EFFECTS OF NITRIDING TEMPERATURE ON MAGNETIC PROPERTIES OF MELT-SPUN $Pr_{1.4}Fe_{10.5}Mo_{1.5}N_x$ AND ITS PHASE ANALYSIS①

Zhang Shengen[1,2], Zhang Jiuxing[1], Yang Hongchuan[1] and Zhou Meiling[1,2]
1 College of Materials Science and Engineering, Beijing Polytechnic University, Beijing 100022, P. R. China
2 Department of Materials Science and Engineering, Central South University of Technology, Changsha 410083, P. R. China

ABSTRACT The phase transition of melt-spun $Pr_{1.4}Fe_{10.5}Mo_{1.5}$ and its nitrides have been studied by means of XRD and TEM. The phases of the alloy are α-Fe(Mo) (containing a little of other phases), $Pr(Fe, Mo)_{12}$, $Pr(Fe, Mo)_7$, $Pr(Fe, Mo)_{12}$ and $Pr(Fe, Mo)_{12}N_x$ in turn after having been arc melted in a purified argon, homogenized, melt-spun, annealed and nitrided. The magnetic properties are obtained on vibrating sample magnetometer (VSM). After annealing at 760 ℃ for 30 min and nitrided at 600 ℃ for 2 h, B_r is 0.349 T and H_c is 115.4 kA•m^{-1}.

Key words melt-spun $Pr(Fe, Mo)_{12}N_x$ phase analysis magnetic properties

1 INTRODUCTION

In 1990, people found $RTiFe_{11}N_{1-\delta}$ (δ ranges from 0 to 0.5) after $RTiFe_{11}$ was nitrided[1]. Neutron diffraction confirmed interstitial 2 b sites of the $ThMn_{12}$-type tetragonal structure (space group I4/mmm)[2]. Because of the interstitial nitrogen atoms, not only the H_c and M_s are increased dramatically, but also the H_A is modified radically[3]. Therefore, the $Pr(Fe, M)_{12}N_x$ (M is Ti, V, Mn, W, Si, or Al) may be a new permanent magnet. Many researchers are keen on the new permanent magnet. Nevertherless the effects of nitriding temperature on the rare-earth permanent magnet's properties have seldom been investigated. Here we have studied the phases of $Pr_{1.4}Fe_{10.5}Mo_{1.5}N_x$ prepared by melt-spun in each technological process and the effects of nitriding temperature on the magnetic properties. The results are represented in detail in this paper.

2 EXPERIMENTAL

Alloys were prepared by arc melting 99% pure Pr, DT-2 pure industrial iron and Fe-60Mo in a purified argon atmosphere. The ingots were heated at 800~1000 ℃ for 7~10 d in high vacuum. Ribbons were prepared by single roller melt spining onto a rotating copper wheel in argon, using surface velocity about 25~30 m/s. The ribbons were pulverized into powders of −320 mesh, the powders were annealed at the optimal temperature of 760 ℃ for 30 min[4]. Subsequently, they were nitrided at different temperature for 2 h. The phase analysis was carried out by XRD and TEM. Hysteresis loops were measured on a vibrating sample magnetometer (VSM).

3 RESULTS AND DISCUSSION

3.1 Phase Analysis of $Pr_{1.4}Fe_{10.5}Mo_{1.5}N_x$

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XRD and TEM analysis showed that the phase constituent is different in the procedures of arc melting, homogenizing, melt spinning, annealing and nitriding. Because of compositional segregation, gravitational segregation and different cooling speed in different part of ingot, the ingot is mainly composed of α-Fe(Mo) and a small amount of Pr(Fig. 1(a)). When the ingot are homogenized, the different kinds of atoms diffuse each other, then the ingot forms a single phase alloy with $ThMn_{12}$-type(space group I4/mmm) stabilized by Mo(Fig. 1(b)). After being melt-spun, the single phase alloy with $ThMn_{12}$-type transfers into $Pr(Fe, Mo)_7$ with $TbCu_7$-type structure(space group p6/mm) (Fig. 2(a, b)). Pinkerkon and Xiao studies show that $Pr(Fe, Mo)_7$ can be easily formed when the rotating copper wheel surface velocity is about 30 m/s, and the lower Mo is, the easier the $Pr(Fe, Mo)_7$ can be formed[5, 6]. As $Pr(Fe, Mo)_7$ is a metastable, when the velocity is 15~ 40 m/s, it can be easily formed. Annealed at 760 ℃ for 30 min, the ribbons of $Pr(Fe, Mo)_7$ transfer into $Pr(Fe, Mo)_{12}$ again. Nitrided at 600 ℃ for 2 h, nitrogen atoms were introduced into crystal lattice, then $Pr(Fe, Mo)_{12}N_x$ was formed which keeps $ThMn_{12}$-type structure. This is the reason why the metastable phase of $Pr(Fe, Mo)_7$ is not stable, it can transfer into the equilibrium phase of $Pr(Fe, Mo)_{12}$ on certain conditions, for

