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Effects of cobalt addition on microstructure and magnetic properties of PrNdFeB/Fe_7Co_3 nanocomposite

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Abstract: The permanent magnetic nanocomposite PrNdFeB/Fe_7Co_3 ribbons were prepared by directly quenching, and the microstructure and magnetic influence of composite materials with Co substitution were studied. The phase identification and the magnetic properties were measured by X-ray diffraction (XRD) and vibrating sample magnetometry (VSM). Microstructure observation was performed using scanning electron microscopy (SEM). The crystallization temperatures of the hard magnetic phase and the soft magnetic phase were measured using differential scanning calorimetry (DSC). The experimental results showed that Co addition improved the Curie temperature of magnets. When the ribbons were melt-spun at 35 m/s, the added content of Co was 4 at.%, and the magnetic properties were the best, which were remanence (B_r) of 0.379 T, coercivity (H_{ci}) of 344.4 kA/m, the maximum magnetic energy product $(BH)_{max}$ of 32.6 kJ/m^3. Besides, the activation energy of each phase was calculated by Kissinger equation, which was 310.4 kJ/mol of Fe_7Co_3 phase and 510.2 kJ/mol of 2:14:1 phase, respectively.

Keywords: nanocomposite materials; melt spinning; magnetic properties; activation energy; rare earths

Nanocomposite permanent magnets consisting of hard magnetic phase with high coercivity and soft magnetic phase with large magnetization, which were realized to have optimized magnetic properties using exchange coupling between two phases in nanoscale, have become new type of functional materials[1–5]. Theoretical prediction[6] showed that the maximum energy products were 1 MJ/m^3 for anisotropic nonocomposite magnets, higher than any single phase materials. Present developments about how to improve magnetic properties for nanocomposite materials were of two aspects: one was adding substitutable elements; the addition of element has influenced not only the intrinsic characteristics for the main phase, but also the microstructures of magnets. For example, the magnetic properties based on Pr matrix owing to higher anisotropic field were better than those based on Nd matrix[7–9]. Zhang et al.[10] pointed out that Co addition decreased the precipitation temperature of crystalline phases, and improved the Curie temperature of magnetic phases. It was shown that Fe replaced partially by Co was an effective method of increasing the thermal stability for Fe-based alloys; but the mechanics of Nb and Zr[11,12] with low solubility in the main phase was to center around grain boundary, refine the grains and increase exchange coupling effect between the magnetically soft and hard grains, thus gain better general magnetic properties. The other aspect was adjusting technics for the sake of ameliorating microstructures for magnets. Li et al.[13] prepared $Nd_2Fe_{14}B$/α-Fe nanocomposite magnets by chemical vapor deposition (CVD), and their results showed that depositing appropriate amount of α-Fe on the NdFeB ribbons could increase interface areas for soft/hard magnetic phase, improved distribution of the soft magnetic phase, and thus enhanced magnetic properties.

In general, most people mainly chose α-Fe as the soft magnetic phase for nanocomposites, and there was little research for Fe_7Co_3 phase which has the excellent moment according to the Slater-Pauling curve. Yang et al.[14,15] prepared Fe_7Co_3 single-phase and Sm_2Co_{17}/Fe_7Co_3 double-phase nanowire arrays via direct-current electrodeposition method, and illustrated that Fe_7Co_3 nanowire was a well-soft magnetic phase compared with Fe nanowire, so we chose Fe_7Co_3 as the soft magnetic phase for nanocomposites. Fischer et al.[16] and Zheng et al.[17] proposed that the magnetic properties were the best for NdFeB nanocomposite magnets with an optimum microstructure consisting of soft magnetic grains (D≈10 nm, $V^{\alpha\text{-Fe}}$≈40%) and hard magnetic grains with a mean grain diameter of about 20 nm owing to the strong exchange coupling actions between the soft magnetic phase

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and the hard magnetic phase. Based on their conclusion, we prepared PrNdFeB/Fe_7Co_3 nanocomposite ribbons with the volume fraction of 40% for Fe_7Co_3 phase, and investigated the effect of Co addition on crystal structure and magnetic properties for nanocomposite PrNdFeB/Fe_7Co_3 ribbons. The action of Co was expected to improve the Curie temperature, and compensate the loss of the temperature by the addition of Pr element. Besides, melt-spinning speed was also an important factor affecting magnetic properties. According to the previous published papers of our research group[18,19], the amorphous state was obtained with the speed of 35 m/s, and then crystallized through appropriate annealing time and temperature, the favorable magnetic properties were gained, so there were only two kinds of spin ribbons speed in the article, and the effect of different roll wheel speeds was also studied.

