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Er-based glassy composites as potential regenerator material for low-temperature cryocooler

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ABSTRACT

Low-temperature specific heat of Er-based metallic glassy composites is investigated. It is found that the low-temperature specific heat of the alloys compares favorably with that of prototype crystalline Er_3Ni which is the low temperature (<15 K) cryocooler regenerator material. The Er-based glassy alloys also have wide temperature range for the large low-temperature specific heat, large magnetic entropy, and the peak of the low-temperature specific heat is tunable. The alloys combining excellent mechanical properties and tunable composition make them a potential regenerator material for small scale low-temperature cryocooler.

1. Introduction

The development of small but highly efficient refrigerators in cryogenic engineering is awaited by industries and some high technology fields [1,2]. The efficiency of such a refrigerator operating below 15 K is mainly determined by the effectiveness of the regenerator materials [1,2]. To increase the regenerator efficiency, the volumetric specific heat (C_p) of the regenerator material must be larger than that of working gas which generally is He gas [3,4]. However, below 15 K, the C_p of currently used regenerator materials such as Cu or Pb, rapidly decreases in the low temperature region, which is too small to obtain the refrigeration capacity at liquid He temperatures.

Some magnetic materials, especially rare-earth intermetallics, which show much larger C_p below 15 K compared with non-magnetic materials, were proposed to be regenerator materials [5–8]. The removal of the magnetic ground state degeneracy by the phase transition can cause a significant magnetic entropy change of the material which brings about a large specific-heat anomaly in the vicinity of the transition temperature [5–8]. However, in most cases the anomaly is in relatively narrow temperature range. For example, the C_p peaks of prototype crystalline cryocooler regenerator material of Er_3Ni and Er_3Co are almost the same as He, but their half width are only half that of He. Therefore, for low-temperature refrigeration, the multilayer regenerator is used to cover different temperature ranges [9,10]. The used regenerator material normally is in the micro scale spherical particles. It is quite difficult to produce micro scale spherical particles of conventional magnetic intermetallic compounds such as Er_3Ni for cryogenic regenerator [9].

Recently, a series of heavy rare earth (Gd, Tb, Dy, Ho, Er, and Tm) based bulk metallic glasses (BMGs) with large magnetic moments and profuse magnetic structure have been developed [11–14]. The large magnetic entropy changes have been obtained at 2–100 K [15–21]. In addition, the magnetic entropy changes peaks are much broader owing to their disorder structure. In view of the large magnetic entropy changes in a broad temperature range, these BMGs may be considered as suitable candidates for low-temperature cryocoolers.

In this paper we report the study of low-temperature special heat of Er-based BMG composites. The large specific-heat in a wide temperature range below 15 K comparable with that of the Er_3Ni alloy has been obtained. Our work shows that the metallic glass based composite could be a potential regenerator material for small scale low-temperature cryocoolers, such as pulse tube refrigerator.

2. Experimental

The Er-based alloys with nominal compositions $Er_{60}Ni_{20}Al_{20-x}Gd_x$ ($x=0$, 1, 2, 3) were prepared by arc melting pure Ni, Al, Er, and Gd in a Ti-gettered argon atmosphere. The ingot was remelted and suck cast into a Cu mold to get a cylindrical rod of 1 mm in diameter. Their structure were ascertained by x-ray diffraction (XRD) using a MAC Mo3 XHF diffractometer with Cu $K\alpha$ radiation and transmission electron microscope (TEM). The special heat dependences of magnetization were measured in physical properties measurement system 6000 of Quantum Design Company. The temperature and field dependences of magnetization were measured in a SQUID magnetometer (Quantum Design).

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3. Results

The XRD, bright-field TEM, high resolution of TEM (HRTEM) and selected area electron diffraction (SAED) images of the $Er_{60}Ni_{20}Al_{17}Gd_3$ alloy are shown in Fig. 1. The XRD pattern in Fig. 1(a) exhibits appreciable crystalline peaks superimposing in the broad diffraction peaks, which indicates the alloy contains both amorphous phase and crystalline phases. The amorphous fraction in the alloy is about 50% estimated roughly form the XRD results. The composites structure is also confirmed by TEM observation (Fig. 1(b)). Fig. 1(c) reveals a series of diffuse halo rings, indicating the amorphous matrix. Fig. 1(d) shows that some Bragg reflection spots come forth near the diffuse halo rings, which indicates there are crystalline phase in amorphous matrix. The HRTEM image of part II (Fig. 1(e)) clearly shows lattice fringes corresponding to crystalline nature, demonstrating that the glassy phase surrounding the nanocrystalline phase. The above results manifest that the alloy has a typical structure of BMG composite.