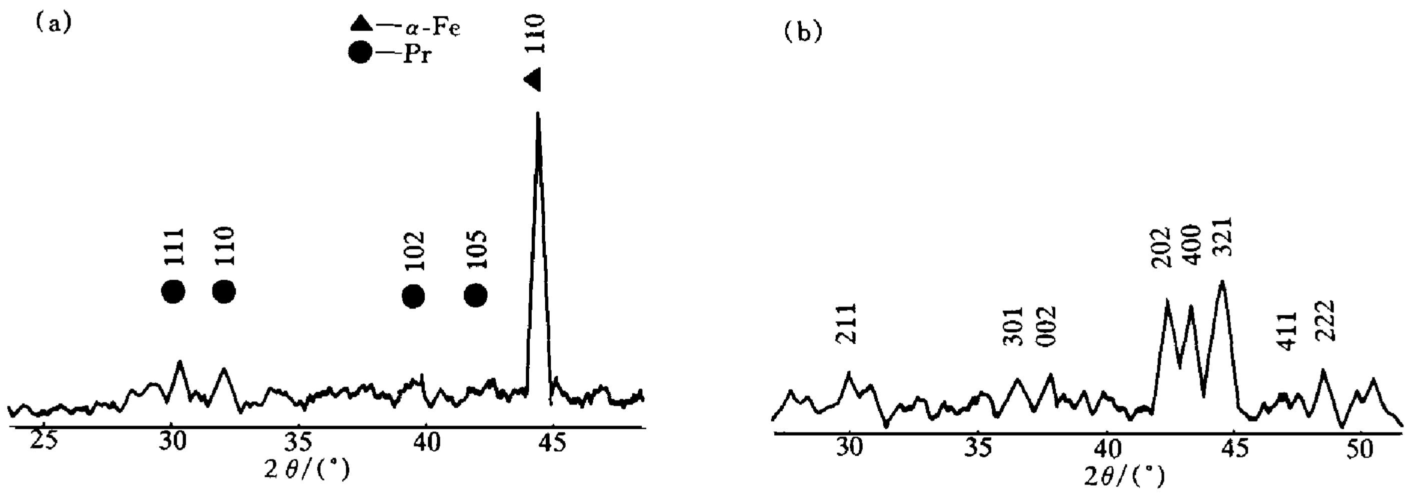

Fig. 1 XRD patterns of $Pr_{1.4}Fe_{10.5}Mo_{1.5}$ alloy
(a) —As-cast; (b) —Homogenized

