The Effect of Niobium Content on the Curie Temperature and Microstructure of the $Pr_{14}Fe_{79.9-x}Co_{16}B_6Nb_x$ Alloys

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Abstract: This study reports the results of investigations carried out to determine the Curie temperature (T_c) of various homogenized praseodymium-based alloys represented by the formula: $Pr_{14}Fe_{79.9-x}Co_{16}B_6Nb_x$ (where x = 0, 0.01, 0.05, 0.1, 0.15, 0.50). The influence of niobium content on the microstructure of these alloys has investigated. The Curie temperature decreased about 3 °C for x = 0.5 at. %. It has been observed a remarkable grain refinement on the microstructure of the $Pr_{14}Fe_{79.8}Co_{16}B_6Nb_{0.1}$ alloy when compared to the niobium-free alloy (x = 0 at. %).

Introduction

The $R_2Fe_{14}B$ compounds (R =Yttrium or a rare earth) have been studied extensively since their discovery in 1983[1]. High energy permanent magnets have been produced with these outstanding materials. Magnets with high energy products have been produced mainly with the Nd/PrFeB system. A major drawback of the this system is their rather low Curie temperature (~300°C)[2]. Improvement of these magnets has been achieved in the 2:14:1 compounds by the substitution of cobalt in the magnetic alloys[3, 4]. The replacement of Fe for Co ($Pr_2Fe_{14-x}Co_xB$) increased the Curie temperature[4]. The $Pr_2Fe_{13}Co_1B$ compound has a higher Tc than $Pr_2Fe_{14}B$[1, 5] and it has been shown that the Co atoms substitute preferentially on Fe sites, involving negative exchange interactions[5]. It has been reported that the Curie temperature of $Nd_2Fe_{14}B$ increases linearly with the Co content at about 11°C per at.%[6]. Recently, it has been shown for $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$ alloys that T_c also increase linearly with the Co content, although at rate slightly inferior to that reported for Nd-based materials (~10.2±0.3°C/at.%)[7,8]. In the $PrCo_{5-x}Ga_x$ system, the Curie temperature decrease with gallium addition[9]. Similarly, the substitution of Fe for Nb also decreases the Curie temperature[1]. The present work was undertaken in order to investigate, in a systematic manner, the progressive effect of Nb substitution for Fe in the Curie temperature and microstructure of some $Pr_{14}Fe_{79.9-x}Co_{16}B_6Nb_x$ alloys, x = 0, 0.01, 0.05, 0.1, 0.15, 0.5.

Experimental

Commercially available alloys in the homogenized state were studied. The chemical analyses of the as-cast alloys are given in Table 1. Homogenization heat treatment was carried out by annealing of the as-cast alloys in vacuum at 1100 °C for 20 h. A susceptibility analyzer was employed for thermomagnetic analysis (TMA) of the alloys in order to investigate their susceptibility versus temperature over the temperature range 50–500°C. A magnetic field of low amplitude (333 Hz) and heating rate of the alloys 1°C / min were employed. $Pr_{14}Fe_{80}B_6$, $Pr_{14}Fe_{64}Co_{16}B_6$ and $Pr_{14}Fe_{79.9}Co_{16}B_6Nb_{0.1}$ alloys were used as standard reference. The microstructures of the annealed alloys were observed using an optical microscope with Kerr effect facility and the chemical composition was observed with a SEM fitted with an EDX system.

Results and Discussion

The variation in the Curie temperature of the annealed Pr-based alloys as a function of niobium content is show in Fig 1. The Curie temperature decreases only 4°C for x = 0.01, 0.05 and 0.1 at.%. For higher Nb-contents, x=0.15 and 0.5, a noticeable diminution in this property has been observed (9 and 11°C, respectively). Table 1 shows a summary of the Curie temperature for the various alloys investigated in this study. The substitution of 0.1 at.% Nb in the $Pr_{14}Fe_{80}B_6$ alloy led to a decrease of 5 °C in T_c. As expected, the substitution of 16 at.% Co in this alloy increased the Curie temperature in 157°C. This has been attributed to decrease of lattice parameters with the substitution (with changes of interatomic distance, which is crucial for exchange interactions)[4]. The Curie temperature, which reflects the overall exchange, increases nearly 50 °C per substituted Fe atom for Co (in region of low Co concentration)[4]. The Curie temperature of the $Pr_2Fe_{14}B$ matrix phase, determined previously by differential thermal analysis (DTA), was ~ 290 °C [10]. It has been reported that compounds of the type $Pr_2Fe_{14-x}Nb_xB$ and $Pr_2Fe_{13-x}Co_1Nb_xB$ showed a decreased to Curie temperature in the composition range $x \leq 2$[1]. Systems of the type $Pr_{1.9}Dy_{0.1}Fe_{13-x}Nb_xCo_1B$ also showed a decrease in this property[1]. For a comparison with the present data these results are given in the table 2. The Curie temperature also decreases with increasing Nb content for these Dy-containing materials.

