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The structure, phase transformation, and magnetic properties of Pr–Fe–C alloys made by mechanical alloying

Y C Sui†, Z D Zhang, W Liu, Q F Xiao, X G Zhao, T Zhao and Y C Chuang
Institute of Metal Research, Academia Sinica, Shenyang 110015, People's Republic of China

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Abstract. The structure, phase transformation, and magnetic properties of mechanically alloyed (MA) [$Pr_{15}Fe_{85-m}C_m$] ($m = 9, 10, 11$) samples have been studied systematically. $Pr_2Fe_{14}C$ can be formed within certain composition ($m \geqslant 10$) and temperature (from 750 °C to 900 °C) ranges. Isothermal annealing of [$Pr_{15}Fe_{74}C_{11}$] at 750 °C for different lengths of time reveals that the formation of $Pr_2Fe_{14}C$ is a nucleation and growth process; excessive prolongation of the annealing time causes the decomposition of $Pr_2Fe_{14}C$ and $Pr_2Fe_{17}C_x$ into carbide and α-Fe. Hexagonal $Pr_2Fe_2C_3$ ($a = 8.66$ Å, $c = 10.40$ Å) and the fcc Pr-rich phase ($a = 5.2$ Å) are formed in the alloys. The best magnetic properties are achieved for [$Pr_{15}Fe_{75}C_{10}$] alloy annealed at 900 °C for 35 minutes, which contains $Pr_2Fe_{14}C$, $Pr_2Fe_{17}C_x$, α-Fe, $Pr_2Fe_2C_3$, a Pr-rich phase, and Pr_2C_3.

1. Introduction

Ternary borides having the tetragonal $Nd_2Fe_{14}B$ structure have been studied in great detail because of their outstanding magnetic properties [1]. References [2–5] on the carbides that are isostructural with $Nd_2Fe_{14}B$ showed that the carbides have some advantages over the borides. Higher magnetocrystalline anisotropies at room temperature were found for $R_2Fe_{14}C$ [6]. Higher coercivities exist in castings of R–Fe–C alloys, without one having to resort to complicated powder metallurgical processing [5].

One problem with understanding the carbides stems from the difficulty of preparing single-phase materials, especially for the light rare-earth system [7]. Buschow made $Nd_2Fe_{14}C$ by annealing the ingot in a temperature window between 830 °C and 890 °C for 21 days [8]. The production of $Pr_2Fe_{14}C$ by Gueramian *et al* involved a process of annealing at 1100 K for 1000 h, followed by a cooling to 700 K in 100 K steps over a period of several months [9]. Both boron and copper addition can accelerate the formation of $R_2Fe_{14}C$ (R = Nd, Pr) [4, 10]. Manganese substitution was found to increase the temperature limit for the formation of $R_2(Fe, M)_{14}C$ (R = Ce, Pr, Nd) [11–13]. Some of the light rare-earth carbides with $Nd_2Fe_{14}B$ structure—for example, $Y_2Fe_{14}C$ and $Ce_2Fe_{14}C$—can be obtained by annealing the melt-spun precursors without substitution [14]. Up to now, the magnetic properties for the $Pr_2Fe_{14}C$-based alloys have been little reported. On the other hand, mechanical alloying (MA) has been proved to be a powerful way of synthesizing magnetic compounds such as $Nd_2Fe_{14}B$ [15], $Nd_2Fe_{14}C$ [16], $Dy_2Fe_{14}C$ [17], $SmFe_7N$ [18], and $SmCo_5$ [19]. In this paper we show that $Pr_2Fe_{14}C$ can also be prepared

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† Author to whom any correspondence should be addressed; e-mail address: wliu@int.syb.ac.cn.