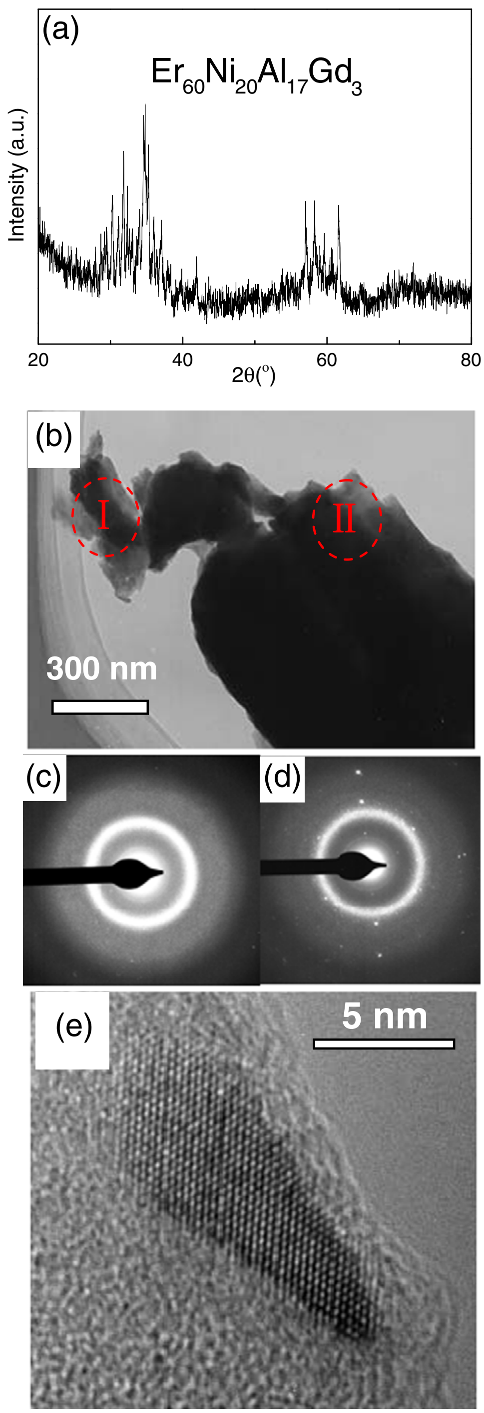

Fig. 1. Microstructure of $Er_{60}Ni_{20}Al_{17}Gd_3$ alloy. (a) XRD pattern of the as-cast $Er_{60}Ni_{20}Al_{17}Gd_3$ rods (diameter is 1 mm), (b) Bright-field TEM image of the alloy, (c) SAED pattern of part I showing in (b), (d) SAED pattern of part II showing in (b), (e) HRTEM image of part II showing in (b).

Fig. 2 shows the comparison of temperature dependence of the volumetric specific heats of the $Er_{60}Ni_{20}Al_{17}Gd_3$ alloy, and prototype cryocooler regenerator materials of He, Pb, and Er_3Ni. The He gas is generally used as the working gas of the refrigerator. Below 15 K, its C_p increases on a superficial state and has a sharp peak as shown in Fig. 2[1]. A good regenerator material should have a large volumetric specific heat compared to that of the working gas. The C_p of lead, usually used as cryocooler martial, rapidly decreases in low temperature region and is not suitable for the cryocooler martial below 15 K. The Er_3Ni is commercial used low-temperature cryocooler material below 15 K [22], but its C_p peak is narrow as shown in Fig. 2. The $Er_{60}Ni_{20}Al_{17}Gd_3$ alloy has a maximum volumetric C_p of 0.7 J/Kcm^3, which is larger than that of Er_3Ni and Pb. The volumetric C_p peak of this alloy has a wide temperature range from 10 to 15 K, which is also larger than that of He, Pb and Er_3Ni. We also note that the cost effectiveness of the present alloy studied is much cheaper than that of the previously reported materials, because the Er-based glassy composites are much easy to be prepared and low content of the rare earth Er. This indicates that the alloy with large C_p has larger cooling power and could be a potential regenerator material for low-temperature cryocoolers.