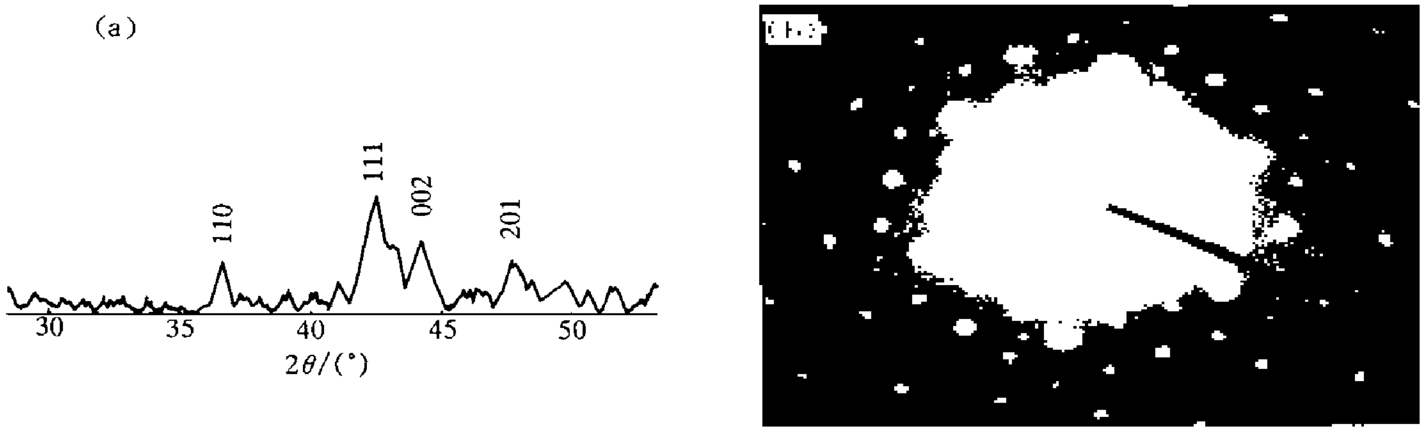

Fig. 2 XRD and TEM of melt-spun $Pr_{1.4}Fe_{10.5}Mo_{1.5}$ ribbons
(a) —XRD; (b) —TEM[0001]

example annealing, and nitriding is that nitrogen atoms occupy interstitial 2 *b* sites, does not change the crystal structure. So the law of the phase change of $Pr(Fe, Mo)_{12}N_x$ is α-Fe(Mo) (containing a little of other phases), $Pr(Fe, Mo)_{12}$, $Pr(Fe, Mo)_7$, $Pr(Fe, Mo)_{12}$ and $Pr(Fe, Mo)_{12}N_x$ in turn after having been arc melted in a purified argon, homogenized, melt-spun, annealed and nitrided.

3.2 Analysis of magnetic properties on $Pr(Fe, Mo)_{12}N_x$

The hysteresis loops of samples after annealing at 760 ℃ for 30 min then at 450 ℃, 500 ℃, 550 ℃ and 600 ℃ for 2 h respectively were measured on VSM. Fig. 3 is a typical hysteresis loop at 600 ℃ nitriding for 2 h. The hysteresis loop shows that the magnetic induction improves rapidly with increasing of the exterior magnetic field; with further increasing of the exterior magnetic field, the B_r and H_c increase slowly; in the magnetic phase with size about single domain, the reverse domains nucleate, then grow till the exterior magnetic field reaching saturation. Evidently, the coercive mechanism is nucleation. The other hysteresis loops are the same. Fig. 4 shows that B_r and H_c influenced by the nitriding temperature have the same law. When the samples are nitrided at 450 ℃, B_r is 0.258 T, H_c is 37.4 kA·m^{-1}; at 500 ℃, B_r and H_c are improved dramatically; at 600 ℃, H_c is 0.349 T and H_c is 115.4 kA·m^{-1}.

Comparing Fig. 4 with Table 1, we also find the nitrogen content *x*, B_r and H_c of $Pr_{1.4}Fe_{10.5}Mo_{1.5}N_x$ have the same law on nitriding temperature. As we know, nitriding is reversible. The absorption and desorption of nitrogen atoms can be easily expressed by $Pr_{1.4}Fe_{10.5}Mo_{1.5} \rightleftharpoons Pr_{1.4}Fe_{10.5}Mo_{1.5}N_x$. When the nitriding

Table 1 Nitrogen content *x* of $Pr_{1.4}Fe_{10.5}Mo_{1.5}N_x$ after annealing at 760 ℃ for 30 min then nitriding at different temperatures for 2 h

