

Phase formation and magnetocaloric effect in (Pr,Nd)-Fe alloys prepared by rapidly quenched method

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Abstract. In this work, $\text{Pr}_{2-x}\text{Nd}_x\text{Fe}_{17}$ ($x = 0 - 2$) ribbons with thickness of about $15 \mu\text{m}$ were prepared by melt-spinning method. The alloy ribbons were then annealed at different temperatures ($900 - 1100^\circ\text{C}$) for various time ($0.25 - 2$ h). The formation of the $(\text{Pr,Nd})_2\text{Fe}_{17}$ (2:17) crystalline phase in the alloys strongly depends on the Pr/Nd ratio and annealing conditions. Annealing time for the completed formation of the 2:17 phase in the rapidly quenched ribbons is greatly reduced in comparison with that of bulk alloys. Curie temperature, T_C , of the alloys can be controlled in room temperature region by changing Pr/Nd ratio. Maximum magnetic entropy change ($|\Delta S_m|_{\text{max}}$) and full width at half the maximum peak (FWHM) of the magnetic entropy change of the alloys were respectively found to be larger than $1.5 \text{ J.kg}^{-1}\text{K}^{-1}$ and 40 K in room temperature region with magnetic field change $\Delta H = 12 \text{ kOe}$.

1. Introduction

Magnetocaloric effect (MCE) is defined as the adiabatic temperature change of a magnetic material upon the application of a magnetic field. The MCE of the material is of interest in research by virtue of its potential application in the field of magnetic refrigeration. The magnetic refrigeration bases on the principle of magnetic entropy change of the material. To have large magnetic cooling efficient, the MCE of the material should be large (magnetic entropy change - ΔS_m , adiabatic temperature variation - ΔT_{ad} and refrigerant capacity - RC should be large) with low field change. In later years, some materials have large magnetocaloric effect (so-called giant magnetocaloric effect - GMCE) were discovered, such as: rare earth-containing alloys, As-containing alloys, La-containing alloys, Heusler alloys, Fe and Mn based rapidly quenched alloys, the ferromagnetic perovskite manganites... [1-8]. Among them, alloys containing rare earth elements (RE) such as Gd, Pr, Nd... are considered as very attractive systems [9-15]. In particular, Fe-rich $\text{RE}_2\text{Fe}_{17}$ alloys exhibit ferromagnetic order with high values for the Fe magnetic moment, and the Curie temperature, T_C , around room temperature in the case of Pr and Nd [16, 17]. Moreover, these alloys show large MCE with the maximum magnetic entropy change ($|\Delta S_m|_{\text{max}}$) of $6 \text{ J.kg}^{-1}\text{K}^{-1}$ under 50 kOe magnetic field at room temperature (for RE = Nd, Pr) [18, 19]. Although ΔS_m of $(\text{Nd,Pr})_2\text{Fe}_{17}$ alloys is lower than that of Gd-Si-Ge alloys [20, 21] and La-Fe-Si alloys [22], the $\text{Pr}_2\text{Fe}_{17}$

and $\text{Nd}_2\text{Fe}_{17}$ alloys have GMCE around room temperature, broad ΔS_m peak around the Curie temperature, low cost and no toxicity, making them become potential candidates for magnetic refrigeration [23-25]. However, there are still some problems in fabricating $(\text{Nd,Pr})_2\text{Fe}_{17}$ single phase and regulating magnetic phase transition for these alloys. Thus, in this paper, we present the results of study on dependence of structure, magnetic properties and magnetocaloric effect on heat treatment and Nd/Pr ratio of $\text{Pr}_{2-x}\text{Nd}_x\text{Fe}_{17}$ (with $x = 0, 1$ and 2) alloy ribbons.

2. Experiment

Ingots with nominal compositions of $\text{Pr}_{2-x}\text{Nd}_x\text{Fe}_{17}$ ($x = 0, 1$ and 2) were prepared from pure components of Pr, Nd and Fe on an arc-melting furnace to ensure their homogeneity. The ribbons were then fabricated on a single wheel melt-spinning system. The quenching rate of the ribbons could be changed by changing tangential velocity, v , of the copper wheel. In this study, the ribbons were prepared with $v = 40 \text{ m/s}$. The ribbons samples with the $\sim 3 \text{ mm}$ width and $\sim 15 \mu\text{m}$ thickness were obtained. Subsequently, the ribbons were annealed from 900°C to 1000°C for various times. All of the arc-melting, melt-spinning and annealing process were performed under Ar atmosphere to avoid oxygenation. Structure of the ribbons was analyzed by X-ray diffraction (XRD). Magnetization measurements in the temperature range of $77 - 600 \text{ K}$ were performed on a

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vibrating sample magnetometer (VSM). The values of magnetic entropy change ΔS_m which 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. Result and discussion