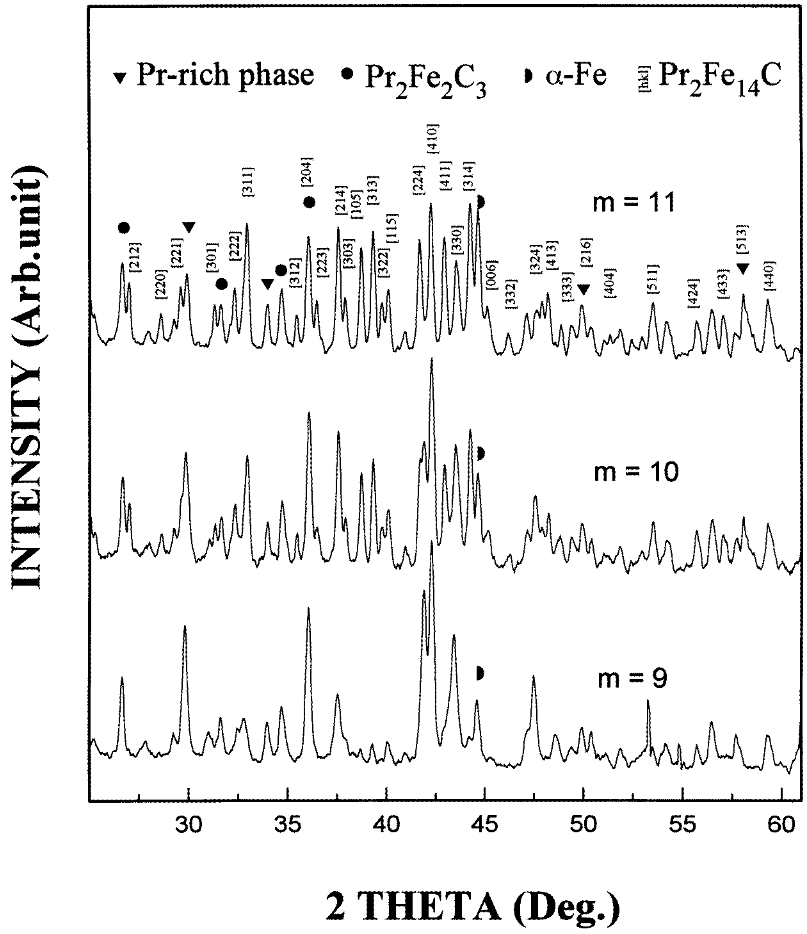

Figure 1. X-ray diffraction patterns of mechanically alloyed $[Pr_{15}Fe_{85-m}C_m]$ alloys annealed at 900 °C for 35 min ($m = 9, 10, 11$).

by MA and subsequent annealing. The relationship between the magnetic properties, phase transformation, composition, annealing time, and temperature will be studied systematically.

2. Experimental details

For the experiments, 99.5%-pure Pr and Fe powders and 99.7%-pure carbon powder were mixed to the desired composition, and sealed under argon in a cylindrical steel container. The milling was performed in a high-energy ball mill designed in our laboratory, for 5 h. After annealing in a vacuum furnace connected to a closed glove box, the Pr–Fe–C powders were embedded in epoxy resin to form bonded samples. The magnetic hysteresis curves were measured using a pulsed-field magnetometer in fields up to 8 T. The magnetization was related to the amounts of the magnetic powders, neglecting the dilution effect of the resin, and assuming that the density of the Pr–Fe–C alloys was 7.6 g cm^{-3}. The powders were routinely analysed by x-ray diffraction and AC initial susceptibility measurement for identification of the structures and Curie temperatures of the phases in the alloys. A

χ_{AC} versus temperature measurement was also performed to verify whether there is any $Pr_2Fe_{17}C_x$ or $Pr_2Fe_{14}C$ present.

