each sample. In addition, the rescaled curves of the as-cast and annealed microwires collapse onto a universal curve using two $T_i$ as seen in Fig. 7c for $\mu_0\Delta H = 5$ T, indicating that they exhibit similar critical exponents. Fig. 7d shows the current density dependence of $\delta\theta$, $n_{\text{min}}$ and FWHM (related to $RCP$ in Equation (4)). With increasing current density, an increasing trend (within the error margin) is observed for $\delta\theta$, $n_{\text{min}}$ and FWHM. This can be attributed to the increasing nanocrystalline phase fraction in the microwires with increasing current density. For materials following the mean-field approach, their $n_{\text{min}} = 2/3$. However, many amorphous MCE materials undergoing SOMT are typically reported with $n_{\text{min}} = 0.75$ [45]. For this study, the $n_{\text{min}}$ values are close to 0.75 for the as-cast, $50 \times 10^6$ and $75 \times 10^6$ A m$^{-2}$ annealed microwires. For $100 \times 10^6$ A m$^{-2}$ annealed microwires, the corresponding $n_{\text{min}}$ is larger than 0.75. For FWHM, it expands with higher current density due to the increase in the fraction of the nanocrystalline phase with low $T_C$ as there is a $T_C$ difference between the amorphous matrix and nanocrystalline phase. Therefore, the $RCP$ values of 686, 703, 681 and 573 J kg$^{-1}$ (5 T) are obtained for the as-cast and $50 \times 10^6$, $75 \times 10^6$ and $100 \times 10^6$ A m$^{-2}$ annealed microwires. The initial annealing ($50 \times 10^6$ and $75 \times 10^6$ A m$^{-2}$) enables the retainment of comparably high $RCP$ with respect to that of the as-cast microwires and reported HE-MGs. Conversely for further annealing to $100 \times 10^6$ A m$^{-2}$, though a large FWHM is attained, $RCP$ decreases due to the reduction in $\Delta S_{\text{max}}$.

Figure 5 Temperature dependence of $-\Delta S_M$ of the as-cast and annealed microwires at $\mu_0\Delta H$ of (a) 0.5, (b) 2, and (c) 5 T. It should be noted that the magnetocaloric curves of the as-cast, $50 \times 10^6$ and $75 \times 10^6$ A m$^{-2}$ overlap at (b, c) due to their similar $\Delta S_M$ values.
in a change in the critical exponents of the amorphous phase. It should be noted that the presence of the nanocrystals, with a transition temperature in the range of <55 K, as indicated by the hump in \(\Delta S_M\) shown in Fig. 5, does not affect the critical behavior of the amorphous phase detected by the magnetocaloric response [32]. Therefore, the modification of the critical exponents of the amorphous phase is solely ascribed to its compositional change. Nevertheless, the modification of the critical exponents is not large enough to significantly alter the collapse of the rescaled \(\Delta S_M\) curves presented in Fig. 7c.

**Literature comparison**

With the aid of power law fitting analysis, the magnetocaloric response of studied microwires can be easily extrapolated to

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**Table 1**  Exponent \(b\) obtained by fitting \(\mu_0\Delta H\) dependences of \(\Delta S_M^{\text{max}}\), RCP and RC for the as-cast and annealed microwires, and the coefficient of determination of the fitting, \(R^2\)

|          | \(\Delta S_M^{\text{max}}\) | \(R^2\)   | \(b\) from RCP | \(R^2\)   | \(b\) from RC | \(R^2\) |
|----------|-----------------------------|-----------|----------------|-----------|---------------|-----------|
| As-cast  | 0.79 ± 0.01                 | 0.99945   | 1.10 ± 0.01    | 0.99982   | 1.12 ± 0.01   | 0.99981   |
| 50 × 10^6 A m\(^{-2}\) | 0.81 ± 0.01                 | 0.99945   | 1.14 ± 0.01    | 0.99978   | 1.13 ± 0.01   | 0.9998    |
| 75 × 10^6 A m\(^{-2}\) | 0.82 ± 0.01                 | 0.99948   | 1.12 ± 0.01    | 0.99972   | 1.12 ± 0.01   | 0.99974   |
| 100 × 10^6 A m\(^{-2}\) | 0.86 ± 0.01                 | 0.9996    | 1.15 ± 0.01    | 0.99995   | 1.14 ± 0.01   | 0.99994   |

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**Figure 7**  The rescaled \(\Delta S_M\) curves (0.45 \(\leq \mu_0\Delta H \leq 5\) T) calculated for the as-cast and annealed microwires using (a) two \(T_r\) and (b) one \(T_r\). The black arrows indicate the width (\(\delta \theta\)) between two rescaled curves at \(\Delta S_M^{\text{max}} = 0.7\). (c) The single universal curve of the studied microwires achieved by using two \(T_r\) at \(\mu_0\Delta H = 5\) T. (d) The current density dependence of various parameters associated to the magnetocaloric behaviors.

**Figure 8**  \(\mu_0\Delta H\) dependences of (a) \(\Delta S_M^{\text{max}}\), (b) RCP, and (c) RC, and their corresponding fitting results.
CONCLUSIONS

In this work, we studied the tuning of magnetocaloric responses of HE-MG microwires by controlling their microstructures through annealing with the current annealing technique: (Gd$_{36}$-Tb$_{20}$Co$_{20}$Al$_{24}$)$_{97}$Fe$_3$ microwires were annealed by current densities of $5 \times 10^6$, $7.5 \times 10^6$ and $100 \times 10^6$ A m$^{-2}$. TEM shows the precipitation of nanocrystals within the amorphous matrix, in which the crystallites are observed to increase in fraction with the increase of current density magnitude. This leads to a compositional difference between the amorphous matrix and the nanocrystalline phase. With the use of two reference temperatures during the scaling procedure, the rescaled magnetic entropy curves collapse onto a single universal curve, avoiding the effects of the presence of multiple phases in the microwires. Overall, the increased current density, whereby within a certain range, enhances the MCE properties of (Gd$_{36}$-Tb$_{20}$Co$_{20}$Al$_{24}$)$_{97}$Fe$_3$ microwires, resulting in broadening working temperature span and simultaneously offering RCP values that are at least 2-fold larger than reported values of many conventional MCE amorphous or amorphous/nanocrystal composite alloys. Compared with the amorphous RE-containing HEAs, our microwires show comparable magnetocaloric properties at the temperature range surpassing the typical <60 K limit. This demonstrates that besides the appropriate compositional design selection, the microstructural control is an effective way to optimize MCE of HEAs.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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