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Structure, thermal stability and magnetostrictive properties of $PrFe_x$ ($1.5 \le x \le 3.0$) alloys

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Abstract

Polycrystalline alloys $PrFe_x$ ($x = 1.5$, $x = 1.8$, $x = 1.9$, $x = 2.0$, $x = 3.0$) have been prepared by arc-melting and subsequent high-pressure synthesis method. Their structure, thermal stability, easy magnetization direction and magnetostriction are investigated. Almost single Laves phase ($MgCu_2$-type) is found in sample with $x = 1.9$. Samples with $x = 2.0$, $x = 3.0$ consist of $PrFe_{1.9}$ phase with $MgCu_2$-type cubic structure and α-Fe phase. The Curie temperature (238 °C) and the decomposed temperature (408 °C) of $PrFe_{1.9}$ alloys are derived from M–T curves. The easy magnetization direction of $PrFe_{1.9}$ Laves phase lies along [1 1 1] axis at room temperature which is verified by Mössbauer spectrum. Furthermore, $PrFe_{1.9}$ alloy shows a large magnetostriction $\lambda_{||} - \lambda_{\perp} = 1081 \times 10^{-6}$ at a magnetic field of 13 kOe.

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Keywords: Rare earth compounds; High-pressure; Magnetostriction

1. Introduction

An excellent magnetostritive material should have low magnetocrystalline anisotropy and large magnetostriction at low magnetic fields. Although the intermetallic compounds $TbFe_2$ and $DyFe_2$ have large magnetostriction at room temperature, they are unsuitable as practical materials in magnetostrictive devices and for applications because these two compounds have high anisotropies. According to the single-ion model [1], $PrFe_2$ should have a larger magnetostriction and much lower magnetocrystalline anisotropy than $TbFe_2$ and $DyFe_2$. Furthermore, a magnetostrictive alloy with high-Pr content should have a good practical prospect because Pr is much cheaper than Tb or Dy. Thus, much effort has been paid to enhance the Pr content in magnetostrictive materials under normal atmosphere in the past years [2–6]. As an example, a single phase cannot be obtained in $(Pr,Tb)Fe_2$ system when the Pr content is over 25 at.% for rare earths [4]. Up to now, an effective method to prepare high-Pr content magnetostrictive materials is still desired. So, it is interesting to synthesize $PrFe_2$ with single cubic Laves phase and systemically study its structure and magnetic properties. It has been reported that $PrFe_2$ alloy which contained an amount of second phase but showed a remarkable magnetostriction constant $\lambda_{||} - \lambda_{\perp} = 1030 \times 10^{-6}$ at room temperature at a magnetic field of 20 kOe [7]. It is possible that the magnetostriction may be improved if $PrFe_2$ single phase can be obtained.

In this paper, polycrystalline alloys $PrFe_x$ ($x = 1.5$, $x = 1.8$, $x = 1.9$, $x = 2.0$, $x = 3.0$) were prepared by arc-melting and subsequent high-pressure synthesis method. Their structures, thermal stability, easy magnetic direction and magnetostriction have been investigated.

2. Experimental details

Ingots with stoichiometric composition of $PrFe_x$ ($x = 1.5$, $x = 1.8$, $x = 1.9$, $x = 2.0$, $x = 3.0$) were prepared by melting the constituent metals in a magneto-controlled arc furnace under a high-purity argon atmosphere. The purities of Pr and Fe are 99.9%, 99.8%, respectively. The as-cast ingots (about 10 mm in diameter and 2 mm in thickness) were wrapped in tantalum foils and pressed into a graphite pipe heater with the shape of cylinder. The heater was then pressed to 6 GPa by a Hall-type hexahedral anvil press and heated to different temperatures and for various time. Conventional X-ray diffraction (XRD) analysis was carried out using Cu Kα radiation with a Rigaku D/Max-gA diffractrometer. The actual composition of the samples was analyzed by the inductively coupled plasma (ICP) spectrometry. The Curie temperature and the decomposed temperature