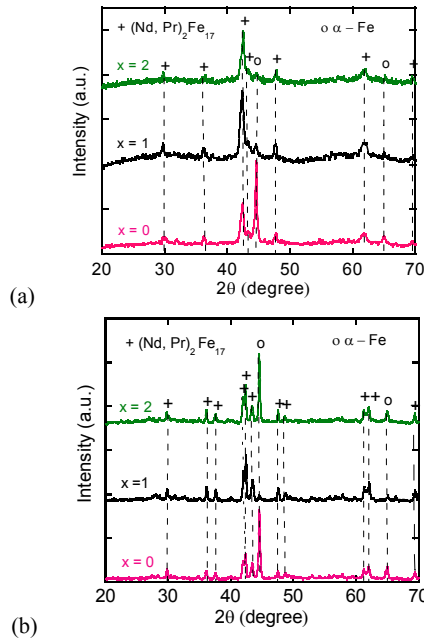


Fig. 1. XRD patterns of $\text{Pr}_{2-x}\text{Nd}_x\text{Fe}_{17}$ ($x = 0, 1$ and 2) ribbons before (a) and after annealing (b).

Figure 1 is the XRD patterns of the $\text{Pr}_{2-x}\text{Nd}_x\text{Fe}_{17}$ ($x = 0, 1$ and 2) alloy ribbons. The results show that the structure of the ribbons clearly depends on Nd-concentration. There are two diffraction peaks of the XRD patterns corresponding to α -Fe phase. Other peaks are of $(\text{Nd, Pr})_2\text{Fe}_{17}$ (2:17) phase. Intensity of diffraction peaks of α -Fe phase is reduced with increasing Nd-concentration. This is important in controlling the formation of undesirable phases of the material. Annealing process has also clearly influenced on the structure of the alloy. After annealing, more diffraction peaks characterizing $(\text{Nd, Pr})_2\text{Fe}_{17}$ phase are formed. Intensity of these peaks is higher and sharper, especially, in the sample with $x = 1$. It should be noted that intensity of diffraction peaks of α -Fe is weakened with Nd/Pr ratio of 1. Thus, the sample is relatively single phase with appropriate Nd-concentration. This will affect the magnetic properties and MCE of the alloy as presented below the alloy.

To determine the coercivity, H_c , and the saturation magnetization, M_s , of the samples, we measured hysteresis loops of $\text{Pr}_{2-x}\text{Nd}_x\text{Fe}_{17}$ ($x = 0, 1$ and 2) ribbons at room temperature (figure 2). The results show that all the samples manifest the soft magnetic behavior. The coercivity of the samples is smaller than 160 Oe. Figure 3 presents the dependence of the saturation magnetization on Nd-concentration. From this figure, we see that the M_s of the samples is quite high, above 50 emu/g. Besides, the saturation magnetization is reduced with increasing Nd-concentration (or reducing Pr-concentration). In detail, the

M_s value of the samples with $x = 0, 1$ and 2 is 105, 101 and 54 emu/g, respectively.

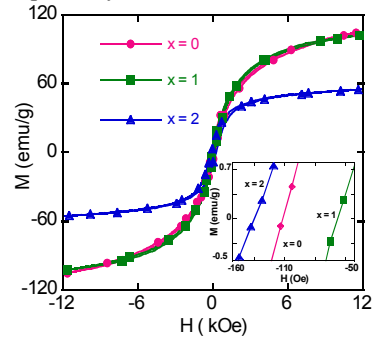


Fig. 2. $M(H)$ loops at room temperature (the inset enlarges the loops at low magnetic field) of $\text{Pr}_{2-x}\text{Nd}_x\text{Fe}_{17}$ ($x = 0, 1$ and 2) ribbons.

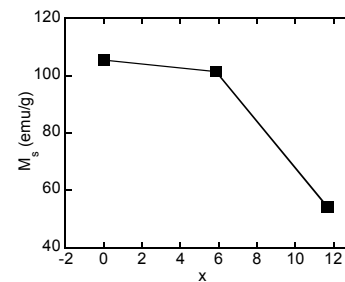


Fig. 3. The dependence of the saturation magnetization on Nd concentration (x) of $\text{Pr}_{2-x}\text{Nd}_x\text{Fe}_{17}$ ($x = 0, 1$ and 2) at room temperature.

