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MAGNETIC PROPERTIES AND MAGNETOCALORIC EFFECT OF $Fe_{90-x}Pr_xZr_{10}$ RAPIDLY QUENCHED ALLOYS

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ABSTRACT

In this paper, we present the results of studying magnetic properties and magnetocaloric effect of $Fe_{90-x}Pr_xZr_{10}$ (x = 1, 2 and 3) rapidly quenched alloys. The alloy ribbons with thickness of about 15 µm were prepared by melt-spinning method on a single roller system. X-ray diffraction patterns of the ribbons manifest their almost amorphous structure. Thermomagnetization measurements show that the Curie temperature of the alloys can be controlled to be near room temperature by changing concentration of Pr (x). When the concentration of Pr is increased, saturation magnetization of the alloys increased from 48 emu/g (with x = 1) to 66.8 emu/g (with x = 2). All the ribbons reveal soft magnetic behavior with low coercive force (H_c < 42 Oe). The magnetic entropy change of the alloys, $|\Delta S_m|_{max} > 0.9$ $J.kg^{-1}K^{-1}$ in magnetic field change ΔH = 12 kOe, shows large magnetocaloric effect at phase transition temperature. On the other hand, the working temperature range is quite large (δ_{FWHM} ~ 70 K) revealing an application potential in magnetic refrigeration technology of these alloys.

Keywords: magnetocaloric effect, magnetic frigeration, amorphous alloy, melt-spinning method.

1. INTRODUCTION

The magnetocaloric effect (MCE) is a property of any magnetic material and defined as the heating or cooling of a magnetic material with variation of magnetic field in an adiabatic process. The MCE of material is concerned to research because it can be used for magnetic refrigeration at room temperature. The magnetic refrigeration bases on the principle of magnetic entropy change of the material. Therefore, the searching for materials, which have high magnetic entropy change (ΔS_m) and wide working range around room temperature with low magnetic field change, Giant Magnetocaloric Effect (GMCE), is concentrated. The application of the magnetocaloric materials in refrigerators has advantages of avoiding environmental pollution (unlike refrigerators using compression gases), improving the cooling efficiency (saving energy), reducing noise and fitting to some special cases. The main problems to be addressed to improve the practical applications of magnetocaloric materials are: (i) creating GMCE in low field, because it is very difficult to create large magnetic field in popular household appliances; (ii) performing the magnetic phase transition of the materials with GMCE at room temperature; and (iii) extending the working temperature range (range with GMCE for material to be cooled in a large temperature range). In addition, some other properties of materials such as heat capacity, electrical conductivity, thermal conductivity, durability etc. should be improved for the application of GMCE materials.

Many researchers have focused on magnetocaloric materials with amorphous or nanocrystalline structure [1-4]. One of the most typical materials is amorphous alloys. Among amorphous alloys, Fe-Zr based rapidly quenched alloys are of particular interests as they have giant magnetocaloric effect (GMCE), broad ΔS_m peak around the Curie temperature T_C, low coercivity, high resistivity, no toxicity and low price [5-9]. For example, the Curie temperature of $Fe_{90-x}Y_xZr_{10}$ alloy is increased from 225 K (for *x* = 0) to 395 K (for *x* = 10) with increasing the concentration of Y [5]. Both the saturation magnetization (M_s) and Curie temperature of the Fe-Zr-B alloy is increased with a slight increase of B-concentration [8], while those of the $Fe_{90-x}Mn_xZr_{10}$ system is decreased with increasing Mn concentration [10-12]

Recently, a lot of research groups have concentrated on magnetocaloric materials prepared by using melt-spinning method [13-21]. Advantages of those materials are easily changing Curie temperature, possessing GMCE, low coercive force, large electric resistivity, cheaper price etc. which are necessary for application in practice. In this paper, we present the results of our study on magnetic properties and magnetocaloric effect of $Fe_{90-x}Pr_xZr_{10}$ (x = 1, 2 and 3) alloys prepared by using melt- spinning method.

