Research articles

Phase composition and magnetic properties in nanocrystalline permanent magnets based on misch-metal

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ABSTRACT

The magnetic properties and phase composition of magnets based on misch-metal (MM) with nominal composition of $MM_{13+x}Fe_{84-x}B_{6.5}$ with x = 0.5, 1, 1.5, 2 and 2.5 using melt-spinning method were investigated. For x = 1.5, it could exhibit best magnetic properties (H_{cj} = 753.02 kA m^{-1}, $(BH)_{max}$ = 70.77 kJ m^{-3}). X-ray diffraction and energy dispersive spectroscopy show that the multi hard magnetic phase of $RE_2Fe_{14}B$ (RE = La, Ce, Pr, Nd) existed in the magnets. The domain wall pinning effect and the exchange coupling interaction between grains are dependent on the abnormal RE-rich phase composition. Optimizing the phase constitution is necessary to improve magnetic properties in MM-Fe-B magnets for utilizing the rare earth resource in a balanced manner.

1. Introduction

Rare earth (RE) permanent magnetic materials play important roles in economics and human life [1]. However, it consumes mainly low-abundance rare earth elements to produce traditional rare earth permanent magnets, leading to the extreme unbalance in the utilization of resources. The consumption of Nd and Pr increases significantly due to the increasing production of Nd-Fe-B permanent magnets in the world [2–5]. Moreover the rare earth minerals are paragenic. Pr and Nd only account for 22% of light rare earth metals in mass, and La ($\geq$25%) and Ce ($\geq$47%) are the most abundant and the least expensive minerals. The market price of Pr and Nd is 10–14 times higher than that of La and Ce. Therefore, it makes sense to search for such a permanent magnetic material with high cost-effectiveness. Developing high abundant rare earth permanent magnets are necessary not only for reducing costs but also for efficient utilization of the resources. Recently, the issue of substitution of Pr-Nd by using the abundant rare earth metals, such as Ce or misch-metal (MM) alloys have attracted renewed attention. However the magnetic properties of magnets based on MM were found to be low [6,7]. The magnitude of coercivity does not meet the application of medium and high-grade products.

Actually, the magnetic properties of $MM_2Fe_{14}B$ prepared in laboratory are much inferior to those of $Nd_2Fe_{14}B$ magnets, and there is some difference in the microstructure and phase constitution between MM-Fe-B and Nd-Fe-B alloys, a small difference in the phase constitution possibly results in a large change in coercivity [8–11]. For $La_2Fe_{14}B$ and $Ce_2Fe_{14}B$, the saturation polarizations $4\pi M_s$ are 13.8 kGs and 11.7 kGs, the magnetocrystalline anisotropy fields (H_A) are 1592 kA·m^{-1} and 2069.6 kA·m^{-1}, but permanent magnet performance cannot be displayed because the phase structure of $La_2Fe_{14}B$ lacks stability [12–14].

Some relevant literature have reported that accumulation of La exists in the RE rich grain-boundary phase [15]. It is found that the inhibitory effect of La on $CeFe_2$ phase and the excess rare elements in MM-Fe-B tend to exist in the form of La-Ce solid solution [16,17]. In our research, we have prepared $MM_{13+x}Fe_{84-x}B_{6.5}$ ribbons by using the misch-metal alloys from Bayan Obo Mine to save the Pr and Nd resources via melt-spinning method, which not only makes the magnetic properties of MM-Fe-B alloys become better, but provides an in-depth understanding of the relationship between phase composition and magnetic properties in MM-Fe-B alloys as well. Phase composition and magnetic properties of MM-Fe-B type magnets with the variation of MM content are investigated at room temperature. Henkel plots were applied to demonstrate the exchange coupling interaction between grains. This method avoids unnecessary separation process of rare earth elements, which utilizes the resources efficiently and protects the environment.

