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Amorphous microwires of high entropy alloys with large magnetocaloric effect

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ABSTRACT

Microwires of $Gd_{20}Ho_{20}Er_{20}Al_{20}TM_{20}$ (TM = Fe, Co and Ni) high-entropy metallic glasses (HE-MGs) are successfully fabricated by a melt-extraction method, which exhibit good magnetocaloric properties. The maximum magnetic entropy change and refrigerant capacity under 5 T of the $Gd_{20}Ho_{20}Er_{20}Al_{20}Co_{20}$ HE-MG microwire can reach 10.2 J kg^{-1}K^{-1} and 625 J kg^{-1}, respectively. In addition, the magnetocaloric properties of the HE-MG microwires can be widely tuned by doping different transition metals. The HE-MG microwires combining high heat-exchange efficiency and excellent mechanical properties are attractive candidates for applications in magnetic refrigeration.

Compared with conventional gas refrigerants, magnetic refrigerants based on a magnetocaloric effect (MCE) exhibit better properties, such as higher efficiency and better environmental friendliness [1–5]. In the past decades, many crystalline materials, such as Gd, $Gd_5Si_2Ge_2$ (at. %) and $LaFe_{11.4}Si_{1.6}$, were developed, and demonstrated their potentials for an application as magnetic refrigerants [1–16]. Metallic glasses (MGs), as a kind of second-order magnetic phase transition materials, manifest a large MCE in a wide temperature range owing to their amorphous nature. Furthermore, MGs also exhibit a high electrical resistivity (meaning a small eddy current heating), a high corrosion resistance, outstanding mechanical properties, and a high thermal stability, which are suitable for the application in the magnetic refrigeration. Recently, high-entropy MGs (HE-MGs) are successfully synthesized [6–9]. Different from the conventional MGs that are usually composed of one or two major elements, the HE-MGs are composed of several elements with equimolar concentrations [6–9]. Due to a strong topological and chemical disorder structure, HE-MGs usually exhibit a large magnetic entropy change (ΔS_M), and refrigerant capacity (*RC*), and thus are promising candidates for the magnetic refrigeration [10–12].

Usually, good magnetic refrigerants, working as both cooling agent, and regenerator medium, are expected to possess a large ΔS_M value and a good capability of heat exchange [13]. To obtain an efficient heat transfer, the magnetic refrigerants must have a high surface area. In this case, decreasing the geometric size of the regenerative substance to be micrometer scale, such as micro-sized spherical particles, thin plates or wires, is favourable for the refrigerate properties. Recently, the MCE of MGs in the forms of bulk [14,15], ribbon [16,17], powder [18,19] and wire [20–23] were extensively studied. Significantly, the MG microwires exhibit better MCE [20–23] compared with their bulk and ribbon counterparts, which are mainly attributed to their better adaptability and higher heat-exchange efficiency. Magnetocaloric materials with a diameter of 50–200 µm (the corresponding surface area is about 10,000–40,000 m^2/m^3) exhibit a good heat-transfer capability under an operating frequency of 1 Hz [24,25]. Furthermore, compared with the spherical and plate shapes, the long wires have a negligible demagnetization factor when the magnetic field is applied along the wire direction [26]. Thus, micro-sized wires with the good MCE are desired to improve the efficiency of magnetic refrigeration system.

In this work, $Gd_{20}Ho_{20}Er_{20}Al_{20}TM_{20}$ (TM = Fe, Co and Ni) HE-MG microwires are fabricated successfully by a melt-extraction method, as schematically shown in Fig. 1a. The effect of component, temperature and magnetic field on the magnetic-transition temperature, the magnetic-entropy change, and the refrigerant capacity are investigated. The results show the HE-MG microwires are suitable candidates for the magnetic refrigerants.

The optical image (Fig. 1b), and SEM images (Fig. 1c, d, e) of the $Gd_{20}Ho_{20}Er_{20}Al_{20}TM_{20}$ microwires show that the HE-MG microwires have a diameter of about 60 µm, and a length of several centimetres. Their amorphous structures are confirmed by XRD patterns and DSC traces, as shown in Fig. 2. From the DSC traces, it can be seen that an endothermic glass transition occurs followed by several exothermic crystallization peaks for each alloy, indicating the formation of glassy

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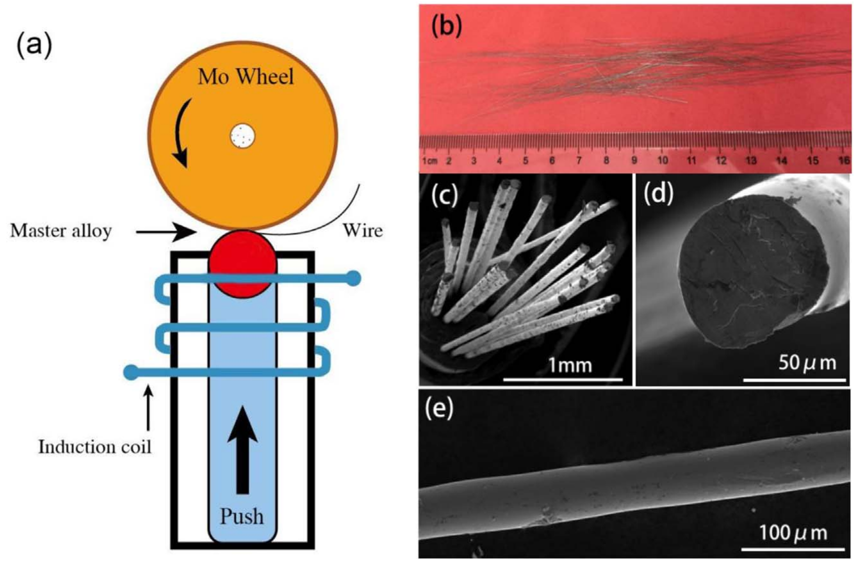

Fig. 1. Experimental setup. (a) The schematic illustration of melt extraction technique, (b) the optical image, and (c), (d), (e) the SEM images of HE-MG microwires.