3. Results

3.1. MA [$Pr_{15}Fe_{85-m}C_m$] annealed at 900 °C for 35 minutes

Figure 1 shows the x-ray diffraction patterns of mechanically alloyed [$Pr_{15}Fe_{85-m}C_m$] alloys annealed at 900 °C for 35 minutes ($m = 9$, 10, 11). When $m = 9$, the main phase of the alloy is $Pr_2Fe_{17}C_x$. Its Curie temperature is 108 °C, which is higher than that of Pr_2Fe_{17} ($T_c = 10$ °C), suggesting that a certain amount of carbon is dissolved in the interstitial sites of this rhombohedral compound. When $m = 10$, the main phases are $Pr_2Fe_{14}C$ and $Pr_2Fe_{17}C_x$, with Curie temperatures of 242 °C and 70 °C respectively. In this case, one may expect that less carbon is dissolved into the lattice of Pr_2Fe_{17} due to the formation of $Pr_2Fe_{14}C$, which depletes the carbon in the remaining $Pr_2Fe_{17}C_x$. When $m = 11$, $Pr_2Fe_{14}C$ ($T_c = 242$ °C) and α-Fe become the main phases; no $Pr_2Fe_{17}C_x$ can be observed by means of either χ_{AC} versus temperature measurements or x-ray diffraction analysis. The amount of $Pr_2Fe_{14}C$ increases with the increment of the carbon content, and that of $Pr_2Fe_{17}C_x$ decreases correspondingly. This indicates that the carbon content is a crucial factor in the formation of $Pr_2Fe_{14}C$. A hexagonal phase, $Nd_2Fe_2C_3$, with lattice parameters $a = 8.61$ Å and $c = 10.26$ Å, was reported for melt-spun carbon-rich Nd–Fe–C samples [20]. A similar hexagonal phase with lattice parameters $a = 8.66$ Å and $c = 10.40$ Å is observed by x-ray diffraction analysis, Thus the composition of this phase is assumed to be $Pr_2Fe_2C_3$. In mechanically alloyed Nd–Fe–C and Dy–Fe–C systems, fcc-structured Nd-rich and Dy-rich phases with lattice parameters of 5.15 Å and 4.98 Å respectively are formed [16, 17]. A similar fcc phase with a lattice parameter of 5.2 Å is formed in the Pr–Fe–C alloys, and is assumed to be a Pr-rich phase. All of the Pr–Fe–C samples contain certain amounts of $Pr_2Fe_2C_3$, α-Fe, a Pr-rich phase, and Pr_2C_3, the amount of α-Fe increasing with the carbon content. The increasing of the carbon content has the effects of facilitating the formation of $Pr_2Fe_{14}C$ and increasing the amount of α-Fe. The former effect would be a benefit, whereas the latter would be a drawback as regards achieving good magnetic properties.

3.2. MA [$Pr_{15}Fe_{74}C_{11}$] annealed at different temperatures

The experimental results reveal that $Pr_2Fe_{14}C$ can be formed within a temperature range of 800 °C to 900 °C upon annealing for 35 minutes. Only the $Pr_2Fe_{17}C_x$-based alloy is obtained if the MA [$Pr_{15}Fe_{74}C_{11}$] powders are annealed at a temperature beyond this range for 35 minutes. Figure 2 shows χ_{AC} versus temperature for MA [$Pr_{15}Fe_{74}C_{11}$] alloy annealed at 750 °C, 900 °C, and 1000 °C for 35 minutes. The temperature limit for the formation of $Pr_2Fe_{14}C$ is 900 °C, which is much higher than that reported for ingot annealing or melt-spun-precursor annealing. This means that mechanical alloying is powerful in the synthesis of magnetic compounds, such as $Pr_2Fe_{14}C$.