Fig. 3 shows the temperature dependence of the C_p of the $Er_{60}Ni_{20}Al_{20-x}Gd_x$ ($x = 0, 1, 2, 3$) alloys. One can see that the substitution of Gd for Al in the alloy shifts the C_p peak to higher temperature. In addition, the magnitudes of the volumetric C_p peaks are greatly increased and the peaks gradually broaden with the content of Gd increasing. The results show clearly that the value, position and width of the C_p peak of the alloy are tunable.

The large C_p anomaly in Er-based BMG composites is due to the larger magnetic entropy changes of the alloys. In a magnetic system the specific heat and the magnetic entropy change (ΔS_m) have the following relations: [13]

$$\Delta S_m = \int_{T_1}^{T_2} \frac{\Delta C_p}{T} dT. \quad (1)$$

As the magnetic transition temperature range is narrow, it is obvious that, near the transition temperature, the larger the magnetic entropy changes, the greater the specific heat anomalies. The ΔS_m of the $Er_{60}Ni_{20}Al_{17}Gd_3$ BMG composite was measured through the isothermal magnetizations at different temperatures. The inset of Fig. 4 displays a set of isothermal magnetization curves of M–H with

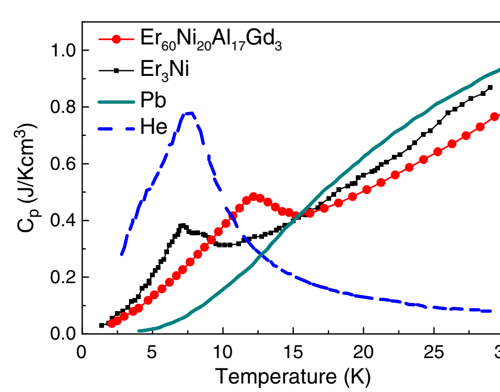

Fig. 2. The comparison of temperature dependence of the volumetric specific heats of He, Pb, Er_3Ni and $Er_{60}Ni_{20}Al_{17}Gd_3$.

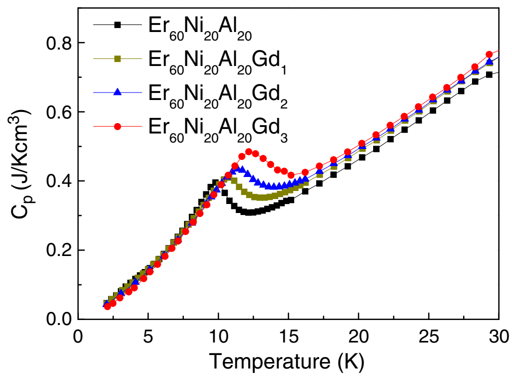

Fig. 3. Temperature dependence of the volumetric specific heats of the $Er_{60}Ni_{20}Al_{20-x}Gd_x$ ($x = 0, 1, 2, 3$) alloys.

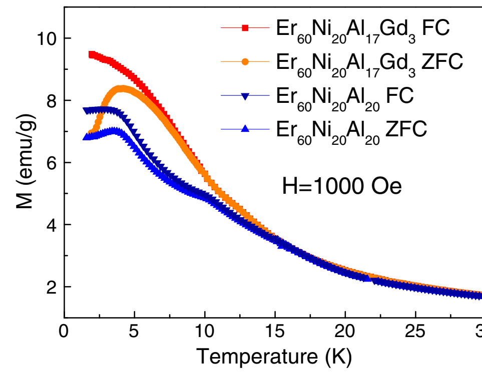

Fig. 5. Temperature dependence of the ZFC and FC magnetization under a magnetic field of 1000 Oe for $Er_{60}Ni_{20}Al_{20}$ and $Er_{60}Ni_{20}Al_{17}Gd_3$ alloys.

increasing filed in a large temperature range. In the isothermal process of magnetization, the total ΔS_m of the system due to the application of a magnetic field can be derived from Maxwell relations by integrating over the magnetic field: [13]

$$\Delta S_m = \int_{H_{\min}}^{H_{\max}} (\partial M/\partial T) dH. \quad (2)$$

