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Investigation of phase formation of $RFe_{11}V_{1-x}Ti_x$ (R = Pr, Ce) compounds

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Phase formation of $PrFe_{11}V_{1-x}Ti_x$ and $CeFe_{11}V_{1-x}Ti_x$ compounds with the $ThMn_{12}$-type structure has been investigated by x-ray diffraction (XRD), differential thermal analysis (DTA) and ac initial susceptibility. The stable temperature range of the 1-12 phase for $PrFe_{11}V_{1-x}Ti_x$ alloys has been constructed as a function of Ti content. It is found that the $PrFe_{11}V$ compound with the $ThMn_{12}$-type structure do not form. The $PrFe_{11}Ti$ compound with the $ThMn_{12}$-type structure can only be obtained by annealing at a narrow temperature range between 1030 °C and 1113 °C. Furthermore, 1-12 phase can be obtained at lower temperature and wider temperature range with decreasing Ti content $x(0.2 \leq x \leq 1)$. The $CeFe_{11}V$ and $CeFe_{11}Ti$ compound with $ThMn_{12}$-type structure can be synthesized, and it is more favorable to synthesis the 1-12 single phase for the pseudotenary $CeFe_{11}V_{1-x}Ti_x$ compounds. For $PrFe_{11}V_{1-x}Ti_x$ compounds with $x = 0.2$–1, the lattice parameters a and c do not vary very much: around 0.860 and 0.479 nm, and Curie temperature T_c is 268 °C–329 °C. For $CeFe_{11}V_{1-x}Ti_x$ compounds the lattice parameters a and c are around 0.857 and 0.478 nm, and Curie temperature T_c is 211 °C–252 °C.

1. Introduction

The ternary Fe-rich $RFe_{12-x}M_x$ alloys (M = Ti, V and Mo etc.) with the tetragonal $ThMn_{12}$-type structure and their nitrides have been extensively studied during the past few years as potential candidates for permanent magnet applications due to their relatively high Curie temperature, saturation magnetization, and favorable magnetocrystalline anisotropy [1]. When R is a heavy rare earth element these compounds can be prepared relatively easily. The situation appears to be more difficult when R is a light rare earth element. No compounds of the $RFe_{10}V_2$ with $ThMn_{12}$-type structure (R = La, Ce and Pr) were reported to be formed [2], and attempts to prepare the $R(Fe, Nb)_{12}$ compounds with rare-earth elements lighter than Sm were unsuccessful [3]. So a further study of the phase formation for these compounds is necessary. In present work, the phase formation of $PrFe_{11}V_{1-x}Ti_x$ and $CeFe_{11}V_{1-x}Ti_x$ ($x = 0 \sim 1$) pseudoternary compounds with $ThMn_{12}$-type have been studied in details.

2. Experimental details

Samples of $PrFe_{11}V_{1-x}Ti_x$ series ($x = 0$, 0.2, 0.4, 0.6, 0.8, and 1) and $CeFe_{11}V_{1-x}Ti_x$ series ($x = 0$, 0.25, 0.5, 0.75, 1) were prepared by melting the constituent metals in a magneto-controlled arc furnace under a high-purity argon atmosphere. The purifies of starting materials were Pr, Ce, V and Ti 99.9%, Fe 99.8%. The relative amount of Ce was in excess of the stoichimetric composition by 5% in order to compensate for the loss of Ce during melting. The as-cast alloys were wrapped in tantalum foils and annealed in sealed quartz capsules between 750 °C and 1140 °C.

X-ray diffraction analysis was performed in the D/max-rA rotating anode X-ray diffractometer and Cu K_α radiation was used. The Curie temperature was determined by measuring the temperature dependence of ac initial susceptibility. Phase transition temperatures were assessed in the LCP-1 model differential thermal analysis (DTA) apparatus under purified argon atmosphere and alumina crucibles were used. The rate of heating was 10 °C/min.