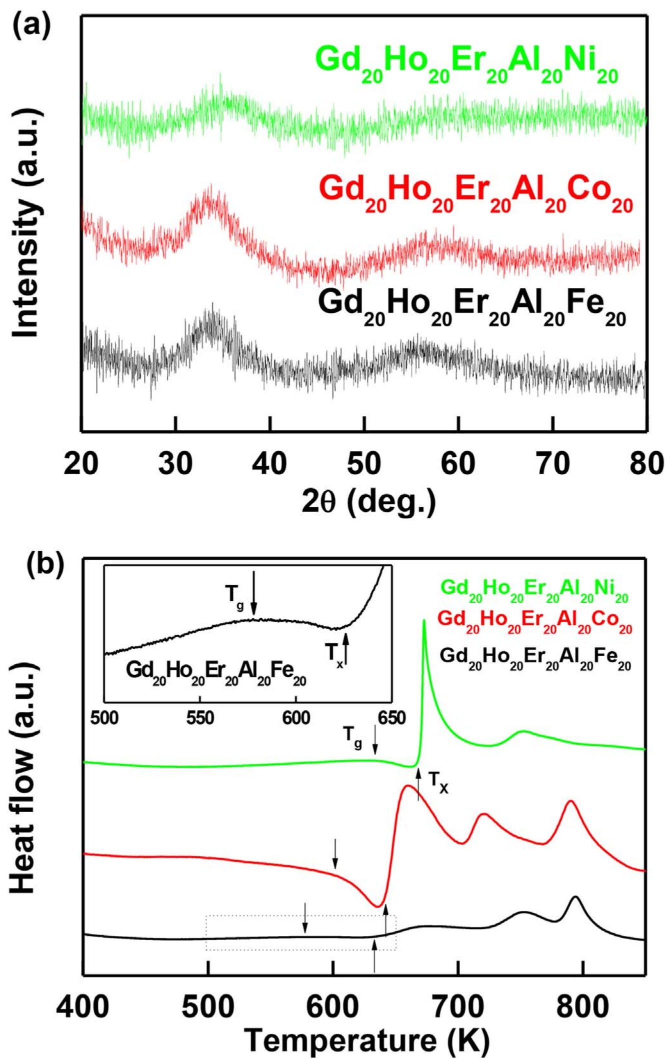

Fig. 2. Structure and thermal properties of $Gd_{20}Ho_{20}Er_{20}Al_{20}TM_{20}$ (TM = Fe, Co and Ni) HE-MG microwires. (a) XRD patterns and (b) DSC traces of HE-MG microwires. The inset shows the magnified DSC trace of $Gd_{20}Ho_{20}Er_{20}Al_{20}Fe_{20}$.

phase. The XRD patterns show a broad diffraction maximum and no sharp Bragg peaks from crystalline phases, which further confirm the amorphous structure. The glass-transition temperature (T_g), first crystallization temperature (T_x) and supercooled-liquid region ($\Delta T_x = T_x - T_g$) are listed in Table 1. A large ΔT_x value suggests a good glass-forming ability (GFA) [27]. The ΔT_x values of these alloys are smaller than those of other rare-earth based MGs, as shown in Table 1, indicating their poor GFA. This may be attributed to the compositions of these HE-MG microwires are deviated from the eutectic points despite their high mixing entropy [10].

The temperature dependence of the magnetization for the HE-MG microwires is measured upon heating under a field of 200 Oe, as shown in Fig. 3a. A spin-freezing transition can be observed in the field cooling (FC) curve. A cusp exists in the zero field cooling (ZFC) curve at the same temperature. The divergence between the FC and ZFC curves is a typical spin-glass-like behavior [28]. The sample of TM = Fe has the widest magnetic-transition temperature (T_C) range among all samples. The T_C values calculated from the differentiation of the FC curves are 55, 39 and 25 K, for the samples of TM = Fe, Co and Ni, respectively, as marked by arrows in the insert of Fig. 3a. Evidently, the T_C value decreases rapidly when TM changes from Fe to Ni. The increase of 3d electrons from Fe ($3d^6$) to Ni ($3d^8$) weakens the magnetic interactions that are dominated by the 3d-electron exchange, and then reduces the exchange energy and the T_C value of the alloys. It is evident that the T_C value can be tuned easily in a large temperature range by alloying different elements in the HE-MG microwire.

To characterize the magnetocaloric effect of these microwires, the ΔS_M values are calculated based on the isothermal-magnetization (*M-H*) curves in a wide temperature range under different external magnetic fields ranged from 0 to 5 T, as shown in Fig. 3b. In an isothermal process of magnetization, the total ΔS_M value of the system caused by a magnetic field (H) can be calculated based on the isothermal *M-H* curves at various temperatures (T_i) using the equation [10],

$$\Delta S_M(T_i, H) = \frac{\int_0^H M(T_i, H)dH - \int_0^H M(T_{i+1}, H)dH}{T_i - T_{i+1}}. \quad (1)$$

Fig. 4a displays the ΔS_M value as a function of the temperature under the magnetic fields of 1, 2, 3, 4 and 5 T for the