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Rare-earth high-entropy alloys with giant magnetocaloric effect

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ABSTRACT

In this paper, we report the development of rare-earth high-entropy alloys (RE-HEA) with multiple principle elements randomly distributed on a single hexagonal close-packed (HCP) lattice. Our work demonstrated that it is the entropy, rather than other atomic factors such as enthalpy, atomic size and electronegativity, that dictates phase formation in the current rare-earth alloy system. The high configuration entropy stabilized the crystalline structure from phase transformation during cooling, whereas a second-order magnetic phase transition occurred at its Neel temperature. The quinary RE-HEA exhibited a small magnetic hysteresis and the largest refrigerant capacity (about 627 J kg^{-1} at the 5 T magnetic field) reported to date, along with respectable mechanical properties. Our analysis indicates that the strong chemical disorder resulted from the high configuration entropy makes magnetic ordering in the HEA difficult, thus giving rise to a sluggish magnetic phase transition and enhanced magnetocaloric effect. Our findings evidenced that RE-HEAs have great potential to be used as magnetic refrigerants and the alloy-design concept of HEAs can be employed to develop novel high-performance magnetocaloric materials.

1. Introduction

Compared with conventional gas refrigerants, magnetic refrigerants based on the magnetocaloric effect (MCE) have advantages of being both highly efficient and environmental friendly [1-4]. The magnetocaloric effect can be characterized by the field-induced entropy change (ΔS_M) due to the alignment of its magnetic spins that occurs under an external magnetic field [5]. According to the involved magnetic phase transitions, magnetic refrigerants can be divided into two categories, i.e., the first and the second order magnetic phase transition materials. Materials in the former category usually show large MCE in a narrow temperature range, but their large thermal and magnetic hysteresis and easy occurrence of cracking and fatigue limited their widespread use as magnetic refrigerators [6]. In contrast, the MCE materials in the second category normally possess gradual and continuous magnetization variation, exhibiting broader peaks with no thermal and magnetic hysteresis. Currently, this type of MCE materials is considered to be an optimal choice for magnetic refrigerants [7]. Up to now, however, very few alloys in this specific category simultaneously having large magnetic entropy change and refrigerant capacity (*RC*) have been developed and fabricated. Exploring novel alloys concurrently possessing large magnetic entropy change and *RC* through innovative routes is paramount for enabling practical applications of magnetic refrigerants.

In recent years, a new alloy-design concept, termed as high-entropy alloys (HEAs), was proposed [8-10]. Generally, HEAs contain multiple principal elements in an equimolar or near-equimolar ratio, which induces formation of disordered solid-solution phases with simple structures due to the high entropy of mixing, such as body-centered cubic (BCC), face-centered cubic (FCC) or hexagonal close-packed (HCP) structures. Formation of ordered crystalline intermetallic phases that often contain

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structurally complex giant unit cells is usually suppressed [11]. The HEA crystallographic structure is characterized by a topologically ordered lattice with an exceedingly high chemical disorder. Such a configurational disorder in MCE materials might hinder thermal motion of magnetic atoms or ions due to the so-called entropy stabilization, which could result in increased heat flow from the ambient environment and lead to large MCE. Rare-earth (RE) elements are known to possess unique magnetocaloric effects, therefore, it is interesting and imperative, both scientifically and technologically, to apply the HEA concept into developing high-performance RE-MCE materials. Recently, Feuerbacher et al. [12] first reported the development of a HCP HEA using pure RE metals, suggesting that our approach is feasible. In this paper, we report design and fabrication of several RE-HEAs which simultaneously have large MCE and *RC*, and the underlying mechanisms will also be explored.

2. Experimental

Alloys with a nominal composition of $Gd_{20}Dy_{20}Er_{20}Ho_{20}Tb_{20}$, $Gd_{25}Er_{25}Ho_{25}Tb_{25}$, $Dy_{25}Er_{25}Ho_{25}Tb_{25}$ and $Er_{33.33}Ho_{33.33}Tb_{33.34}$ were prepared by arc-melting a mixture of high-purity Gd (99.9%), Dy (99.9%), Er (99.9%), Ho (99.9%) and Tb (99.9%) in a Ti-gettered high-purity argon atmosphere. The ingots were re-melted at least six times to ensure chemical homogeneity and subsequently drop-cast into a copper mold with a dimension of Φ10 mm × 60 mm. Phase constitutions were identified by X-ray diffraction (XRD) using Cu-Kα radiation. Chemical composition was analyzed by energy dispersive spectrometer (EDS) in a scanning electron microscopy (SEM) with field emission using a Zeiss Supra55 operated at 15 kV. SEM, TEM (transmission electron microscopy) and STEM (scanning transmission electron microscopy) were employed to characterize the microstructures. The SEM samples were sequentially ground and mechanically polished using 0.04 μm silica suspensions. The TEM samples were first mechanically ground to ~20 μm thick and then ion-milled at −30 °C under liquid-nitrogen to avoid oxidation. Temperature and field dependences of magnetization as well as specific heat were measured by a physical property measurement system (PPMS) from Quantum Design Company.