3. Results and discussion

3.1. $PrFe_{11}V_{1-x}Ti_x$ alloy series

The as-cast samples consist of a essentially single phase with the tetragonal $ThMn_{12}$-type structure ($x = 1$) or the mixture of Pr-rich and α-Fe(V, Ti)

phases ($x = 0, 0.2, 0.4, 0.6, 0.8$). The phase structure in $PrFe_{11}V_{1-x}Ti_x$ alloys is varied significantly with different annealing temperature and Ti content. When annealed at 850 °C, the samples consist of an almost single phase having the $ThMn_{12}$-type structure ($x = 0.2, 0.4, 0.6, 0.8$) except for the sample with $x = 0$ and 1, for which no trace of this phase was found on the X-ray pattern and ac susceptibility measurements. The sample with $x = 0$ consists of the mixture of Pr-rich and α-Fe(V), and the sample with $x = 1$ contains an amount of the phase having the rhombohedral $ThZn_{17}$-type structure. As an example, the X-ray diffraction patterns and the corresponding ac initial susceptibility curves of $PrFe_{11}Ti$ alloy annealed at 1000 °C, 1100 °C, and 1140 °C are shown in Figs 1 and 2 respectively. Alloy annealed at 1100 °C present the $ThMn_{12}$-type structure with a small amount of α-Fe(Ti) impurity (Fig. 1b), the curie temperature of 1-12 phase is about 268 °C (Fig. 2b), which is correspondent to that reported by [4]. Annealed at 1140 °C, no magnetic order transition is observed from room temperature to 320 °C, and an amount of α-Fe(Ti) phase precipitate, indicating that the 1-12 phase disappears and 1140 °C exceeds the decomposition temperature of $PrFe_{11}Ti$ compound. This result is similar to the that of Kalogiron *et al.* [5] that $PrFe_{11}Mo$ is unstable at 1120 °C. Annealing the 1-12 compound at 1000 °C results in a decomposition to the mixture of the 2-17, Fe_2Ti and α-Fe(Ti) (Fig. 1a). Curie temperature of the 2-17 phase (Fig. 2a) is 130 °C which is higher than that of Pr_2Fe_{17} ($T_c = 10$ °C), suggesting a certain amount of Ti atoms are dissolved into the lattice of Pr_2Fe_{17} compound. Substitution of V for Ti hinders the decomposition of 1-12 to 2-17 structure. When $x = 0.8$, the $ThMn_{12}$-type structure is stable annealing at 850 °C and slowly decompose to 2-17, Fe_2Ti and α-Fe(V, Ti) at 800 °C. When $x \leq 0.6$, The $ThMn_{12}$-type structure remains unchanged at lower annealing temperature (for example, 750 °C).

The DTA curves of heating and cooling for the $PrFe_{11}V_{1-x}Ti_x$ alloys ($x = 0.2, 0.6, 0.8, 1$) annealed at 850 °C are shown in Fig. 3. It can been seen that for $PrFe_{11}Ti$ alloy only one endothermal peak, in which the 1-12 phase decomposes, was observed when heated (Fig. 3a). According to the result annealed at 1000 °C and at 1100 °C, the phase transition from 2-17 to 1-12 occurs in the temperature range 1000 °C to 1100 °C, however, this phase transformation was not detected by DTA. This may be due to the rate of transformation being very slow, also the thermal effect produced is too small to be detected. On cooling curve, two obviously exothermal peaks appear. 1-12 phase forms at 1110 °C and decompose to 2-17 phase at 1030 °C. The stable temperature range of 1-12 phase is only 80 °C, so it is very difficult to synthesis single phase $PrFe_{11}Ti$ compound with $ThMn_{12}$-type structure as reported by Akayama *et al.* [5]. When $x \leq 0.8$, only a endothermal peak on heating curve, in which the 1-12