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of the sample were derived from M–T curves measured by a vibrating samples magnetometer at field of 2 kOe. The ^{57}Fe Mössbauer spectrum was collected on a constant accelerated spectrometer with the transmission geometry at room temperature. The source is ^{57}Co in Pd matrix with an activity about 25 mCi. The spectrum was calibrated with a standard α-Fe foil and analyzed by Lorentzian lines in 256 channels using software Klencsar and MossWinn [8]. The linear magnetostriction was measured using standard strain-gauge technique in directions parallel ($\lambda_{||}$) or perpendicular ($\lambda_{\perp}$) to applied magnetic fields up to 13 kOe at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns for $PrFe_x$ with the different Fe content. The samples were synthesized at 900 °C and 6 GPa for 30 min. It is found that samples with $x = 1.5$ and $x = 1.8$ comprise $MgCu_2$-type Laves cubic phase and a little amount of hcp-Pr phase. The sample exhibits almost a single Laves phase when x is up to 1.9. The ICP spectrometry analysis shows the actual atom ratio of Fe to Pr is about 1:1.9, which is in accordance with the starting stoichiometric composition. When x increases to 2.0 and 3.0, the samples consist of $PrFe_{1.9}$ with $MgCu_2$-type cubic phase and α-Fe phase. The lattice parameters of cubic laves phase derived from XRD patterns of the samples with different Fe contents are 7.532 Å ($x = 1.5$), 7.488 Å ($x = 1.8$), 7.479 Å ($x = 1.9$), 7.468 Å ($x = 2.0$) and 7.453 Å ($x = 3.0$). The lattice parameters become smaller as increasing Fe content in the alloys, therefore we can deduce that Pr–Fe cubic Laves phase can exist within a narrow composition range near $x = 1.9$. As we know, it is difficult to obtain α-Fe phase coexisting with $MgCu_2$-type cubic phase in the RE-Fe (such as, Tb-Fe, Dy-Fe or Sm-Fe) alloys because $REFe_3$ and RE_2Fe_{17} phases would appear if Fe content exceeds 67 at.% in alloys. And almost all the RE-Fe compounds, such as $REFe_2$, $REFe_3$ and RE_2F_{17} phases are mechanically brittle. Therefore, $PrFe_x$ alloys with $x > 1.9$, such as $x = 3.0$, that contain a little amount of α-Fe phase, not only can keep a large magnetostriction (as shown in Fig. 6) but also can be much easier machinable in comparison with brittle RE-Fe compounds with single phase.

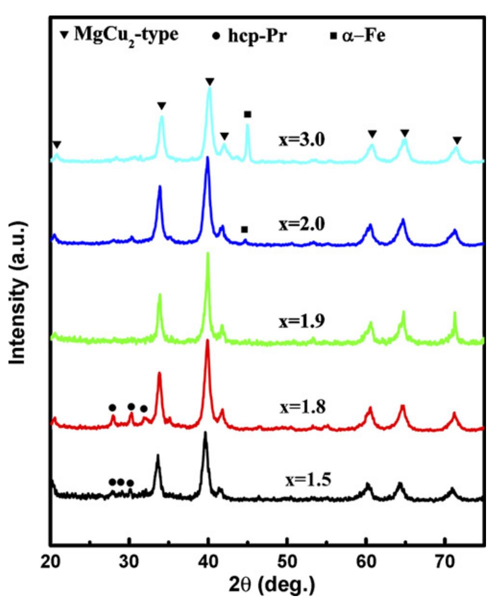

Fig. 1. XRD patterns of $PrFe_x$ with different x. All the alloys were synthesized at 6 GPa and 900 °C for 30 min.

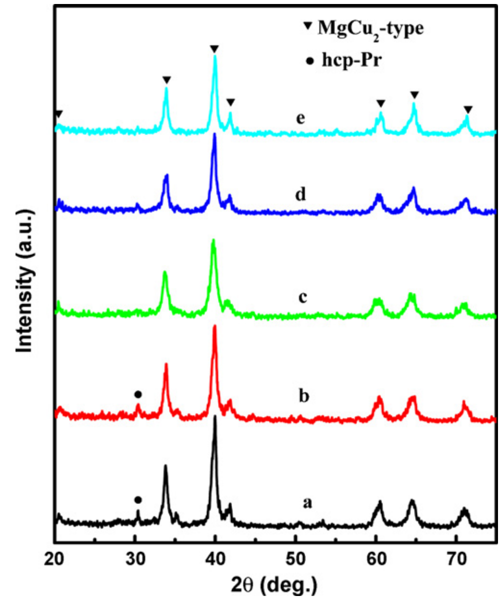

Fig. 2. XRD patterns of $PrFe_{1.9}$ alloys which were synthesized at 6 GPa and different temperature for different time. (a) Synthesized at 600 °C for 30 min. (b), (c), (d) and (e) are corresponding to the samples synthesized at 900 °C for 5 min, 15 min, 60 min and 90 min.

Fig. 2 shows XRD patterns of $PrFe_{1.9}$ which were synthesized at 6 GPa at different temperature for different time. As is shown in Fig. 2, Laves phase can be obtained by annealing at 900 °C for the time longer than 5 min and it is easier to obtain a single Laves phase when annealed for the longer time. The sample synthesized at 600 °C for 30 min presents the Laves phase and a little amount of hcp-Pr phase. From results above, we can see that a single cubic Laves phase for Pr–Fe alloy can be synthesized by the high-pressure synthesis method. It is thought that the atomic size plays an important role in the synthesis of the Laves phase compounds. For the RE-Fe_2, the ideal radius ratio of RE and Fe for the formation of a Laves phase is 1.225 [9]. Since the radius ratio of Pr and Fe is 1.333, which is much larger than 1.225, it is difficult to synthesis Pr–Fe cubic Laves phases in an ambient atmosphere and it can only be synthesized by a high-pressure method.