3.3. Isothermal annealing of MA [$Pr_{15}Fe_{74}C_{11}$] at 750 °C

Figure 3 and figure 4, respectively, demonstrate x-ray diffraction patterns and χ_{AC} versus temperature curves for [$Pr_{15}Fe_{74}C_{11}$] alloy annealed at 750 °C for 30 min, 6 h, and 12 h. It is shown clearly that the formation of $Pr_2Fe_{14}C$ is a nucleation and growth process. $Pr_2Fe_{17}C_x$ is formed quickly at the initial stage of the isothermal annealing. When the annealing

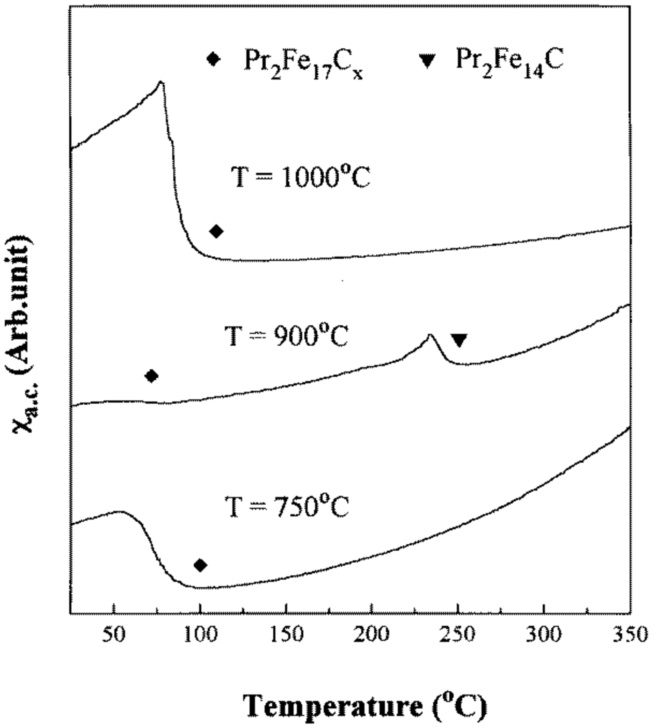

Figure 2. χ_{AC} versus temperature for mechanically alloyed [$Pr_{15}Fe_{74}C_{11}$] alloys annealed at 750 °C, 900 °C, and 1000 °C for 35 min.

time (t_a) is shorter than 35 min, no $Pr_2Fe_{14}C$ is observed by means of thermomagnetic measurement and x-ray diffraction analysis. When $t_a > 35$ min, a trace of $Pr_2Fe_{14}C$ could be detected. When $t_a = 6$ h, a large amount of $Pr_2Fe_{17}C_x$ was transformed into $Pr_2Fe_{14}C$. When $t_a < 6$ h, the amounts of $Pr_2Fe_{14}C$ and α-Fe increase simultaneously with the extension of the annealing time. When $t_a > 6$ h, both the amount of $Pr_2Fe_{14}C$ and that of $Pr_2Fe_{17}C_x$ decrease, and that of α-Fe increases indefinitely with further extension of annealing time. Those results indicate that both $Pr_2Fe_{14}C$ and $Pr_2Fe_{17}C_x$ are metastable compounds during isothermal annealing. They decompose into α-Fe, $Pr_2Fe_2C_3$, and a Pr-rich phase with excessive extension of the annealing time. The solid-state reactions taking place during the isothermal annealing are rather complicated, involving (a) MA Pr–Fe–C powders transforming into $Pr_2Fe_{17}C_x$, (b) $Pr_2Fe_{17}C_x$ reacting with carbide to form $Pr_2Fe_{14}C$, and (c) $Pr_2Fe_{17}C_x$ and $Pr_2Fe_{14}C$ decomposing into α-Fe, $Pr_2Fe_2C_3$, and a Pr-rich phase. The formation of $Pr_2Fe_{14}C$ is confined within a time range during isothermal annealing which is determined partly by the thermodynamics of the system and partly by kinetic factors.

