Original Article

Magnetocaloric effect and critical behavior in Fe-La-Zr rapidly quenched ribbons

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A B S T R A C T

Fe90-xLa xZr10 (x = 1 and 2) rapidly quenched ribbons with thickness of about 15 μm were prepared by the melt-spinning method. X-ray diffraction analysis shows that the structure of the ribbons is mostly amorphous. The Curie temperature, Tc, of the alloy considerably increased, from ~262 K for x = 1 to ~302 K for x = 2, with increasing La-concentration. The maximum magnetic entropy change, (∆SM)max, of the alloy is about 1.1 J·kg⁻¹·K⁻¹ for a magnetic field change ∆H = 12 kOe. A quite large refrigerant capacity (RC ~ 74 J·kg⁻¹) for a magnetic field change ∆H = 12 kOe near the room temperature region is obtained for the alloy. A thorough analysis on critical exponents around the ferromagnetic-paramagnetic phase transition, using the Arrott–Noakes plots and Kouvel–Fisher method, sheds light on the critical magnetic behavior and its association with the magnetocaloric effect in the Fe-La based alloys.

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1. Introduction

In recent years, an emerging refrigeration technology based on the magnetocaloric effect (MCE) has been attracting many scientists and engineers. The MCE is known to be due to an adiabatic temperature change (∆Tad) or an isothermal magnetic entropy change (∆Sm) in a magnetic material when it is magnetized or demagnetized. In comparison with the conventional gas-compression refrigeration, magnetic refrigeration is more environmentally friendly and energetically efficient. Currently, it is necessary to find magnetocaloric materials with large values of ∆Sm and refrigerant capacity (RC) in the room temperature region.

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Up to now, a large number of magnetic materials possessing large MCEs have been discovered, such as Gd-containing alloys, As-containing alloys, La-containing alloys, Heusler alloys, amorphous alloys, and ferromagnetic perovskite maganites [1,2]. The materials (for example: As-containing alloys, La-containing alloys, Heusler alloys), which undergo a first-order phase transition (FOPT), have a large magnetic entropy change. However, the large MCE of these alloys only occurs in a narrow temperature range due to the nature of the FOPT. Thus, the practical application of FOPT materials in magnetic refrigeration is quite limited [3–5]. On the other hand, materials such as amorphous alloys, Gd-containing alloys, rare-earth intermetallic compounds having a second-order magnetic phase transition (SOPT) exhibit a moderate magnetic entropy change, but its temperature distribution spans over a wide temperature range [6–8]. Such a typical example of magnetocaloric materials is amorphous alloys. Among the amorphous alloys, Fe-Zr based rapidly quenched alloys are of particular interest as they possess the giant magnetocaloric effect (GMCE), with broad ∆Sm peaks around the Curie temperatures, low coercivity, high

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resistivity, no toxicity and low price [9–13]. To tune the Curie temperature and improve the glass forming ability (GFA) for these materials, other elements such as Co, Ni, B, Y, Cr, Mn have been incorporated [9–17]. However, the effects of the additional elements on the GFA and Tc of the alloy were widely various. For example, the Curie temperature of Fe90-xLaxZr10 alloy increased from 225 K for x = 0 to 395 K for x = 10 with increasing Y concentration [9]. Both the saturation magnetization (Ms) and Curie temperature (Tc) of the Fe-Zr-B alloy increased with a slight increase of B-concentration [12], while those of the Fe90-xMnxZr10 system decreased with increasing Mn concentration [14–16]. These studies concentrated mainly on the La-Fe alloys with crystalline structure but hardly with amorphous structure. In this work, we have investigated the influence of La on the structure, magnetic properties and magnetocaloric effect of Fe90-xLaxZr10 (x = 1 and 2) rapidly quenched ribbons prepared by the melt-spinning method. A thorough analysis on the critical exponents and their association with the MCE near the paramagnetic-ferromagnetic (PM-FM) phase transition for these alloys has been made.