The temperature dependences of magnetizations of the alloys were measured in a low magnetic field of 2 kOe to determine the Curie temperature and the stability of $PrFe_{1.9}$ alloys. As an example, the thermal magnetic curve of $PrFe_{1.9}$ which was synthesized at 900 °C for 30 min is shown in Fig. 3. The rate of heating and cooling is 10 °C/min. As the temperature increases from room temperature, the curve is smooth and there is no trace of Pr_2Fe_{17} phase whose Curie temperature is near room temperature. With the temperature increasing the magnetic moment of the sample decreases sharply near 238 °C at which is the Curie temperature of $PrFe_{1.9}$ alloy. The following decomposed process can be divided into two different periods: with the temperature increasing from 408 °C to 512 °C, the sample is decomposing into Pr and α-Fe which leads to the increase of the magnetic

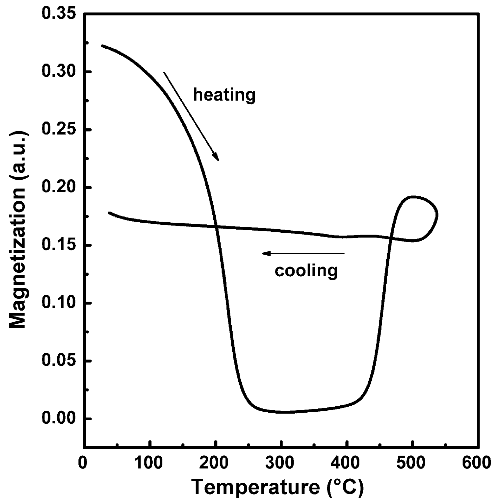

Fig. 3. Magnetization of $PrFe_{1.9}$ synthesized at 900 °C for 30 min as a function of temperature in the magnetic field 2 kOe.

moment; with further increasing temperature from 512 °C, the magnetic moment decreases because Pr and Fe is reacting with each other and forming Pr_2Fe_{17}. These results are also illustrated by XRD pattern in Fig. 4. The samples synthesized at 900 °C for 30 min were wrapped in tantalum foils and vacuum annealed in sealed quartz capsules at 450 °C and at 550 °C for 2 h. It can be seen that the sample annealed at 450 °C mainly contains hcp-Pr and α-Fe phase and the one annealed at 550 °C mainly contains hcp-Pr and Pr_2Fe_{17} phase.

^{57}Fe Mössbauer spectrum for the $PrFe_{1.9}$ alloy was recorded at room temperature, as shown in Fig. 5. The profile of the measured points is similar to that of cubic Laves phase compounds of $Ho_{0.6}Tb_{0.4}Fe_2$ (above 150 K), which indicates that the easy magnetization direction may parallel to the [1 1 1] direction [10]. The assumption was examined by the resolving the gross spectrum into two sextets assigned to the two inequivalent types of iron sites due to different orientation of the spin direction with respect to the principle axis (V_{zz}) of electric field gradient (EFG). The

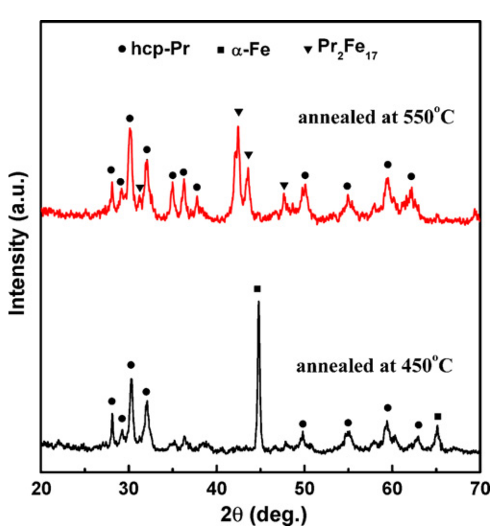

Fig. 4. XRD patterns of $PrFe_{1.9}$ alloys which were annealed at 450 °C and 550 °C for 2 h.