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2. Experiment

The $MM_{13+x}Fe_{84-x}B_{6.5}$ ingots with x = 0.5, 1, 1.5, 2 and 2.5 were prepared by induction melting of constituent elements in an argon atmosphere of high purity. Each ingot was remelted at least two times to ensure composition homogeneity. In our experiment, MM alloys come from Bayan Obo Mine in Baotou, Inner Mongolia, China. It consists of La 28.63 wt%, Ce 50.13 wt%, Pr 4.81 wt%, Nd 16.38 wt% and other inevitable impurities. The purity of starting materials are 99.9% for Fe and 99.2% for Fe-B alloys. The ribbons were obtained by ejecting the melt of the ingot in a quartz tube onto the surface of a rotating copper wheel by pressurized argon atmosphere. The surface velocity of the copper wheel was varied in the range 20–25 m/s for optimizing the magnetic properties. X-ray diffraction (XRD) measurements on the ribbon samples were performed using Cu K_α radiation to determine the crystal structure. Magnetic properties at room temperature were measured by vibrating sample magnetometer (VSM) with a maximum magnetic field of 2388 kA·m^{-1}. The morphologies were studied by transmission electron microscopy (TEM) with an energy dispersive spectroscopy (EDS).

3. Results and discussion

Fig. 1 shows the hysteresis loops for the $MM_{13+x}Fe_{84-x}B_{6.5}$ magnet with x = 0.5, 1, 1.5, 2 and 2.5 obtained by optimum direct quenching at room temperature. The speed of the copper wheel ranges from 20 to 25 m/s. In our research about the effects of MM content on magnetic properties, the optimal speed is found to be 22 m/s, which is used in all the samples. With an increase of MM atomic percent the saturation magnetization decrease, which should partially result from the more amount of RE-rich phases. The variations of coercivity with MM percent content are shown in the inset of Fig. 1. The magnetic properties, i.e., coercivity, remanence, energy product and cost performance are listed in Table 1. With the increase of MM content, the coercivity increases monotonically, but both the remanence and energy product are abnormally dependent on the MM atomic percentage. As the MM atomic percentage increases to 14.5, the MM magnet consists of nearly perfect magnetic properties with the coercivity of 753.02 kA·m^{-1} and the maximum energy product of 70.77 kJ·m^{-3}. With the continuing increase of the MM atomic percentage, the coercivity decreases. The maximum magnetization of each loop
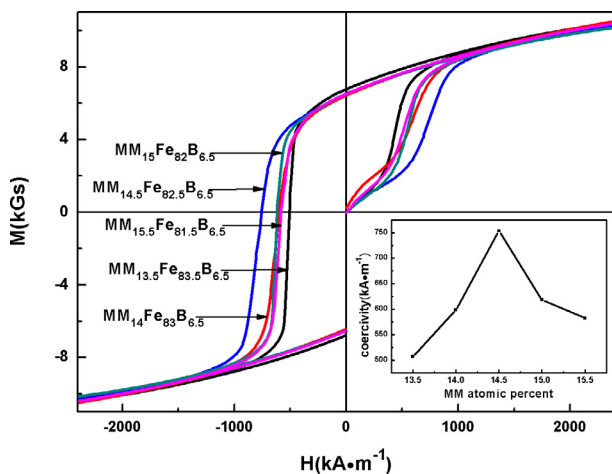
in the first quadrant which were also plotted in this figure, the values of magnetization is low and increases slowly at low field, which then indicates that the domain wall pinning is dominant in the process of magnetization reversal [18]. The domain wall pinning effect of $MM_{14.5}Fe_{82.5}B_{6.5}$ ribbons is the strongest through a comparison of analysis. In order to compare the performance and economic value of MM-Fe-B and PrNd-Fe-B accurately under the same experimental condition, we calculated the Cost Performance (CP, as listed in Table 1) of the sample only considering the cost of experimental materials. Herein, CP is defined as CP = FP · FG^{-1} · · MP^{-1}, and is the cost performance of different REFeB magnets; FP is the total price of various elements in U.S. Dollar/$; FG is the atomic weight of the molecular formula of REFeB magnets; and MP is the REFeB magnetic properties (H_c, $(BH)_{max}$). The smaller the value of CP is, the higher cost-effectiveness the samples can obtain. Table 1 shows that the value of CP(H_c) of $MM_{13+x}Fe_{84-x}B_{6.5}$ is in the range of 0.73–0.82 $/kA·m^{-1}/kg, while CP($H_c$) of the commonly-used PrNd-Fe-B is 2.17 $/kA·m^{-1}/kg; CP($(BH)_{max}$) of $MM_{13+x}Fe_{84-x}B_{6.5}$ ranges from 0.07 to 0.08 $/kJ·m^{-3}/kg, while the CP($(BH)_{max}$) of PrNd-Fe-B is 0.18 $/kJ·m^{-3}/kg . The CP of MM-Fe-B are much less than those of PrNd-Fe-B, suggesting that the MM-Fe-B magnets have higher economic value. In a word, MM-Fe-B magnets have attained excellent magnetic properties and cost-effectiveness.