2. EXPERIMENTAL

The alloys with nominal composition of $Fe_{90-x}Pr_xZr_{10}$ ribbons (x = 1, 2 and 3) were prepared from pure metals (99.99%) of Fe, Pr and Zr on an arc-melting furnace to ensure their homogeneity. After the samples were obtained by arc-melting, we weighed the volume of the samples. The calculations have shown that deficit of volume was less than 0.01%. The ribbons were then fabricated by rapidly quenching on a single copper wheel with a tangential velocity of 40 m/s. All the arc-melting and melt-spinning were performed under Ar atmosphere to avoid oxygenation. Structure of the ribbons was analyzed by X-ray diffraction (XRD) using a Bruker made machine of model: D2 Phaser. Magnetization measurements in the temperature range of 77 – 400 K were performed on a hand made vibrating sample magnetometer (VSM).

The values of magnetic entropy change ΔS_m, which is caused by a variation of applied magnetic field, was calculated via:

$$\Delta S_m = \int_0^H \left(\frac{\partial M}{\partial T} \right) dH . \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. Structure of the $Fe_{90-x}Pr_xZr_{10}$ (x = 1, 2 and 3) rapidly quenched alloy ribbons

Crystalline structure of the $Fe_{90-x}Pr_xZr_{10}$ (x = 1, 2 and 3) rapidly quenched alloy ribbons with thinkness of 15 µm were analyzed by XRD method. Figure 1 shows XRD patterns of the ribbons. We can see that, all the patterns exhibit an XRD peak corresponding to $FeZr_2$ phase at 2θ of 43.2°. However, intensity of this XRD peak is low. That means volume fraction of the crystalline phase in the ribbons is small. Except for the XRD peak of the sample with x = 3, which is a litle bit sharp, the other ones are broad, characterizing for nearly-full amouphous structure in the alloy ribbons. As reported [1-4, 9], the magnetic phase transition temperature (Curie temperature) of the Fe-based alloys could be lowered to room temperature region by making their structure amouphous. On the other hand, coercive force of amorphous structure is also smaller than that of cystalline structure. Those are requirements for application of magnetocaloric materials (magnetic refrigeration) at room temperature.

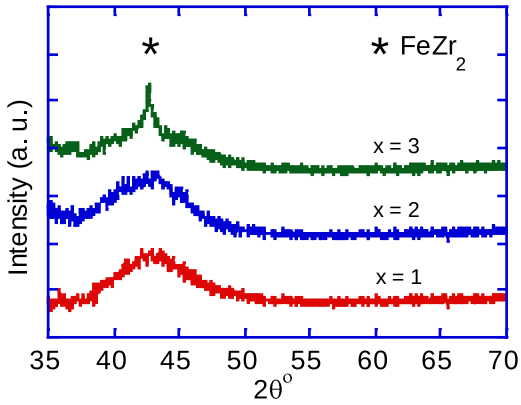

Figure 1. XRD patterns of $Fe_{90-x}Pr_xZr_{10}$ (x = 1, 2 and 3) rapidly quenched alloy ribbons.

3.2. Magnetic properties of $Fe_{90-x}Pr_xZr_{10}$ (x = 1, 2 and 3) rapidly quenched alloy ribbons

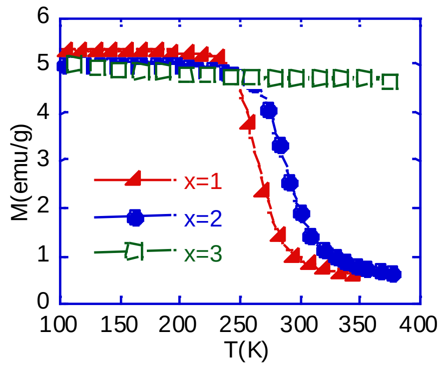

Figure 2. Thermomagnetization curves of $Fe_{90-x}Pr_xZr_{10}$ (x = 1, 2 and 3) alloy ribbons in an applied magnetic field of 100 Oe .