3.4. Magnetic properties

The magnetic properties are sensitive to the microstructural parameters of the alloy, such as the distribution of phases, the chemical composition and crystal structure of the phases, and the grain size distribution. $Pr_2Fe_{14}C$ is the only hard magnetic phase in the multiple-phase alloys; its formation depends sensitively on the annealing temperature and the carbon content, so the magnetic properties are correlated directly with the annealing temperature

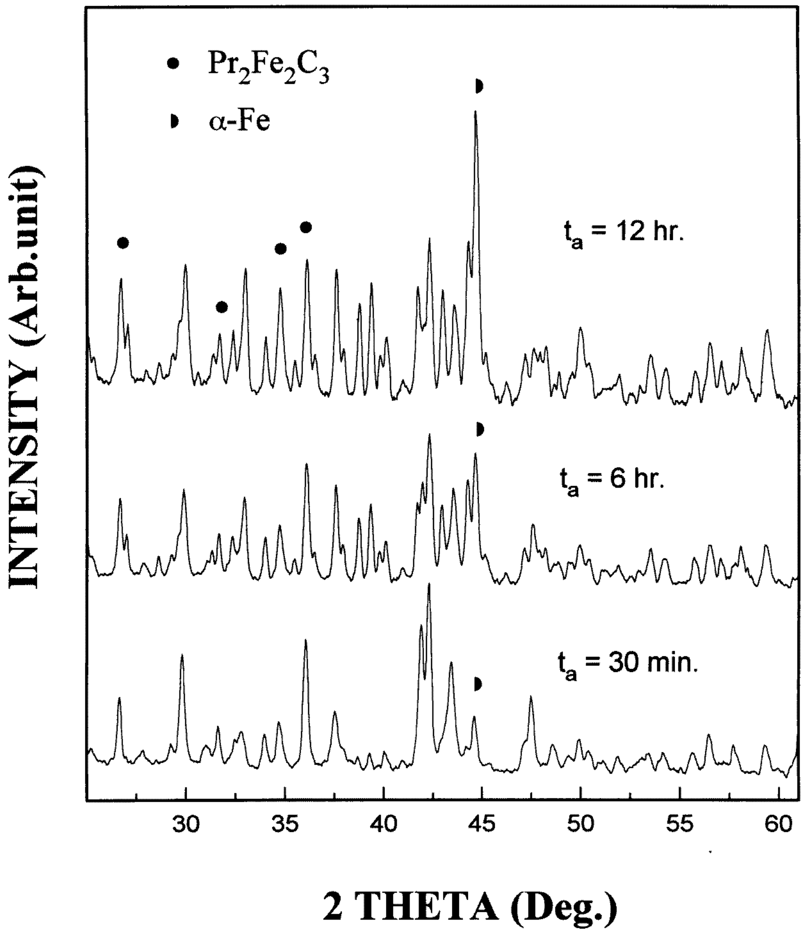

Figure 3. X-ray diffraction patterns of mechanically alloyed [$Pr_{15}Fe_{74}C_{11}$] alloys annealed at 750 °C for 30 min, 6 h, or 12 h.

and alloy composition. The largest intrinsic coercivity and the highest energy product are achieved for [$Pr_{15}Fe_{75}C_{10}$] alloy annealed at 900 °C for 35 min, for which the remanence, intrinsic coercivity, and maximum energy product are 4.99 kG, 4.47 kOe, and 3.59 MG Oe, respectively. When the annealing temperature is higher or lower than 900 °C, less $Pr_2Fe_{14}C$ is formed in the MA [$Pr_{15}Fe_{75}C_{10}$] alloy, and thus a lower coercivity and a lower maximum energy product are achieved.

Figure 5 demonstrates the hysteresis loops of MA (a) [$Pr_{15}Fe_{74}C_{11}$] and (b) [$Pr_{15}Fe_{75}C_{10}$] samples annealed at 900 °C for 35 min. Although more $Pr_2Fe_{14}C$ is present in [$Pr_{15}Fe_{74}C_{11}$] alloy than in [$Pr_{15}Fe_{75}C_{10}$] alloy, the magnetic properties of the latter are much better than those of the former. In MA Nd–Fe–C samples, the main phase of the [$Nd_{16}Fe_{75}C_9$] alloy is $Nd_2Fe_{14}C$, while the main phases of the [$Nd_{16}Fe_{76}C_8$] alloys are $Nd_2Fe_{14}C$ and $Nd_2Fe_{17}C_x$, the latter having a larger coercivity than the former [16]. Neither $Nd_2Fe_{17}C_x$ nor $Pr_2Fe_{17}C_x$ show easy-axis anisotropy, but they do not accelerate the reverse magnetization process in Pr/Nd–Fe–C alloys. On the contrary, their presence increases the coercivity of the corresponding alloys compared with that of the $Nd_2Fe_{17}C_x$-free alloys. A tentative