2. Experimental

The alloys with nominal compositions of Fe90-xLaxZr10 (x = 1 and 2) were prepared from pure metals (99.9%) of Fe, La and Zr. An arc-melting method was first used to ensure the homogeneity of the alloys. The ribbons were then fabricated on a single wheel melt-spinning method using a copper wheel. The tangential velocity, v, was 40 m/s. All of the arc-melting and melt-spinning processes were performed under Ar atmosphere to avoid oxygenation. The structure of the ribbons was analyzed by X-ray diffraction (XRD). The magnetic properties of the alloys were measured by a sample vibrating magnetometer (VSM). The magnetocaloric effect of the ribbons was assessed indirectly by deducing the magnetization versus magnetic field, M(H), at various temperatures, using Maxwell relationship.

3. Results and discussion

The thickness of the obtained ribbons is about 15 μm. Fig. 1 shows the XRD diffraction patterns of Fe90-xLaZr10 alloy ribbons at room temperature. The results reveal that the structural characteristic of the samples is quite similar. All the ribbons have a coexistence of amorphous and crystalline phases. The diffraction peaks corresponding to the crystalline phase of α-Fe and Fe2Zr are observed in these patterns, although they are very weak. This means that the prepared alloy ribbons are almost amorphous. In our previous work [17], the undoped ribbons of Fe90Zr10 with different thicknesses were investigated. Respectively, the undoped ribbons showed a large crystalline fraction and an amorphous structure with thicknesses of 30 μm and 15 μm. The amorphous phase is mainly responsible for the magnetic properties and MCE of the Fe-Zr based alloy ribbons in the vicinity of room temperature.

Fig. 2 presents hysteresis loops at room temperature and reduced thermomagnetization curves (M/M_{100K}) in a magnetic field of 100 Oe for Fe90-xLaZr10 (x = 1 and 2) alloy ribbons. From the hysteresis loops (Fig. 2a), the saturation magnetization Ms (approximately taken at H = 12 kOe) and the coercivity Hc of the alloy ribbons were obtained. The ribbons show a soft magnetic feature with low coercivity of less than 80 Oe (see the inset of Fig. 2a). The Ms values determined for the samples with x = 1 and 2 are ~30 and ~52 emu/g, respectively [17]. Thus, the additional element of La slightly increases the Hc of the alloy. Interestingly, the La addition significantly improves the Ms of the alloy. The reduced thermomagnetization curves (Fig. 2b) indicate that La clearly influences the Tc of the alloy. The value of Tc was determined from the minimum of the dM/dT versus T curve (see inset of Fig. 2b). The samples with x = 1 and 2 have the Tc values of 262 and 302 K, respectively. The magnetization of both the samples does not reduce to zero after the magnetic phase transition. This is probably due to the coexistence of the crystalline phases that have higher Curie temperatures, such as α-Fe. This is in good agreement with the structural analysis (Fig. 1). The Tc value determined for the sample with x = 0 is 245 K [17]. This means that the Tc of the alloy increases with increasing La-concentration. It should be noted that, the magnetic transition phase temperature of the alloy ribbons increased to room temperature with the La-concentration of 3 at.%. The effect of La-addition on the Curie temperature of the Fe-Zr based alloys has a significant meaning in controlling the working temperature of the magnetic refrigerators. The enhancements of the Curie temperature and the saturation magnetization of the alloy by adding La can be explained by the strengthened coupling between 3d-electrons of Fe with 4f-electrons of La. The change in distance of Fe-Fe atoms by the addition of La could also improve the ferromagnetic interaction in these alloys.