In order to investigate influence of annealing process on magnetic properties of the alloy, we measured thermomagnetization curves of the samples before and after annealing. Figure 4 reveals the dependence of reduced magnetization on temperature of the as-quenched ribbons in an applied magnetic field of 100 Oe. In as-quenched state, the samples manifest the multi-phase behavior. These ribbons have magnetic phase transitions in the temperature range of 250 - 450 K. After the first transition, the magnetization of these ribbons does not decrease to zero, but maintains values characterizing the other crystalline phase. The $x = 0$ sample has a magnetic phase transition at about 300 K. The $x = 1$ sample owns the first phase transition at 380 K and the second phase transition at 425 K. Similarly, the $x = 2$ sample has a phase transition at 370 K and the next phase transition at 440 K. With purpose to create single phase for the alloy, heat treatment was carried out. Figure 5 is the reduced thermomagnetization curves in an applied field of 100 Oe of $\text{Pr}_{2-x}\text{Nd}_x\text{Fe}_{17}$ ($x = 0, 1$ and 2) alloy ribbons after annealing at 900°C for 2 h. The results show that the magnetic properties are considerably improved after annealing. Specially, the ferromagnetic-paramagnetic (FM-PM) transition of the $x = 1$ sample is quite sharp. According to XRD patterns of the samples (figure 7), the sample with $x = 0$ is almost single phase with the 2:17 structure after annealing. As for the samples with $x = 0$ and $x = 2$, diffraction peaks of the α -Fe crystalline phase are comparable with those of the 2:17 phase. That is reason for the single magnetic phase feature of the sample with $x = 1$ and the multi-magnetic phase behavior of the

samples with $x = 0$ and $x = 2$. Curie temperature of the α -Fe phase is higher than that of the 2:17 phase leading to the maintenance of magnetization in high temperature region after the transition of the 2:17 magnetic phase near room temperature.

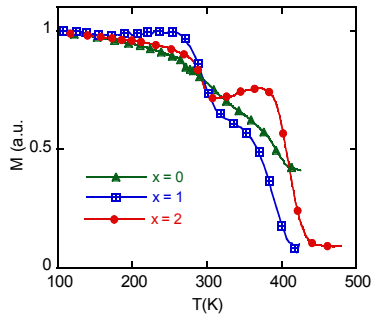


Fig. 4. Reduced thermomagnetization curves in an applied magnetic field of 100 Oe of $\text{Pr}_{2-x}\text{Nd}_x\text{Fe}_{17}$ ($x = 0, 1$ and 2) as-quenched ribbons.

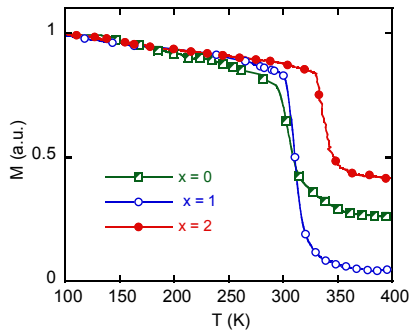


Fig. 5. Reduced thermomagnetization curves in an applied magnetic field of 100 Oe of $\text{Pr}_{2-x}\text{Nd}_x\text{Fe}_{17}$ ($x = 0, 1$ and 2) ribbons after annealing at 900°C for 2 h.

Figure 6 displays the reduced thermomagnetization curves in an applied magnetic field of 100 Oe of $\text{Pr}_{2-x}\text{Nd}_x\text{Fe}_{17}$ ($x = 0, 1$ and 2) annealed at different temperatures (900 - 1100°C) for various time (0.25 - 2 h). From obtained results, we see that the $x = 1$ sample annealed at 950°C for 2h has the sharp phase transition. The Curie temperature (T_C) of this sample is 310 K. In particular, its magnetization is almost zero after the first magnetic transition. This shows that this sample is almost single magnetic phase transition.

From figure 6b, it is apparent that the $x = 1$ sample annealed at 950°C for 2h has a quite strong magnetic phase transition, revealing the possibility of a large MCE. On the other hand, the T_C of this sample is around room temperature. Therefore, with the goal of finding magnetocaloric materials that possess magnetic transition temperature close to room temperature, we chose NdPrFe_{17} ribbon annealed at 950°C for 2 h to investigate its MCE. We calculated magnetic entropy change (ΔS_m) basing on thermomagnetization curves of this ribbon at various magnetic fields ranging from 0.01 to 12 kOe (figure 7). From the thermomagnetization curves for the samples in various magnetic fields, we can deduce the magnetization versus magnetic field, $M(H)$,

at various temperatures (figure 8). According to previous results [26, 27], to check this derivation procedure, we compared data deduced from thermomagnetization curve with data of virgin magnetization ones and we found that the data obtained from the two different ways are coincided. Then, the magnetic entropy change, ΔS_m , is determined from $M(H)$ data by using equation (1).