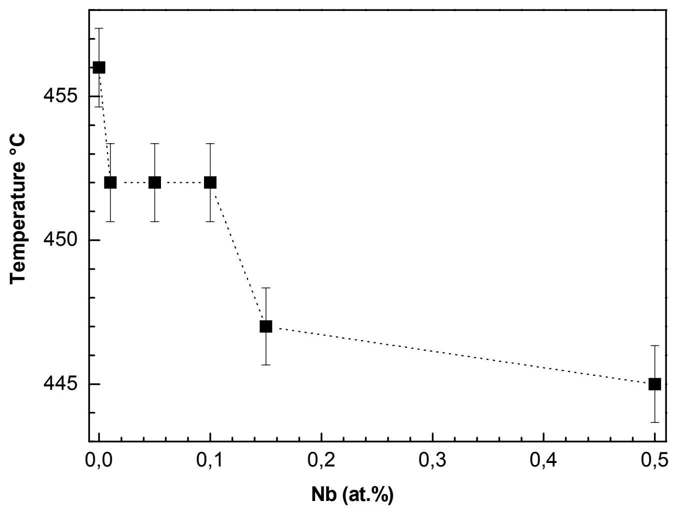


Figure 1 – Curie temperature versus niobium content for $Pr_{14}Fe_{79.9-x}Co_{16}B_6Nb_x$ magnetic alloys.

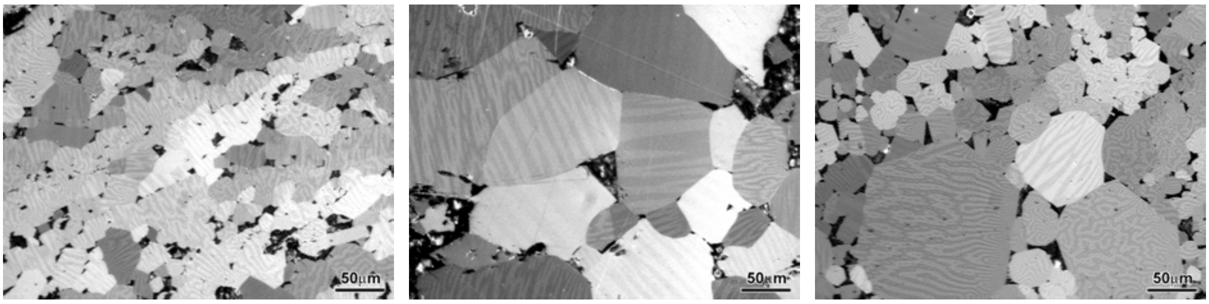
Table 1 - Curie temperature obtained in this study for magnetic alloys.

Alloys composition [at %]	T_c [°C]
$Pr_{14}Fe_{80}B_6$	299
$Pr_{14}Fe_{79.9}B_6Nb_{0.1}$	294
$Pr_{14}Fe_{64}Co_{16}B_6$	456
$Pr_{14}Fe_{63.99}Co_{16}B_6Nb_{0.01}$	452
$Pr_{14}Fe_{63.95}Co_{16}B_6Nb_{0.05}$	452
$Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$	452
$Pr_{14}Fe_{63.85}Co_{16}B_6Nb_{0.15}$	447
$Pr_{14}Fe_{63.50}Co_{16}B_6Nb_{0.5}$	445

Table 2 - Curie temperature for similar systems[1].