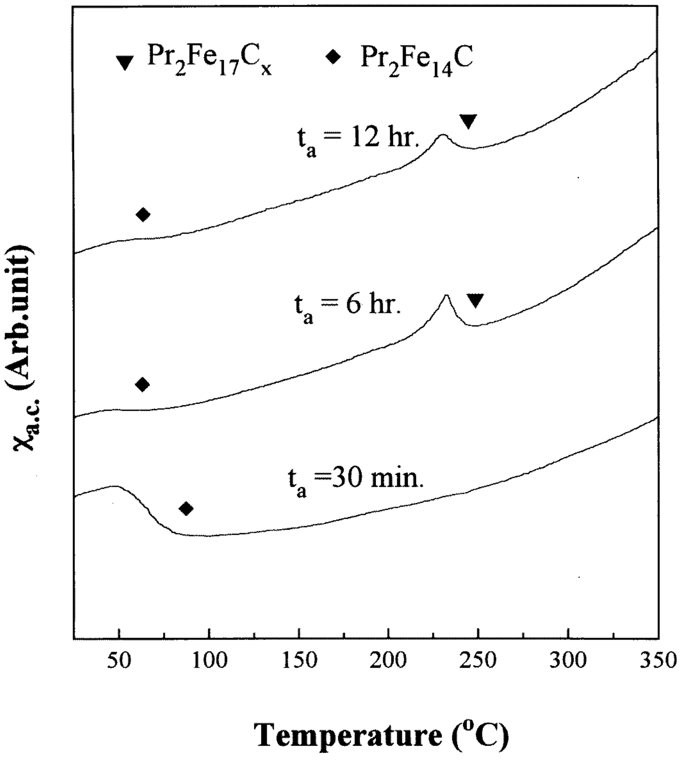

Figure 4. χ_{AC} versus temperature for mechanically alloyed [$Pr_{15}Fe_{74}C_{11}$] alloys annealed at 750 °C, for 30 min, 6 h, or 12 h.

explanation is given below.

There are many parallels between $Nd_2Fe_{14}B$ and Nd_2Fe_{17} compounds, including the layered arrangement and the presence of hexagonal transition metal nets surrounding rare-earth atoms in each structure [21], and the fact that the Fe (j_2) atoms in $Nd_2Fe_{14}B$ correspond magnetically and crystallographically to the Fe (c) atoms in Nd_2Fe_{17} [22]. It is reasonable to believe that the above-mentioned parallels exist between $R_2Fe_{14}C$ and $R_2Fe_{17}C_x$ (R = Nd, Pr) compounds. The lattice parameters of Nd_2Fe_{17} (a = 8.57 Å, c = 12.44 Å) approach those of $Nd_2Fe_{14}C$ (a = 8.83 Å, c = 12.03 Å). Because the hard magnetic phase $R_2Fe_{14}C$ grows out of $R_2Fe_{17}C_x$, it is possible to assume that $R_2Fe_{14}C$ is surrounded by $R_2Fe_{17}C_x$, and is crystallographically coherent with $R_2Fe_{17}C_x$. Due to the lattice parameter and intrinsic magnetic property differences, imperfections and stress exist in the interfaces, where the domain walls are strongly pinned; thus higher coercivity is obtained in Pr/Nd–Fe–C alloys with $R_2Fe_{17}C_x$ and $R_2Fe_{14}C$ as the main phases.