Maximal value of 5 T was used in our experiments. The ΔS_m is due to the change of the degree of the alignment of the magnetic moments driven by the variation of the external magnetic field. From Eq. (2), it is clear that a large ΔS_m can be observed near the transition temperature when the magnetization varies sharply in a constant field. Fig. 4 presents the calculated ΔS_m from the Maxwell equation of the $Er_{60}Ni_{20}Al_{17}Gd_3$ alloy. The peak value under a field change of 5 T can reach 12.8 J kg^{-1} K^{-1}, which is comparable to that of Gd and the rare earth based BMGs [13,16]. In addition, the glass phase in the BMG composite leads to a broader peak in the ΔS_m due to fluctuation of the exchange integral. The large magnetic entropy change extends the large specific heat into larger temperature range.

4. Discussions

The large C_p and the tunable specific heat peaks below 15 K are owing to the magnetic transitions and the tunable magnetic transition temperature of the alloys at low temperatures. Fig. 5 shows the temperature dependence of the magnetization determined in an applied field of 1000 Oe for the $Er_{60}Ni_{20}Al_{20}$ and $Er_{60}Ni_{20}Al_{17}Gd_3$ alloys. The zero field cooling (ZFC) branch was measured on heating after initially cooling from 300 to 2 K in zero field. The field cooling (FC) branch was measured on heating after initially cooling to 2 K in the same measuring field. From the FC curves a spin freezing transition can clearly be seen, while in the ZFC curve a cusp is observed at the same temperature where divergence appeared between the FC and the ZFC branches showing typical spin-glass-like behavior. The transition temperatures T_f for the $Er_{60}Ni_{20}Al_{20}$ and $Er_{60}Ni_{20}Al_{17}Gd_3$ alloys determined from the ZFC curves are 3.5 K and 4 K, respectively. This indicates that the T_f of the composites can be tuned easily by alloying different rare earth elements [23], and the volumetric C_p peak of the alloys then can be modulated. We also note that the glassy composites have relatively high corrosion resistance, good mechanical properties, high electrical resistance, and polymer-like thermoplastic formability [13]. The metallic glass show good micro- and even nano-formability using thermoplastic forming near room temperature [24]. The advantage of the wide choice of the magnetic transition temperature tuned by composition and combining properties makes these alloys attractive regenerator material at low temperatures.

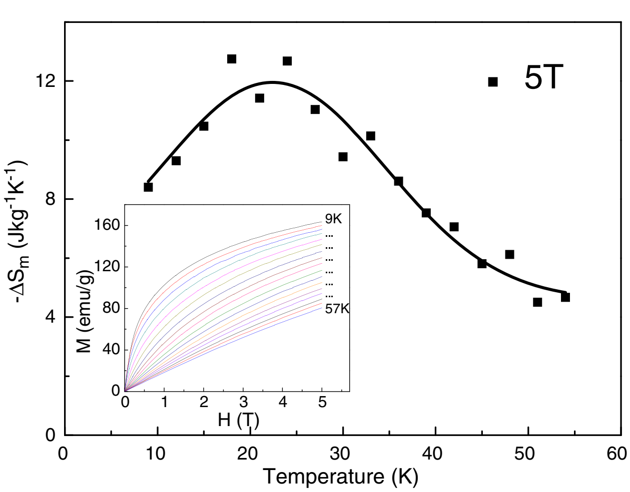

Fig. 4. The calculated magnetic entropy change from the Maxwell equation of the $Er_{60}Ni_{20}Al_{17}Gd_3$ alloy under 5 T. The insert shows the magnetization isotherms of the $Er_{60}Ni_{20}Al_{17}Gd_3$ alloy.

5. Conclusions

Large low-temperature specific heat has been observed in the Er-based BMG composites. Their maximum value of the specific heat compares favorably with that of the known crystalline magnetic regenerator material Er_3Ni. Furthermore, the BMG composites have much wide temperature range of the large low-temperature specific heat and tunable C_p peak. The results presented are repeatable and verified. In manufacturing, the glassy composite alloys are much easily to be fabricated compared to that of the compounds. All these advantages of the alloys make it attractive candidates of regenerator material for low-temperature cryocoolers.

Acknowledgements

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