Alloys composition [at %]		T_c [°C]
$Pr_{11.8}Fe_{82.3}B_{5.9}$	($Pr_2Fe_{14}B$)	293
$Pr_{11.76}Fe_{81.91}Nb_{0.58}B_{5.75}$	($Pr_2Fe_{13.9}$ $Nb_{0.1}B$)	290
$Pr_{11.71}Fe_{81.21}Nb_{1.16}B_{5.92}$	($Pr_2Fe_{13.8}Nb_{0.2}B$)	287
$Pr_{11.79}Fe_{76.79}Co_{5.53}B_{5.89}$	($Pr_2Fe_{13}Co_1B$)	355
$Pr_{11.79}Fe_{75.91}Nb_{0.58}Co_{5.83}B_{5.89}$	($Pr_2Fe_{12.9}Nb_{0.1}Co_1B$)	352
$Pr_{11.76}Fe_{75.31}Nb_{1.16}Co_{5.85}B_{5.92}$	($Pr_2Fe_{12.8}Nb_{0.2}Co_1B$)	348
$Pr_{11.19}Dy_{0.6}Fe_{76.51}Co_{5.82}B_{5.88}$	($Pr_{1.9}Dy_{0.1}Fe_{13}Co_1B$)	359
$Pr_{11.16}Dy_{0.58}Fe_{75.94}Nb_{0.58}Co_{5.84}B_{5.9}$	($Pr_{1.9}Dy_{0.1}Fe_{12.9}Nb_{0.1}Co_1B$)	357
$Pr_{11.19}Dy_{0.58}Fe_{75.31}Nb_{1.16}Co_{5.85}B_{5.91}$	($Pr_{1.9}Dy_{0.1}Fe_{12.8}Nb_{0.2}Co_1B$)	354

Fig 2 shows the microstructure of the reference alloys. The $Pr_{14}Fe_{80}B_6$ alloy exhibits fine and elongated grains. Conversely, the $Pr_{14}Fe_{79.9}B_6Nb_{0.1}$ alloy exhibits larger grains of the matrix phase. The microstructure of the $Pr_{14}Fe_{64}Co_{16}B_6$ alloy is composed of rounded grains. It is well known that in steels Nb acts as refinement of grains through carbide precipitation. A quantitative elemental analysis using EDX showed large amount of boride $Pr_{1+\varepsilon}(FeCo)_4B_4$ precipitated in the grain boundaries of the $Pr_{14}Fe_{80}B_6$ alloy, which could be the reason for the small grain size of this alloy. The figures 3 and 4 show the microstructures of $Pr_{14}Fe_{63.99}Co_{16}B_6Nb_{0.01}$ and $Pr_{14}Fe_{63.95}Co_{16}B_6Nb_{0.05}$ alloys, respectively. The microstructures of these alloys are very similar, which would be expected since the variation in Nb content also was very small. In both cases, it is noticeable the increase in the grain size in relation to the Nb-free alloy.



(a) (b) (c)

Figure 2 – Kerr effect image of the (a) $Pr_{14}Fe_{80}B_6$, (b) $Pr_{14}Fe_{79.9}B_6Nb_{0.1}$ and (c) $Pr_{14}Fe_{64}Co_{16}B_6$ alloys.

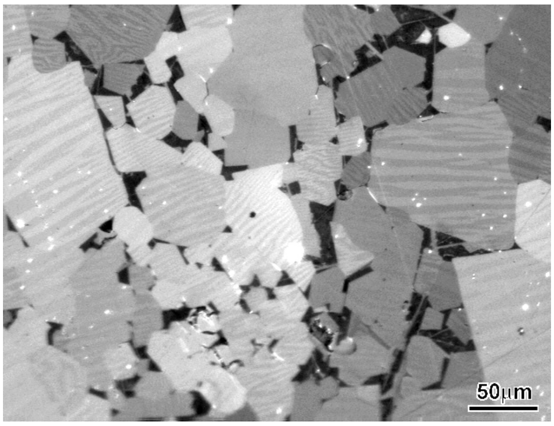


Figure 3 – Kerr effect image of the $Pr_{14}Fe_{63.99}Co_{16}B_6Nb_{0.01}$ alloy.

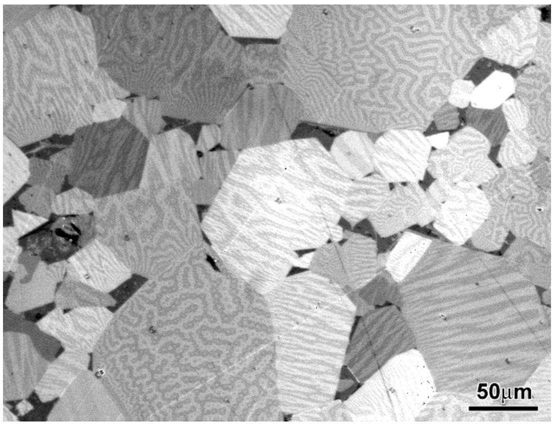


Figure 4 – Kerr effect image of the $Pr_{14}Fe_{63.95}Co_{16}B_6Nb_{0.05}$ alloy.