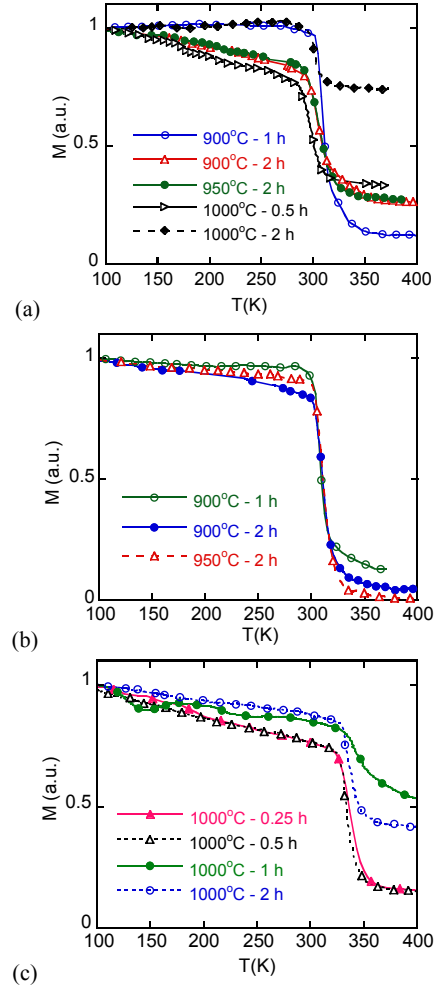


Fig. 6. Reduced thermomagnetization curves of $\text{Pr}_2\text{Fe}_{17}$ (a), NdPrFe_{17} (b) and $\text{Nd}_2\text{Fe}_{17}$ (c) ribbons after annealing at different temperatures for various time.

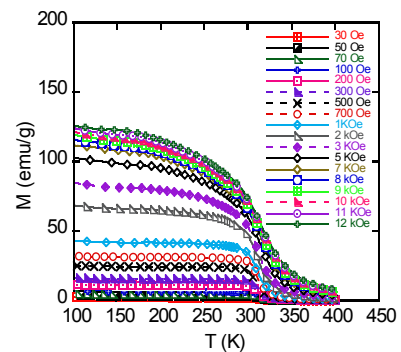


Fig. 7. Thermomagnetization curves in various magnetic field of NdPrFe_{17} ribbon.

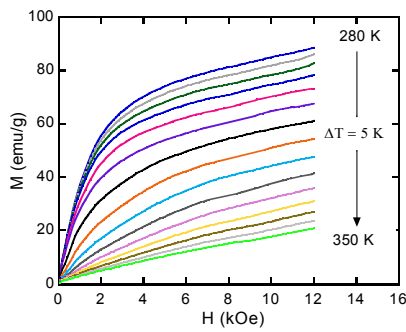


Fig. 8. Magnetization versus magnetic field at various temperatures deduced from thermomagnetization curves of PrNdFe₁₇ ribbon.

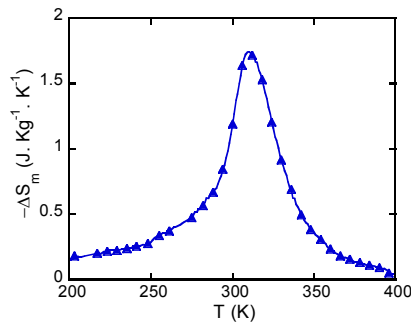


Fig. 9. $-\Delta S_m(T)$ curves (with $\Delta H = 12$ kOe) of PrNdFe₁₇ ribbon.

Figure 9 is the temperature dependence of $-\Delta S_m$ of NdPrFe₁₇ ribbon after annealing at 950°C for 2h in a magnetic field change of 0 – 12 kOe. The maximum magnetic entropy change, $|\Delta S_{m|_{max}}$, is 1.72 J.kg⁻¹.K⁻¹ at 310 K. The refrigerant capacity (RC) of the samples, which is defined as product of maximum entropy change ($|\Delta S_{m|_{max}}$) and full width at half maximum (δT_{FWHM}) of entropy change peak, was also calculated. The δT_{FWHM} value is also mentioned as the working temperature range of magnetic refrigerant. The working temperature range of the alloys is about 40 K. The refrigerant capacity, which is determined for NdPrFe₁₇ ribbon, is 69 J/kg. This value is comparable to higher than that of Pr₂Fe₁₇ and Nd₂Fe₁₇ alloys [11, 18, 19].

4. Conclusion

The influence of Pr/Nd ratio and annealing process on structure, magnetic properties and magnetocaloric effect of (Pr,Nd)-Fe alloy ribbons has been investigated. The formation of (Pr,Nd)₂Fe₁₇ crystalline phase strongly depends on Pr/Nd ratio and annealing conditions. (Pr,Nd)₂Fe₁₇ phase is dominantly formed in the sample after annealing. Magnetic properties of the alloy changed markedly with annealing temperature and time. The sample with Pr/Nd ratio of 1 is relatively single phase after annealing. The maximum magnetic entropy change ($|\Delta S_{m|_{max}}$) of NdPrFe₁₇ ribbon was determined to be 1.72 J.kg⁻¹.K⁻¹ at 310 K with magnetic field change $\Delta H = 12$ kOe.

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