1 Experimental

Alloy ingots with chemical composition of $Pr_{2.5}Nd_{7.5}Fe_{84-x}Co_xB_6/Fe_7Co_3$ (x=0, 2, 4, 6) were prepared by melting 99.9% pure Pr, Nd, Co, Fe and Fe-B (B%= 19.6%) alloy, and then remelted four times to ensure its homogeneity. An excessive content of about 5 wt.% Pr and Nd was added to compensate the mass loss due to their evaporation. Spin ribbons were obtained with the speed of 25 m/s or 35 m/s. These techniques were conducted in a high purity Ar atmosphere. Phase structure identification was characterized by X-ray diffraction (XRD) with Cu Kα radiation. Microstructure observation and the atomic percentage of melt spun ribbons were performed using scanning electron microscopy (SEM, S-4800) and energy dispersive X-ray spectroscopy (EDS), respectively. The magnetic properties were measured by a vibrating sample magnetometer (VSM, Lakeshore-7407) with a field up to 1600 kA/m. The crystallization temperatures of the magnetic phase were determined by using differential scanning calorimetry (DSC, SDT-Q600) at various heating rates under N_2 atmosphere, and the activation energy of each phase was calculated by Kissinger equation.

2 Results and discussion

2.1 Phase identification of ribbons

The XRD patterns of all alloys melt-spun ribbons with the speed of 35 m/s are shown in Fig. 1, which shows it involves mainly the soft magnetic Fe_7Co_3 phase and the hard magnetic 2:14:1 phase. Compared with $Nd_{15}Fe_{77}B_8$ ribbons in the literature[20], the diffraction peaks of ribbons Pr instead of Nd are the same, which indicates that Nd is partly replaced by Pr in the main phase and forms $(Pr,Nd)_2(Fe,Co)_{14}B$ phase. Besides, it should be noticed

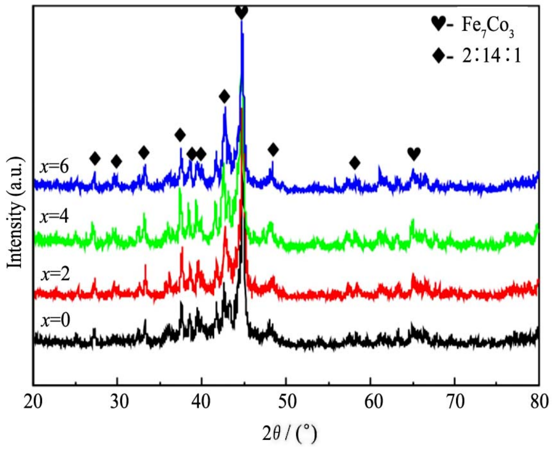

Fig. 1 XRD patterns of $Pr_{2.5}Nd_{7.5}Fe_{84-x}Co_xB_6/Fe_7Co_3$ ribbons with the speed of 35 m/s (x=0, 2, 4, 6)

that the characteristic peaks of Fe_7Co_3 phase and 2:14:1 phase shift toward higher angle with the increase of Co content, which means their crystal lattice constants decrease. Among these, the crystal lattice constant of Fe_7Co_3 phase decreases from 0.2864 to 0.2858 nm, and the crystal lattice constants a and c of 2:14:1 phase decrease from 0.8793 and 1.218 nm to 0.8766 and 1.214 nm. Furthermore, the mean grain size for the Fe_7Co_3 and 2:14:1 phases using Scherrer's equation are estimated to be about 26.5 and 59.5 nm, respectively. Corresponding to the references[16,17], the thick grains of two phases are the possible reasons of the unfavourable magnetic properties. In this article, the contents of the soft magnetic phase and the hard magnetic phase were determined by X-ray semi-quantitative component analysis (RIR method). As shown in the following formula:

$$w_i = \frac{I_i / RIR_i}{\sum_{i=1}^{N} I_i / RIR_i} \tag{1}$$

Table 1 shows the integrated intensities of the diffraction peaks of the soft magnetic phase and the hard magnetic phase and corresponding *RIR* values. After analyzing the diffraction peak height, the volume percent of Fe_7Co_3 phase is calculated to be about 33.8%, which has a minor error with the original composition design because of the statistical error of experimental data.

Table 2 shows the structural and magnetic parameters of $Pr_2Fe_{14}B$, $Nd_2Fe_{14}B$ and $Nd_2Co_{14}B$ monocrystals. In contrast to these parameters, saturation magnetic polarization of $Pr_2Fe_{14}B$ is a little lower than that of $Nd_2Fe_{14}B$, but the anisotropy field is about 1.3 times larger than that one. The anisotropy field is proportionate to the smallest

Table 1 RIR values of two phases and their intensities

Magnetic phase	RIR	Peak (2θ)/(°)	Intensity	Weight percent/%	Volume percent/%
2:14:1	1.65	42.640	65	65	66.2
Fe_7Co_3	10.40	44.742	214	35	33.8