In order to investigate the MCE of the alloy ribbons, their magnetic entropy change ∆Sm was calculated using the thermomagnetization data at various magnetic fields ranging from 0.01 to 12 kOe (Fig. 3). From these thermomagnetization curves, we deduced the magnetization versus magnetic field, M(H), at various temperatures (Fig. 4). According to our previous results [17,18], we compared the data deduced from the thermomagnetization curves with those from the virgin magnetization ones and we found a good agreement between these two methods. Then, the magnetic entropy change, ∆Sm, is determined from the M(H) data by using the following relation:

$$\Delta S_m = -\int_{0}^{H} \left(\frac{\partial M}{\partial T}\right) dH$$

(1)

The temperature dependence of -∆Sm of the Fe90-xLaZr10 ribbons for different magnetic field changes (∆H = 4, 6, 8, 10 and 12 kOe) is represented in Fig. 5. It can be observed that the value of ∆Sm increases with increasing the magnetic field change. For ∆H = 12 kOe, the maximum magnetic entropy change, ∆S_{m,max} determined for the samples with x = 1 and 2 are 1.0 and 1.1 J·kg⁻¹·K⁻¹, respectively. These values are equivalent or higher than those reported in the literature for rapidly quenched Fe-based alloys.
MCE alloys, including Fe-Mn-Zr [15], Fe-Cr-Mo-Cu-Ga-P-C-B [19], Fe-Mo-Cu-B [20], (Fe55Co10Cr15)Zr7B2 [21], (Fe70Ni30)Zr7B4 [22,23], Fe-Zr-Cr [24], Fe-Y-Zr [25], Fe-Zr-B-Cu [26], and Fe-Nb-B [27].

The refrigerant capacity (RC) of the samples, which is defined as the product of the maximum entropy change ($\Delta S_{\text{m,\,max}}$) and the full width at half maximum ($\delta T_{\text{FWHM}}$) of the entropy change peak, was also calculated. The value of $\delta T_{\text{FWHM}}$ was also referred as the working temperature range of a magnetic refrigerant. The working temperature range of these ribbons is determined to be about 45 and 67 K for $x = 1$ and 2, respectively. The maximum RC of about 74 J·kg⁻¹ around room temperature was achieved for the 2 at.% La-added sample.

To clearly understand the critical magnetic behavior near the second order PM-FM phase transition for the present ribbons, the Arrott plots or $M^2/H/M$ plots were constructed from the $M(H)$ data and the results are shown in Fig. 6. Because the PM-FM transition at the Curie temperature is a continuous phase transition, the power
law dependence of spontaneous magnetization $M_s(T)$ and inverse initial susceptibility $\chi^{-1}(T)$ on reduced temperature $\varepsilon$ with the set of critical exponents of $\beta$, $\gamma$, $\delta$, etc., can be determined by using the following Arrrott–Noakes relations [28]:

$$M_s(T) = M_0 (-\varepsilon)^\beta \quad \varepsilon < 0$$

(2)

$$\chi_0^{-1}(T) = H_0 M_0^{-\gamma} \quad \varepsilon > 0$$

(3)

$$H = DM^{1/\delta} \quad \varepsilon = 0$$

(4)

where $M_0$, $H_0$, $D$ and $\delta$ are the critical amplitudes and $\varepsilon = (T - T_C)/T_C$ is the reduced temperature.

The $\delta$ parameter can be calculated using the Widom scaling relation [29]:

$$\delta = 1 + \gamma/\beta$$

(5)

The spontaneous magnetization $M_s(T)$ and inverse initial susceptibility $\chi^{-1}(T)$ of the ribbons can be obtained from constructing and linearly fitting of Arrrott plot of $M^2$ versus $H/M$ at high magnetic fields. The values of $M_s(T)$ and $\chi^{-1}(T)$ as functions of temperature $T$ are plotted for the Fe$_{90-x}$La$_x$Zr$_{10}$ ribbons (Fig. 7). In accordance with equations (2) and (3) for $M_s(T)$ and $\chi^{-1}(T)$, the power law fittings are used to extract $\beta$, $\gamma$ and $T_C$ (Fig. 7). The resulted values of $\beta$ and $\gamma$ were then used to calculate the $\delta$ parameter based on equation (5). As a result, the sample with $x = 1$ has the critical parameters of $\beta = 0.437$, $\gamma = 0.834$, $\delta = 2.91$ and $T_C = 262$ K. Similarly, for the sample with $x = 2$, those values are $\beta \approx 0.445$, $\gamma \approx 1.178$, $\delta \approx 3.64$ and $T_C \approx 301$ K. The values of $T_C$ of the alloys obtained from the fittings are mostly equal to those directly determined from the thermomagnetization measurements. This means that the procedures for calculating the critical exponents are correct.