In order to study the effect of concentration Pr on Curie temperature of $Fe_{90-x}Pr_xZr_{10}$ (x = 1, 2 and 3) ribbon alloys. The measurements of magnetization versus temperature are carried out and illustrated in Figure 2. As seen from the graph, ferromagnetic-paramagnetic transition (FM-PM) temperature of the alloy ribbons is depended on Pr concentration. With x = 3, no magnetic phase transition is observed in the thermomagnetization curves M(T). While, the M(T) curves of samples with x = 1 and 2 demonstrate a quite sharp FM-PM phase transition at 282 K and 302 K, respectively. Thus, for the x = 2 sample, the phase transition temperature is in room temperature region.

Figure 3 shows the hysteresis loops of the $Fe_{90-x}Pr_xZr_{10}$ (x = 1 and 2) samples at room temperature. From the hysteresis loops, we can determine the coercivity H_c and saturation magnetization M_s. The samples exhibit soft magnetic behavior with small coercivity. In detail, the H_c values determined for the samples with x = 1 and 2 are 42 and 26 Oe, respectively (see inset of Fig.3). On the other hand, we can see that the saturation magnetization of the alloy ribbons also depends on the Pr concentration. The magnetization saturation of the samples is increased with increasing the Pr concentration. The magnetization saturation M_s of the samples with x = 1 and 2 are 48 and 66.8 emu/g, respectively.

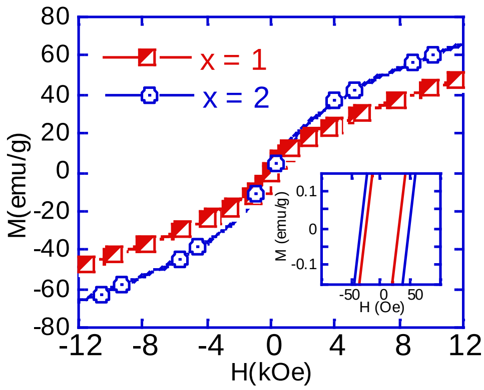

Figure 3. Hysteresis loops of $Fe_{90-x}Pr_xZr_{10}$ (x = 1 and 2) alloy ribbons at room temperature.

3.3. Magnetocaloric effect of $Fe_{90-x}Pr_xZr_{10}$ (x = 1 and 2) rapidly quenched alloy ribbons

In order to study magnetocaloric effect, thermomagnetization curves, M(T), in various magnetic field of the $Fe_{90-x}Pr_xZr_{10}$ (x = 1 and 2) alloy ribbons were measured (Fig. 4). From these M(T) curves, the magnetization versus magnetic field curves, M(H), could be deduced (Fig. 5). Based on M(H) curves, magnetic entropy change (ΔS_m) was calculated using equation (1). Temperature dependence of the magnetic entropy change $\Delta S_m(T)$ in magnetic change ΔH = 4, 6, 8, 10 and 12 kOe are depicted in Figure 6.

The results show that the maximum magnetic entropy change $|\Delta S_m|_{max}$ is achieved near the Curie temperature T_C of the samples. The $|\Delta S_m|_{max}$ determined for the sample with x = 1 is 0.92 $J.kg^{-1}.K^{-1}$ at 282 K (with ΔH = 12 kOe). The working temperature range (δ_{FWHM}), which is defined by full width at half maximum (FWHM) of magnetic entropy change peak, of this ribbon is 69 K. As for the sample with x = 2, $|\Delta S_m|_{max}$ is 0.99 $J.kg^{-1}.K^{-1}$ at 302 K (with ΔH = 12 kOe), and the working temperature range is 70 K (Table 1).