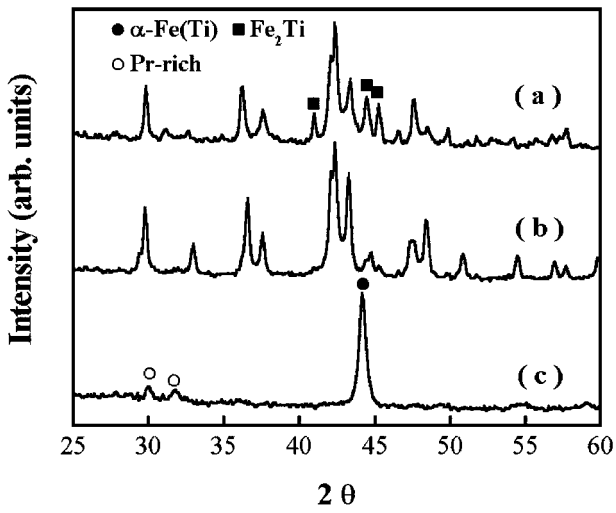

Figure 1 X-ray diffraction patterns of $PrFe_{11}Ti$ alloys at different annealing temperatures. (a) at 1000 °C for 120 h, (b) at 1100 °C for 48 h, (c) at 1140 °C for 2 h.

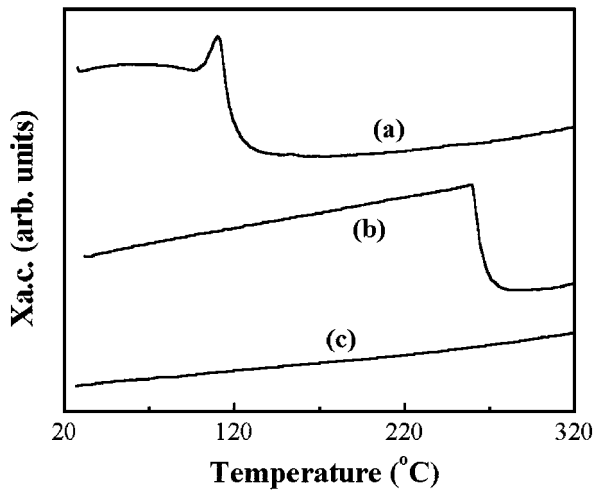

Figure 2 The ac initial susceptibility curve of $PrFe_{11}Ti$ alloy at different annealing temperatures (a) at 1000 °C for 120 h, (b) at 1100 °C for 48 h, (c) at 1140 °C for 2 h.

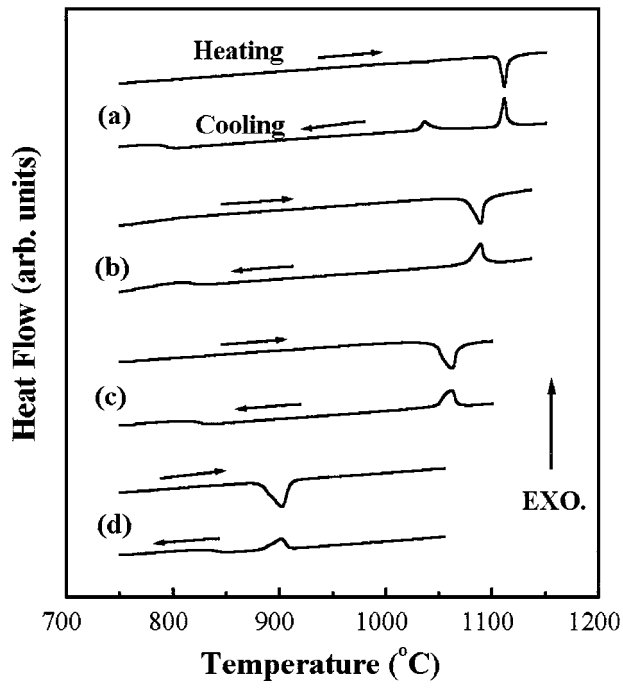

Figure 3 The DTA curves of heating and cooling for $PrFe_{11}V_{1-x}Ti_x$ alloys annealed at 850 °C for 120 h. (a) $x = 1$, (b) $x = 0.8$, (c) $x = 0.6$, (d) $x = 0.2$.

phase decomposes, and a obviously exothermal peak on cooling curve in which the 1-12 phase forms, were observed. The phase transformation from 1-12 phase to 2-17 phase for the sample with $x = 0.8$, which occurs in the temperature range 800 °C to 850 °C according to the annealing results, was not detected by DTA. This may be attributed to the substitution the small amount of V for Ti slowing down the rate of decomposition from 1-12 phase to 2-17 phase.