When more carbon is added, $Pr_2Fe_{17}C_x$ disappears, and this disappearance is accompanied with the increase of the content of carbide and α-Fe. It is reported that the R carbides deplete the coercivity strongly [23]; therefore, the drastic disappearance of magnetic properties in [$Pr_{15}Fe_{74}C_{11}$] alloy can be ascribed mainly to the increase in the α-Fe and $Pr_2Fe_2C_3$ content.

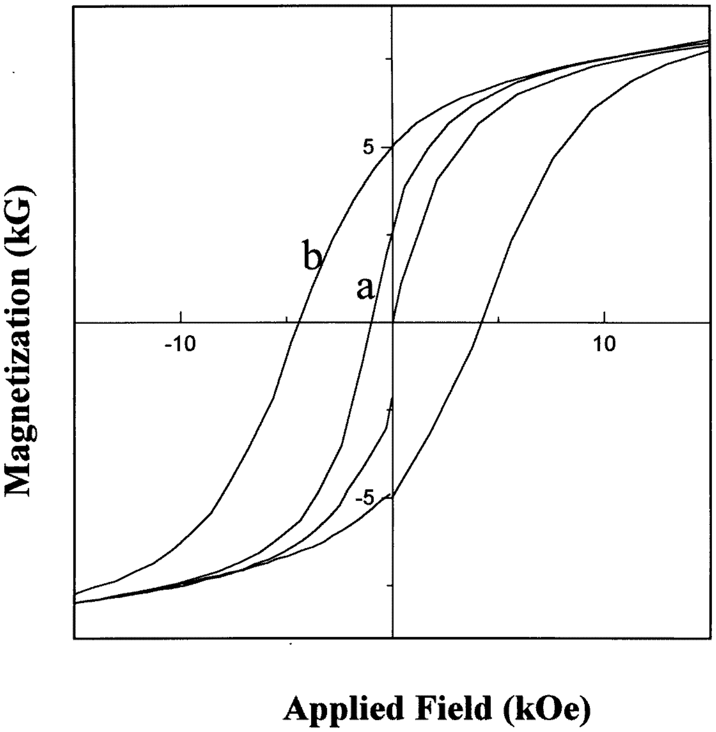

Figure 5. Hysteresis loops at room temperature of MA (a) [$Pr_{15}Fe_{74}C_{11}$] and (b) [$Pr_{15}Fe_{75}C_{10}$] alloys annealed at 900 °C for 35 min.

4. Conclusions

By means of mechanical alloying and a subsequent solid-state reaction, $Pr_2Fe_{14}C$ can be synthesized within certain composition and temperature ranges. The temperature limit for the formation of $Pr_2Fe_{14}C$ is 900 °C, which is much higher than that reported for ingot annealing or melt-spun-precursor annealing. Isothermal annealing of [$Pr_{15}Fe_{74}C_{11}$] at 750 °C for different lengths of time reveals that the formation of $Pr_2Fe_{14}C$ is accomplished within an appropriate time range. The solid-state reactions take place during this process, involving (a) MA Pr–Fe–C powders transforming into $Pr_2Fe_{17}C_x$, (b) $Pr_2Fe_{17}C_x$ reacting with carbide to form $Pr_2Fe_{14}C$, and (c) $Pr_2Fe_{17}C_x$ and $Pr_2Fe_{14}C$ decomposing into α-Fe, $Pr_2Fe_2C_3$, and a Pr-rich phase. The best magnetic properties are achieved for [$Pr_{15}Fe_{75}C_{10}$] alloys annealed at 900 °C for 35 minutes, which contain $Pr_2Fe_{14}C$, $Pr_2Fe_{17}C_x$, α-Fe, $Pr_2Fe_2C_3$, a Pr-rich phase, and Pr_2C_3. The remanence, intrinsic coercivity, and maximum energy product of [$Pr_{15}Fe_{75}C_{10}$] alloy are 4.99 kG, 4.47 kOe and 3.59 MG Oe, respectively.

Acknowledgments

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