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Complete suppression of metastable phase and significant enhancement of magnetic properties of B-rich PrFeB nanocomposites prepared by devitrifying amorphous ribbons

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Abstract

The effect of refractory element addition on phase transformation, crystallization behavior and magnetic properties of $Pr_{8.5}Fe_{81.5}B_{10}$ (addition-free) and $Pr_{8.5}Fe_{81.5}M_2B_{10}$ (M = V, Cr, Nb, Zr, Ti) ribbons has been investigated. The annealed addition-free ribbon as well as the samples with V or Cr additions are mainly composed of the metastable $Pr_2Fe_{23}B_3$ phase, whereas annealed ribbons with Nb, Zr or Ti additions primarily consist of $Pr_2Fe_{14}B$ and a minor amount of Fe_3B/boride. The complete suppression of the metastable $Pr_2Fe_{23}B_3$ phase due to Nb, Zr or Ti additions leads to a significant enhancement of the magnetic properties. For example, the remanence, the coercivity and the energy product are remarkably increased from 2.5 kG, 0.4 kOe and 0.2 MG Oe for the addition-free material to 9.2 kG, 4.7 kOe and 7.6 MG Oe for the specimens with Nb addition. The successful elimination of the metastable $Pr_2Fe_{23}B_3$ phase is believed to profit from two factors: (a) Nb, Zr or Ti atoms substitute the Pr site, comparatively increase the Pr content, and thus inhibit the nucleation of Pr-lean $Pr_2Fe_{23}B_3$ phases, and (b) the formation of Nb, Zr, or Ti borides consumes some part of B, which hinders the generation of the B-rich $Pr_2Fe_{23}B_3$ phase.

Keywords: Metastable phase; Amorphous; Anneal; Magnetic properties

Exchange-spring nanocomposite magnets consisting of a soft magnetic phase exchange coupled to a hard magnetic phase have been extensively studied due to their remanence enhancement effect, high energy product and low cost [1–4]. Micromagnetic calculations show that the remanence enhancement results from the intergrain exchange-coupling action (IECA) between the magnetic phases, which is demonstrated to sensitively depend on microstructure parameters, such as grain size, phase composition and distribution [5,6]. The ideal microstructure for strong IECA should have a fine grain size, a homogenous phase distribution and no impurity phases such as metastable and nonmagnetic phases [5]. It is known that in B-rich RFeB nanocomposites, when the R content is less than 9 at% and the B content is more than 6 at%, metastable phases usually appear, which reduces the IECA between the hard and soft phases and deteriorates the magnetic properties [7–9]. Hence, suppressing the formation of metastable phases is a key problem to improve the magnetic properties of B-rich RFeB nanocomposites. The formation and type of metastable phases is strongly affected by the alloy composition [10] and the heating rate during crystallization [11]. Recently, Nb, Cr, Ti and Zr additions were found to effectively restrain the growth of the metastable phase and increase the concentration of the hard phase [7,12,13]; however, the reason why such additions can successfully restrain the metastable phase is not well understood.

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In this work, we select $Pr_{8.5}Fe_{81.5}B_{10}$ as the basic composition in which the metastable $Pr_2Fe_{23}B_3$ phase can easily be generated, and investigate the effect of V, Cr, Zr, Nb or Ti addition on the phase transformation, the crystallization process and the magnetic properties of melt-spun ribbons. Because the generation of the metastable $Pr_2Fe_{23}B_3$ phase can be fully inhibited by Zr, Nb or Ti additions, the magnetic properties of the samples are considerably improved. The grain size of the samples with Zr, Nb or Ti additions is larger than the critical grain size for full IECA, so the magnetic properties can be further enhanced by optimizing the annealing process and by refining the microstructure. In our experiments, the devitrification of fully amorphous melt-spun ribbons was used to prepare nanocomposites, because the samples prepared by this method have comparable microstructure and magnetic properties in comparison with specimens produced by direct quenching [14,15].

Alloy ingots with compositions $Pr_{8.5}Fe_{81.5}B_{10}$ (addition-free) and $Pr_{8.5}Fe_{79.5}M_2B_{10}$ (M = V, Cr, Zr, Ti, Nb) were prepared by vacuum induction melting. Pieces of the ingots were melt-spun from a quartz tube having an orifice diameter of about 1 mm at a wheel speed of 40 m/s. The annealing temperature was selected by measuring differential scanning calorimeter (DSC) curves at a heating rate of 20 K/min. The structure of the ribbons was analyzed using a Siemens transmission X-ray diffraction (XRD) diffractometer with Mo K_α radiation. The Curie temperature was determined from the constant-rate heating DSC curves. The mean grain size of the specimens was estimated with the Scherrer equation from the half-width of the strongest three diffraction peaks. The magnetic properties were measured in a superconducting quantum interference device (SQUID) magnetometer under an applied field up to 50 kOe. The external field was parallel to the length direction of the ribbons.