The substitution of 0.1 at.% Nb led to a significant change in the microstructure of the alloys, as shown in Fig. 5. The grain size is comparable to that observed in the $Pr_{14}Fe_{80}B_6$ alloy (Fig 2a). Chemical analyses showed the presence of a $Pr(FeCo)_2$ in the grain boundaries. This Laves phase has been identified previously[6, 11, 13].

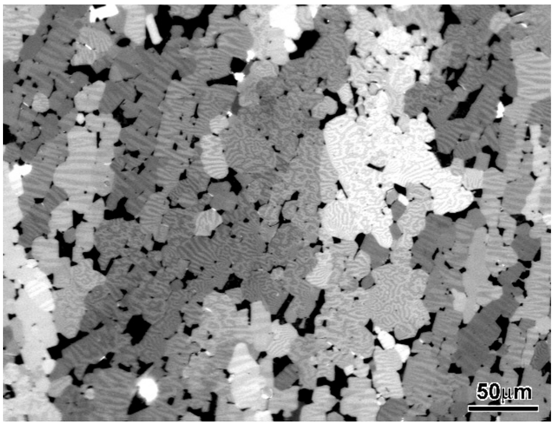


Figure 5 – Kerr effect image of the $Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$ alloy.

The increase in the Nb content to 0.15 at.% promoted some grain growth, as can be observed in the microstructure shown in Fig. 6. Chemical analyses in these alloys showed the presence of a Fe_2Nb phase[7]. The alloy containing 0.5 at.% Nb also showed some change in the structure of the matrix phase grains, as shown in Fig 7. Chemical analyses showed the presence of a Laves phase and a new FeNb phase. It is possible that higher Nb content lead the formation of precipitates in the grains boundaries, which could modify the structure of the grains.

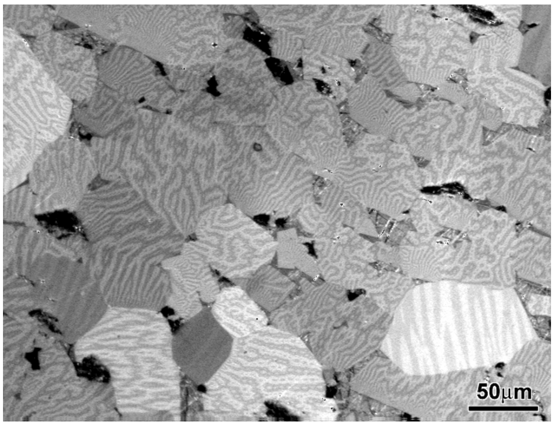


Figure 6 – Kerr effect image of the $Pr_{14}Fe_{63.85}Co_{16}B_6Nb_{0.15}$ alloy.

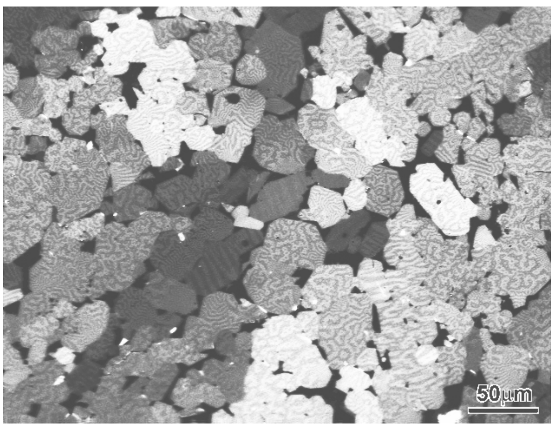


Figure 7 – Kerr effect image of the $Pr_{14}Fe_{63.50}Co_{16}B_6Nb_{0.5}$ alloy.

Conclusions

It has been shown that niobium substitution in the rare earth-iron-boron-system led to a decrease in the Curie temperature. This diminution is quite noticeable when the niobium content is larger. Single substitution of Co and Nb led to the grain growth of the homogenized PrFeB-type alloy. Niobium acts as a grain refining only when cobalt is present in the Pr-based homogenized alloy. At the concentration of 0.1 at.% Nb this effect seem to be more evident. Grain refinement has been attributed to boride and Nb precipitates.

Acknowledgments

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