It also can be seen from Fig. 3 that the peak of 1-12 phase decomposition on heating curve appeared sharp at $x = 1$, which is typical for congruantly melting compound. When $x \leq 0.8$ the width of the peak of 1-12 phase decomposition on heating curve became relatively broad. This is believed to be attributed to the peritectic reaction. Furthermore, with decreasing x the strength of the peak of 1-12 phase formation on cooling curve is more and more weak compared with that of the 1-12 phase decomposition on heating curve, indicating that the rate of 1-12 phase formation on cooling is more and more slow. This supports the results that it is easy to obtain the 1-12 phase for the as-cast sample with $x = 1$ and difficult for the as-cast samples with $x \leq 0.8$.

From DTA, and x-ray diffraction patterns we construct in Fig. 4 the stable temperature range of 1-12 phase. When annealed at a temperature higher than the solid line, the $ThMn_{12}$ structure compound starts to decompose into the mixture of α-Fe(V, Ti) and a Pr-rich phase. When annealed at the temperature lower than the dotted line the $ThMn_{12}$-type structure compound start to decompose into the mixture of 2-17, Fe_2Ti and α-Fe(V, Ti) phase. The Pr-rich phase and α-Fe(V) are obtained when $PrFe_{11}V$ alloy is annealed between 750 °C and 1100 °C, and $PrFe_{11}V$ compound with $ThMn_{12}$-type structure do not exist. $PrFe_{11}Ti$ compounds with the $ThMn_{12}$ structure exist in a very narrow temperature range between 1130 °C and 1110 °C. As shown in Fig. 4, the stable temperature range of the 1-12 phase is wider and the formation temperature of the 1-12 phase is lower with decreasing Ti content. This is very favorable for obtaining high hard magnetic properties which rely on the formation of $ThMn_{12}$-type material at low annealing temperature prior to nitriding in order to obtain the required nanometer sized grains by mechanical alloying or melting-spinning technique.

TABLE I Lattice parameters a and c, Curie temperature T_c of $PrFe_{11}V_{1-x}Ti_x$ and $CeFe_{11}V_{1-x}Ti_x$

Compound	a (nm)	c (nm)	T_c (°C)
$PrFe_{11}V_{0.8}Ti_{0.2}$	0.859	0.478	329
$PrFe_{11}V_{0.6}Ti_{0.4}$	0.860	0.479	305
$PrFe_{11}V_{0.4}Ti_{0.6}$	0.860	0.479	300
$PrFe_{11}V_{0.2}Ti_{0.8}$	0.861	0.479	284
$PrFe_{11}Ti$	0.861	0.479	268
$CeFe_{11}V$	0.856	0.477	252
$CeFe_{11}V_{0.75}Ti_{0.25}$	0.856	0.478	237
$CeFe_{11}V_{0.5}Ti_{0.5}$	0.857	0.478	230
$CeFe_{11}V_{0.25}Ti_{0.75}$	0.858	0.478	216
$CeFe_{11}Ti$	0.858	0.479	211

The composition dependence of the lattice parameter and Curie temperature of $PrFe_{11}V_{1-x}Ti_x$ pseudoternary system with $x \geq 0.2$ is shown in Table I. It can be seen that with increasing Ti content x the lattice parameter remains almost unchanged, however, Curie temperature remarkably decreases.