Fig. 1 shows XRD patterns of $Pr_{8.5}Fe_{81.5}B_{10}$ (addition-free) and $Pr_{8.5}Fe_{79.5}M_2B_{10}$ (M = V, Cr, Zr, Ti, Nb) ribbons spun at a wheel speed of 40 m/s. These patterns exhibit only one broad diffuse-diffraction maximum around $2\theta = 18^\circ$, indicating that all the ribbons with different composition are amorphous.

Fig. 2 presents the DSC curves of the amorphous ribbons. All samples crystallize through one exothermic peak. The crystallization peak temperature (T_p) shifts to higher values due to the introduction of additional elements. For instance, the T_p value for the addition-free sample is 903 K and that for the specimens with the Nb addition is 922 K. Nb addition leads to the highest T_p. This indicates that the element addition enhances the thermal stability of the amorphous ribbons. To realize magnetic hardening of amorphous ribbons and to check the effect of element addition on the phase transformation behavior, an isothermal devitrification anneal is necessary. The corresponding temperature, at which the crystallization reaction finishes, was chosen to anneal the amorphous samples for 15 min.

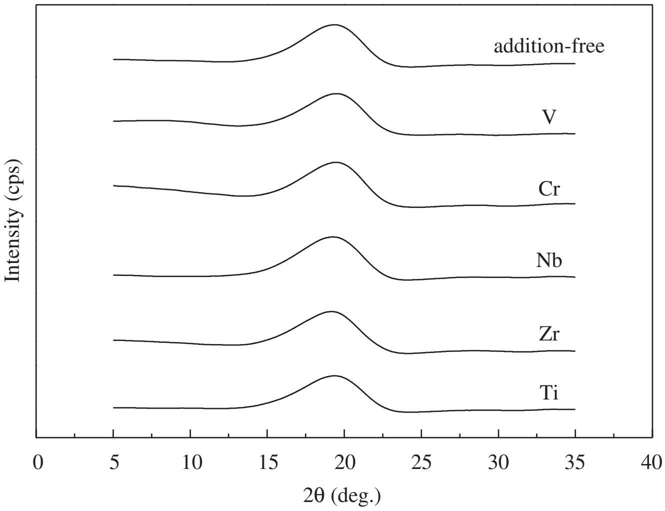

Fig. 1. XRD patterns of $Pr_{8.5}Fe_{81.5}B_{10}$ (addition-free) and $Pr_{8.5}Fe_{79.5}M_2B_{10}$ (M = V, Cr, Zr, Ti, Nb) ribbons spun at a wheel speed of 40 m/s.

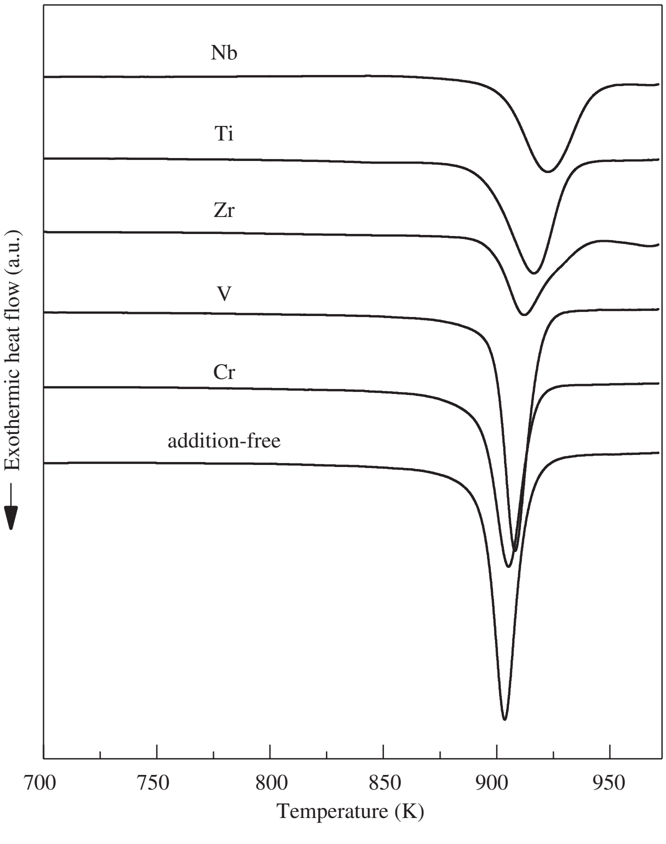

Fig. 2. DSC curves of the $Pr_{8.5}Fe_{81.5}B_{10}$ (addition-free) and $Pr_{8.5}Fe_{79.5}M_2B_{10}$ (M = V, Cr, Zr, Ti, Nb) amorphous ribbons.

The XRD patterns of annealed $Pr_{8.5}Fe_{81.5}B_{10}$ (addition-free) and $Pr_{8.5}Fe_{79.5}M_2B_{10}$ (M = V, Cr, Zr, Ti, Nb) ribbons are shown in Fig. 3. The addition-free ribbons as well as the ribbons with V or Cr additions consist of the $Pr_2Fe_{23}B_3$ metastable phase with cubic structure and a lattice parameter of 1.418 nm [16], and a minor amount of