Refrigerant capacity (RC) of the samples, which is defined as product of maximum magnetic entropy change and working temperature range (δ_{FWHM}), is determined (Table 1). We can realize that, the working temperature of these alloy ribbons is about 70 K. and their refrigerant capacity RC is larger than 64 J/kg at near room temperature with Pr concentration of 1 – 2%. The RC value of the $Fe_{90-x}Pr_xZr_{10}$ (x = 1 - 2) alloys is in the same order with that of other amorphous and nanocrystalline alloys such as $Fe_{68.5}Mo_5Si_{13.5}B_9Cu_1Nb_3$, $Fe_{83-x}Co_xZr_6B_{10}Cu_1$, $Fe_{91-x}Mo_8Cu_1B_x$, $Fe_{60-x}Mn_xCo_{18}Nb_6B_{16}$ and $Fe_xCo_yB_zCuSi_3Al_5Ga_2P_{10}$ [22]. These alloys have manifested promising features for magnetic refrigeration technology at room temperature.

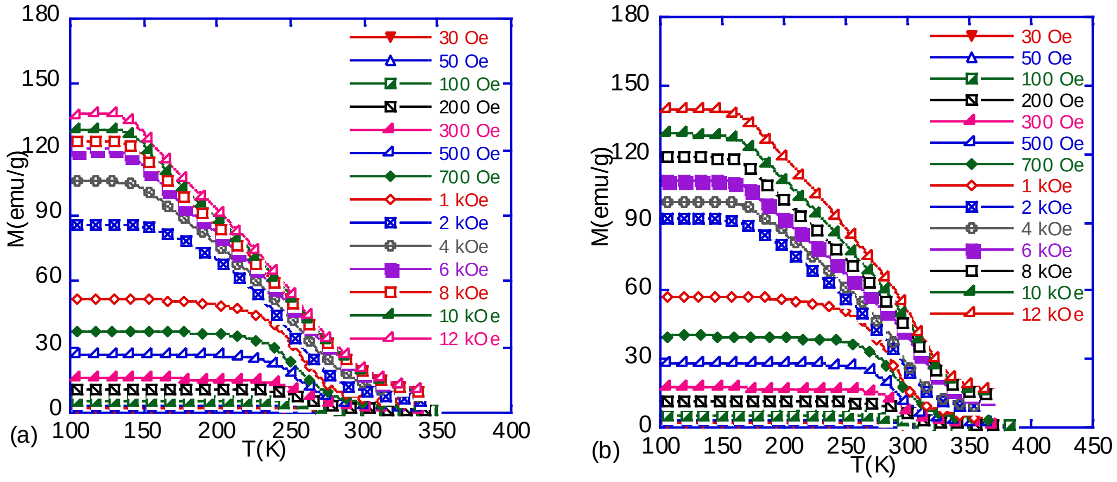

Figure 4. Thermomagnetization curves in various magnetic field of $Fe_{90-x}Pr_xZr_{10}$ alloy ribbons with x = 1 (a) and 2 (b).