3.2. $CeFe_{11}V_{1-x}Ti_x$ alloy series

The results of x-ray diffraction patterns and ac initial susceptibility show that the samples annealed at 850 °C consist of a essentially 1-12 single phase with $x = 0.25$, 0.5 and 0.75, and the 1-12 phase dominates for the samples with $x = 0$ and 1. As an example, Figs 5 and 6 give, respectively, the XRD patterns and the corresponding ac initial susceptibility curves of the $CeFe_{11}V_{1-x}Ti_x$ alloys with $x = 0, 0.5$ and 1. When $x = 1$ the XRD pattern can be indexed the $ThMn_{12}$-type structure and a little amount of α-Fe(Ti) impurity. In addition, one phase on the ac initial susceptibility curve is observed with Curie temperature of 211 °C (Fig. 6). This temperature is in agreement with that reported for $Ce(Fe, Ti)_{12}$ [4]. For $x = 0$, the XRD pattern shows that there exist an amount of α-Fe(V) impurity except for the 1-12 main phase, the ac susceptibility curve reveals that

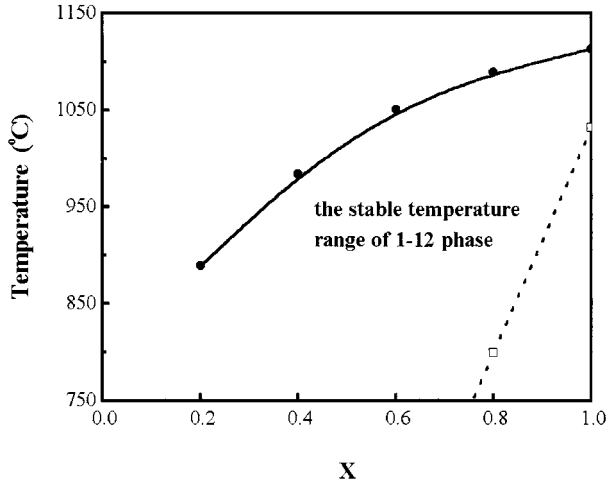

Figure 4 The stable region of the 1-12 phase for $PrFe_{11}V_{1-x}Ti_x$ alloys as a function of composition and temperature.

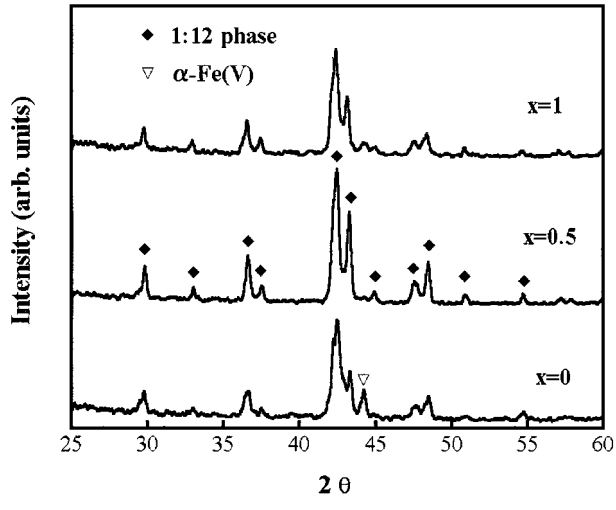

Figure 5 X-ray diffraction patterns of $CeFe_{11}V_{1-x}Ti_x$ alloys annealed at 850 °C for 48 h. (a) $x = 0$, (b) $x = 0.5$, (c) $x = 1$.

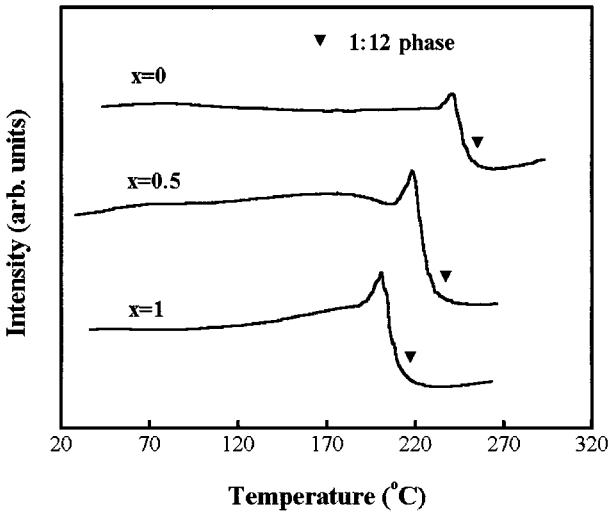

Figure 6 The ac initial susceptibility cures of $CeFe_{11}V_{1-x}Ti_x$ alloys annealed at 850 °C for 48 h. (a) $x = 0$, (b) $x = 0.5$, (c) $x = 1$.