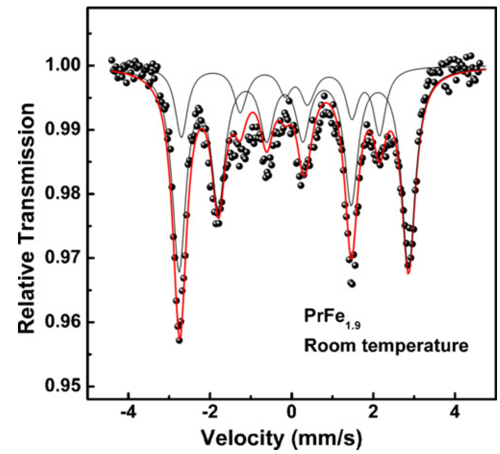

Fig. 5. Mössbauer spectrum at room temperature for $PrFe_{1.9}$ alloy which was synthesized at 6 GPa and 900 °C for 30 min.

relative areas were confined by 1:3 and a static Hamilton model with hyperfine interaction and quadrupole splitting interaction was used to obtain the possible relative orientation of hyperfine field with V_{zz}. As $PrFe_{1.9}$ has a cubic Laves phase structure, the Fe atoms occupy only one crystallographic site with space group of $\bar{3}m$, and the asymmetry factor, $\eta = (V_{xx} - V_{yy})/V_{zz}$, was confined as zero, where V_{xx}, V_{yy}, and V_{zz} denote the diagonal components of the EFG tensor. The relative angles of hyperfine fields to V_{zz} (β) were calculated as 0° and 74.9° for the two inequivalent sites respectively, which are close to the ideal values of 0° and 70.5° and is in good agreement with the expected easy magnetization direction of [1 1 1]. The corresponding parameters are listed in Table 1.

The room-temperature magnetostriction of the $PrFe_x$ alloys with different Fe content is shown in Fig. 6. All the samples were synthesized at 6 GPa and 900 °C for 30 min. It can be seen that $PrFe_{1.9}$ alloy shows a large magnetostriction value ($\lambda_{||} - \lambda_{\perp} = 1081 \times 10^{-6}$) at 13 kOe. With decreasing Fe content, the magnetostrictions of samples ($x = 1.5$ and $x = 1.8$) decrease owing to the second phase Pr in the samples. With increasing Fe content, the magnetostriction of the sample is not dropped dramatically. The sample shows a large magnetostriction $\lambda_{||} - \lambda_{\perp} = 900 \times 10^{-6}$ at 13 kOe even the Fe content increases to $x = 3.0$. As we know, the high-pressure technique is also an effect method to fabricate nanocrystalline and nanocomposite system [11], it is hopeful that $PrFe_{1.9}$/α-Fe nanocrystalline can be prepared by combining melt-spinnng and high-pressure technique and the magnetostriction of the nanocrystalline Pr–Fe alloys at low magnetic fields is hopeful

Table 1
Mössbauer parameters of $PrFe_{1.9}$

	Parameters					
	CS	V_{zz}	H_{hf}	β (°)	Line width	Ratio (%)
Site 1	−0.06(0)	1.3(2)	17.4(3)	0	0.40(4)	75
Site 2	−0.08(5)	7.5(4)	13.7(6)	74.9	0.36(6)	25

The CS, linewidth are given in mm/s, H_{hf} is given in T, V_{zz} is given in 10^{21} V/m^2, CS is relative the spectrum center of α-Fe.

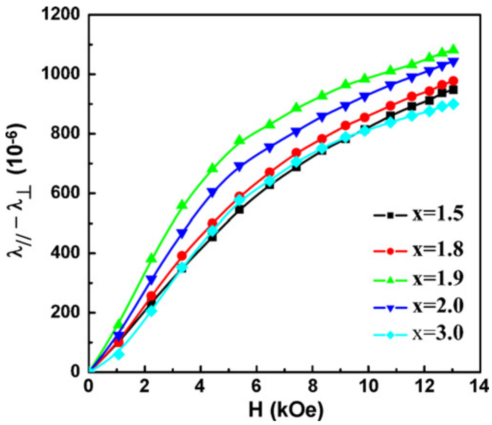

Fig. 6. Magnetic field dependence of $\lambda_{||} - \lambda_{\perp}$ at room temperature for $PrFe_x$ ($x = 1.5$, $x = 1.8$, $x = 1.9$, $x = 2.0$, $x = 3.0$) alloys.

to be improved. The investigation on the magnetostriction of $PrFe_{1.9}$/α-Fe nanocrystalline is now in progress.

4. Conclusion

In conclusion, $PrFe_{1.9}$ alloys with Laves single phase and $PrFe_x$ ($x \geq 1.9$) alloys with Laves phase coexisting with α-Fe phase have been synthesized by arc-melting and subsequent high-pressure synthesis method. $PrFe_{1.9}$ with single Laves phase has a Curie temperature of 238 °C and a low decomposed temperature of 408 °C. Since easy magnetization direction of $PrFe_{1.9}$ Laves phase is [1 1 1] at room temperature, $PrFe_{1.9}$ shows a large magnetostriction $\lambda_{||} - \lambda_{\perp} = 1081 \times 10^{-6}$ at 13 kOe at room temperature. Containing cheaper rare-earth Pr, $PrFe_{1.9}$ alloy should be a potential candidate for use as a magnetostrictive material.

Acknowledgements

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