3. Results

3.1. Microstructure

Fig. 1a shows XRD patterns of the as-cast $Gd_{20}Dy_{20}Er_{20}Ho_{20}Tb_{20}$, $Gd_{25}Er_{25}Ho_{25}Tb_{25}$, $Dy_{25}Er_{25}Ho_{25}Tb_{25}$, and $Er_{33.33}Ho_{33.33}Tb_{33.34}$ alloys. For the quinary $Gd_{20}Dy_{20}Er_{20}Ho_{20}Tb_{20}$ alloy, all the XRD peaks can be indexed to a HCP structure. The corresponding SEM image of this alloy is shown in Fig. 1b in which irregular-shaped grains are seen, indicating formation of a mostly single crystalline phase. While for the quaternary $Gd_{25}Er_{25}Ho_{25}Tb_{25}$ and $Dy_{25}Er_{25}Ho_{25}Tb_{25}$ alloys, and ternary $Er_{33.33}Ho_{33.33}Tb_{33.34}$ alloy, another crystalline phase with a trigonal (TRI) structure was found in addition to the HCP phase, indicating that configuration entropy of these alloys is insufficient to induce formation of a single phase. The actual composition was determined to be $Gd_{19.5}Dy_{21.1}Er_{19.3}Ho_{20}Tb_{20.1}$ (in atomic percent) with 0.5% uncertainty from the EDS measurements, which is in good agreement with the target. XRD patterns of $Gd_{20}Dy_{20}Er_{20}Ho_{20}Tb_{20}$ as a function of temperature from 20 K to room temperature are shown in Fig. 1b. Clearly, the XRD patterns stayed almost the same at different temperatures, suggesting neither structural change nor structure-induced phase transformation during cooling down to 20 K. Nevertheless, the XRD peaks were found to be quite broad, as compared with those in conventional alloys, which may be due to the distorted HCP lattice

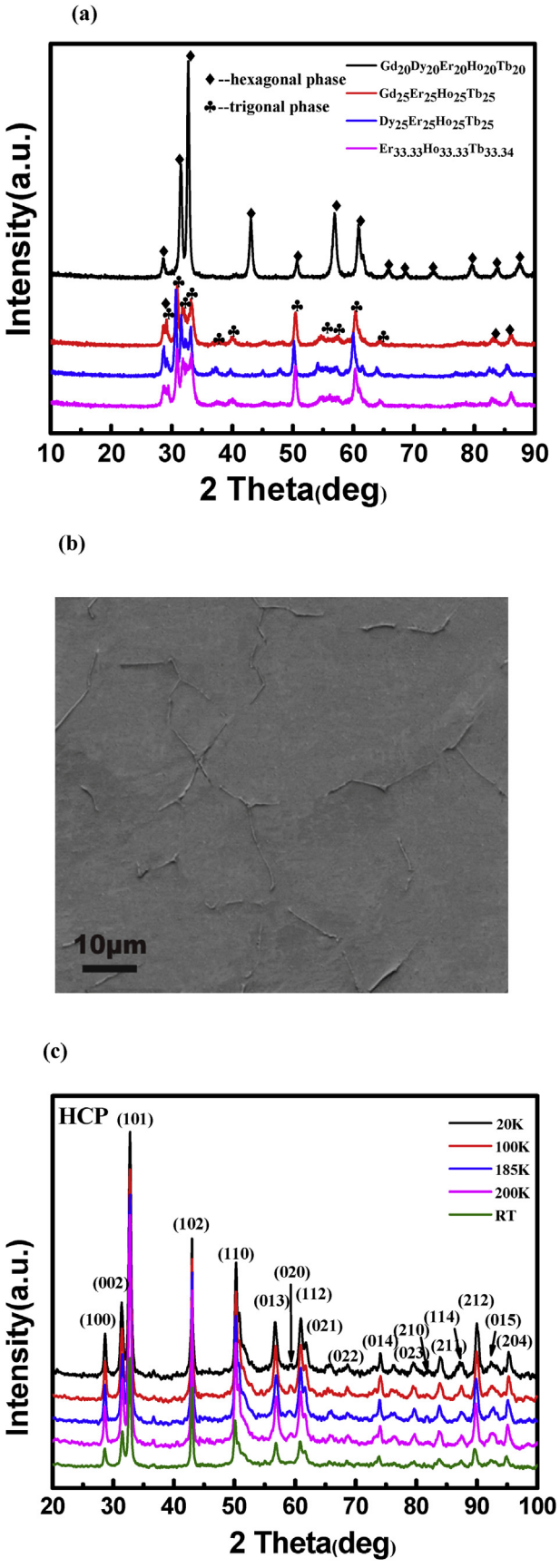

Fig. 1. (a) XRD patterns of the $Gd_{20}Dy_{20}Er_{20}Ho_{20}Tb_{20}$, $Gd_{25}Er_{25}Ho_{25}Tb_{25}$, $Dy_{25}Er_{25}Ho_{25}Tb_{25}$ and $Er_{33.33}Ho_{33.33}Tb_{33.34}$, (b) SEM image of the $Gd_{20}Dy_{20}Er_{20}Ho_{20}Tb_{20}$ alloy, (c) XRD patterns of the $Gd_{20}Dy_{20}Er_{20}Ho_{20}Tb_{20}$ HEA from 20 K to room temperature.