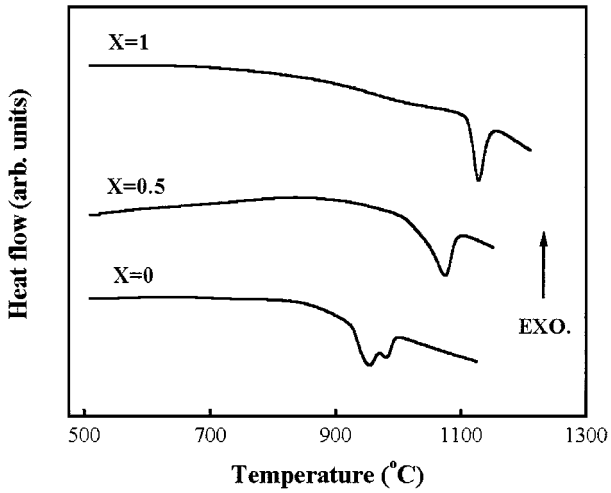

Figure 7 The DTA curves of heating for $CeFe_{11}V_{1-x}Ti_x$ compounds with $x = 0$, 0.5 and 1 annealed at 850 °C for 48 h.

the $CeFe_{11}V$ compound with $ThMn_{12}$-type structure has a Curie temperature of 252 °C. For $x = 0.5$, one Curie temperature at 230 °C is observed (Fig. 6), and the XRD pattern is well indexed to the 1-12 single phase. This result indicates that it is favorable to synthesis the 1-12 single phase for pseudoternary $Ce(Fe, V, Ti)_{12}$ alloys.

In order to identify the stability of the 1-12 phases, differential thermal analysis (DTA) is carried out. The DTA curves for the $CeFe_{11}V_{1-x}Ti_x$ alloys annealed at 850 °C are shown in Fig. 7. In the compound with $x = 1$ the peak of 1-12 phase decomposition appears sharp, which is typical for congruantly melting compound. With further decrease in x the width of the peak of 1-12 phase decomposition became broader and when $x = 0$ the peak appears as a doublet which is attributed to the peritectic reaction, implying that it is difficult to obtain the 1-12 single phase by annealing the as-cast sample with $x = 1$. The above results are similar to those of $PrFe_{11}V_{1-x}Ti_x$ alloy series. Table 1 gives lattice parameters and Curie temperature of $CeFe_{11}V_{1-x}Ti_x$ compounds.

4. Conclusion

Phase formation of $RFe_{11}V_{1-x}Ti_x$ (R = Pr, Ce) is studied. $PrFe_{11}V$ compound with $ThMn_{12}$-type structure do not form and $PrFe_{11}Ti$ compound with $ThMn_{12}$-type structure form only at a narrow temperature range between 1030 °C and 1110 °C. The stable temperature range of the 1-12 phase is wider and 1-12 phase can be formed at lower temperature with lower Ti content ($0.2 \leq x \leq 1$). This is very favorable for obtaining high hard magnetic properties which are rely on the formation of $ThMn_{12}$-type material at low annealing temperature prior to nitriding in order to obtain the nanometer sized grains by mechanical alloying or melting-spinning technique. Phase formation studies indicate that $CeFe_{11}V$ compound with $ThMn_{12}$-type structure is successfully synthesized and it is more favorable to synthesis the 1-12 single phase compounds for the pseudoternary $Ce(Fe,V,Ti)_{12}$ compound.

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