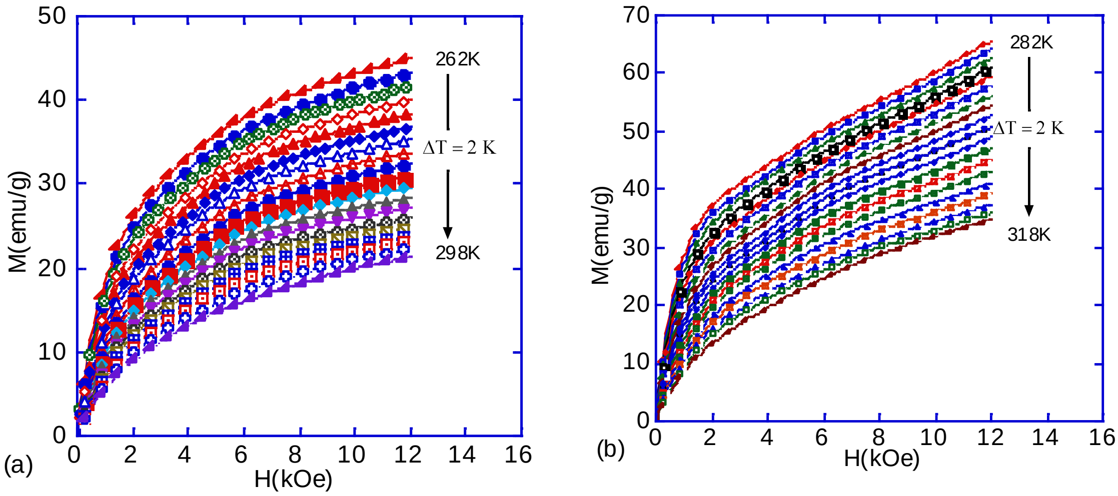

Figure 5. Magnetization versus magnetic field at various temperatures of $Fe_{90-x}Pr_xZr_{10}$ alloy ribbons with x = 1 (a) and 2 (b).

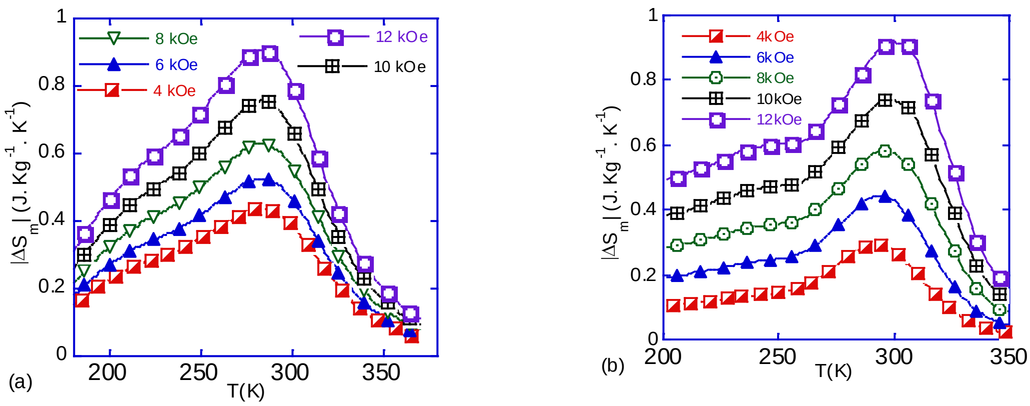

Figure 6. Temperature dependence of magnetic entropy change of $Fe_{90-x}Pr_xZr_{10}$ alloy ribbons with x = 1 (a) and 2 (b) in various magnetic field change.

Table 1. Influence of Pr concentration (x) on saturation magnetization (M_s), Curie temperature (T_C), maximum magnetic entropy change ($|\Delta S_m|_{max}$), working temperature range (δT_{FWHM}) and refrigerant capacity (RC) of the $Fe_{90-x}Pr_xZr_{10}$ (x = 1 and 2) alloy ribbons (ΔH = 12 kOe).

x (%)	M_s (emu/g)	T_C (K)	$\|\Delta S_m\|_{max}$ (J/kg.K)	δ_{FWHM} (K)	RC (J/kg)
1	48	282	0.92	69	64
2	65	302	0.99	70	70

4. CONCLUSION

The influence of Pr concentration on the magnetic properties and magnetocaloric effect of the $Fe_{90-x}Pr_xZr_{10}$ (x = 1, 2 and 3) rapidly quenched alloy ribbons have been investigated. The ribbons manifest their almost amorphous structure and soft magnetic behavior. Magnetic phase transitions of the alloy ribbons can be regulated by changing the Pr concentration. The largest magnetocaloric effect has achieved on the alloy for x = 2 with Curie temperature T_C = 302 K, maximum magnetic entropy change $|\Delta S_m|_{max}$ = 0.99 $J.kg^{-1}.K^{-1}$, working temperature range δ_{FWHM} = 70 K and refrigerant capacity RC = 70 $J.kg^{-1}$ (with magnetic filed change ΔH = 12 kOe). These papameters show application potential of the alloy in magnetic refrigeration at room temperature.

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