By using the Kouvel - Fisher method [30], the critical parameters of the alloy ribbons can be obtained more accurately. Similar to the Arrrott–Noakes method, the values of $M_s(T)$ and $\chi^{-1}(T)$ are also determined by plotting $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$ curves. Then, the critical parameters $T_C$, $\beta$ and $\gamma$ can be obtained from fitting $M_s(T)$ and $\chi^{-1}(T)$ data by using the following relations:

$$M_s(T) \left( \frac{d H_s/d T} 1 \right)^{-1} = (T - T_C)/\beta$$

(6)

$$\chi_0^{-1}(T) \left[ d \chi_0^{-1}(T)/dT \right]^{-1} = (T - T_C)/\gamma$$

(7)

Fig. 8 indicates the Kouvel–Fisher curves for the alloy ribbons. As shown in this figure, the fitting results of the critical parameters yield $\beta = 0.432$, $\gamma = 0.843$ and $T_C = 263$ K for the $x = 1$ sample and $\beta = 0.448$, $\gamma = 1.180$ and $T_C = 302$ K for the $x = 2$ sample. By using the relation (5), the $\delta$ values of the samples are calculated to be 2.951 for $x = 1$ and 3.634 for $x = 2$. The values of the critical parameters obtained from the Kouvel–Fisher method are in good agreement with those determined from the Arrrott–Noakes fittings.

In comparison with some standard models, such as the mean-field theory ($\beta = 0.5$, $\gamma = 1$ and $\delta = 3.0$), 3D-Heisenberg model ($\beta = 0.365$, $\gamma = 1.336$ and $\delta = 4.8$) and 3D-Ising model ($\beta = 0.325$, $\gamma = 1.241$ and $\delta = 4.82$ [31], the critical parameters attained for the
Fe$_{90-x}$La$_x$Zr$_{10}$ alloy ribbons are close to those of the mean field theory of long-range ferromagnetic order. This means that the samples are mainly of long-range ferromagnetic order. The fact that the critical parameters of the samples fall between those of the mean-field and 3D-Heisenberg models reveals part of short-range magnetic orders coexisting with the long-range magnetic orders in the alloy ribbons. According to the previous study[32], the as-quenched Fe$_{90}$Zr$_{10}$ ribbons show a short-range ferromagnetic order with $\beta = 0.365$ and $\gamma = 1.615$. This may suggests that the critical parameters of the Fe-Zr based alloys with La-addition are closer those of the mean field theory of long-range ferromagnetic orders. The addition of La plays an important role in establishing the long-range ferromagnetic order in the Fe$_{90-x}$La$_x$Zr$_{10}$ ribbons. The dominance of the long-range ferromagnetic order is consistent with the enhancements of the Curie temperature and saturation magnetization observed for the La-added alloy ribbons. It is the coexistence of long- and short-range ferromagnetic orders that broadens the working temperature range of the Fe-La based alloys.

4. Conclusion

The influence of La addition on the structure, magnetic properties, magnetocaloric effect and critical parameters of Fe$_{90-x}$La$_x$Zr$_{10}$ ($x = 1$ and 2) ribbons was investigated systematically. The Curie temperature of these alloys can be tuned to the region of room temperature by choosing an appropriate La-concentration. The maximum entropy change, $\Delta S_m_{\text{max}} = 1.1$ J·kg$^{-1}$·K$^{-1}$ for $\Delta H = 12$ kOe and the wide working range around room temperature, $\Delta T = 70$ K, reveal potential use of the rapidly-quenched Fe-La-Zr based alloys in magnetic refrigerators. A detailed analysis of the critical parameters of the Fe$_{90-x}$La$_x$Zr$_{10}$ ribbons indicates the dominance of long-range ferromagnetic order that coexists with a short-range magnetic order. Controlling the ratio of these phases may provide an effective way for tuning the magnetocaloric effect and broadening the working temperature range of magnetocaloric materials.

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