Temperature/ ℃	Ni content *x*
450	0.15
500	0.78
550	0.89
600	1.06

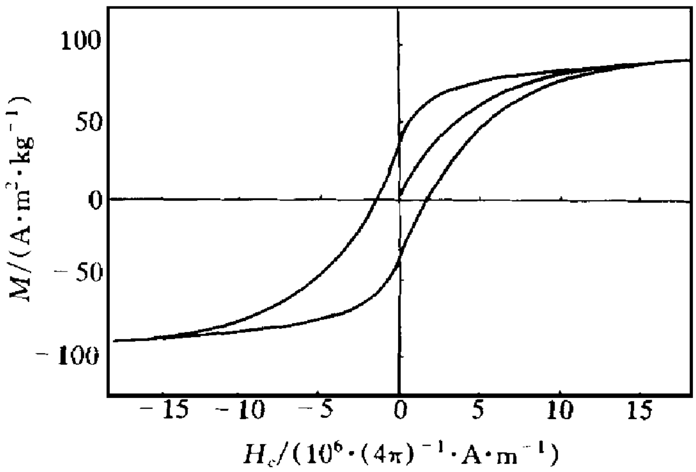

Fig. 3 A typical hysteresis loop of $Pr_{1.4}(Fe, Mo)_{12}N_x$

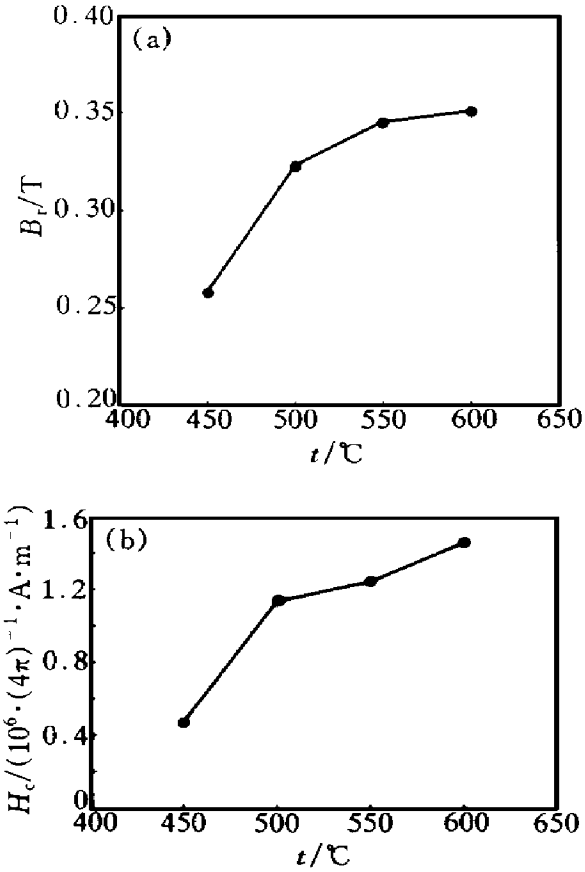

Fig. 4 B_r(a) and H_c(b) of $Pr_{1.4}Fe_{10.5}Mo_{1.5}N_x$ annealed at 760 ℃ for 30 min and nitrided at different temperatures for 2 h

temperature is 450 ℃, nitration is insufficient, nitrogen content x is 0.15, the effect of nitrogen atoms are not evident. When the annealing temperature is 500 ℃, nitrogen content x reaches 0.78, nitrogen atoms occupy the most interstitial 2 b sites, the effect of nitrogen atoms are evident, resulting in the improvement B_r and H_c. When the annealing temperature is 600 ℃, nitrogen content x exceeds 1, B_r and H_c have a sharp improvement.

Undoubtedly, when $x \leq 1.0$, the nitrogen atoms occupy the interstitial 2 b sites. In fact, x probably exceeds 1.0. Shun Suzuki etc found that nitrogen content x exceeded 1.0 and nitrogen atoms occupied not only the interstitial 2 b sites, but also other unknown crystal sites[7]. Fujii etc found that when nitrogen content x is 1.9, the (001) peak disappeared in the XRD pattern, which induced the crystal to lose the periodicity[8]. So we deduce that nitration can be divided into two stages. The first stage is that the nitrogen atoms penetrate into the interstitial 2b sites till nitrogen content x reaches 1.0. The second stage is that the nitrogen atoms penetrate into the other unknown crystal sites. However, when the nitrogen content x is 1.0, the best magnetic properties can be obtained.

4 CONCLUSIONS

(1) The phases of $Pr_{1.4}Fe_{10.5}Mo_{1.5}N_x$ are α-Fe(Mo) containing a little of other phase, $Pr(Fe, Mo)_{12}$, $Pr(Fe, Mo)_7$, $Pr(Fe, Mo)_{12}$ and $Pr(Fe, Mo)_{12}N_x$ in turn after having been arc melted in a purified argon, homogenized, melt-spun, annealed and nitrided.

(2) Annealed at 760 ℃ for 30 min, the suitable nitriding temperature of $Pr_{1.4}Fe_{10.5}Mo_{1.5}N_x$ is 600 ℃, B_r is 0.349 T and H_c is 115.4 $kA \cdot m^{-1}$ respectively.

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