To understand the pinning effect on domain wall motion, we investigate magnetization behavior in $MM_{14.5}Fe_{82.5}B_{6.5}$ ribbons. Fig. 2 shows the dependence of M_s, H_c and M_r on the applied field in minor loops of $MM_{14.5}Fe_{82.5}B_{6.5}$ ribbons at room temperature. The inset in Fig. 2 shows the original minor hysteresis loops. Fig. 2 reveals the dependence of normalized coercivity and remanence in minor loops on the applied field. Asymmetric minor loops were observed when the maximum applied field (Fig. 2) for certain minor loops is lower than the intrinsic coercivity. This phenomenon may result from the pinning effect of domain wall movements during the magnetization process [18,19]. The normalized coercivity increases faster than remanence, which is an additional evidence for the dominant role of the pinning mechanism on the coercivity of $MM_{14.5}Fe_{82.5}B_{6.5}$ ribbons.

The magnetization reversal is strongly dependent on the intergranular exchange coupling. Henkel plots could be used to investigate the exchange coupling between grains, the expression of δm is defined as $\delta m = [2M_r(H) + M_d(H)]/M_r - 1$. Here $M_r(H)$ is the remanence obtained after the applied field; $M_d(H)$ is the remanent magnetization obtained by applying a reversal field of H; and M_r is the saturated remanence. The δm curve with a positive peak indicates that exchange coupling is dominant over the dipolar interaction. Fig. 3 shows δm values for all samples of $MM_{13+x}Fe_{84-x}B_{6.5}$ ribbons at room temperature, and the peak of δm at the field around coercivity on the curve is shown. The maximum of δm is very low, indicating a weak intergranular exchange coupling in the $MM_{14.5}Fe_{82.5}B_{6.5}$ ribbons with the highest coercivity, which should partially result from the more amount of the RE-rich phase [18–20]. The RE-rich phase exists among the boundaries of the grains, which weakens the coupling between the hard phase grains. Magnets with homogenous distribution of RE-rich phase normally exhibit more excellent coercivity.

The XRD patterns of the $MM_{13+x}Fe_{84-x}B_{6.5}$ magnet with x = 0.5, 1, 1.5, 2 and 2.5 is shown in Fig. 4. It can be seen from Fig. 4 that the magnets consist mainly of $RE_2Fe_{14}B$ phase (RE = La, Ce, Pr, Nd). A small amount of RE-rich phases are observed in the all samples. It can be noticed that the intensity of the diffraction peak of RE-rich phase becomes disorganized with the decrease of the MM atomic percentage. The RE-rich phase cannot be identified which should be responsible for its low content. It can be seen on the XRD patterns that the diffraction peaks are not very smooth, indicating a small amount of amorphous phase and metastable phases

Fig. 1. The hysteresis loops for all samples of $MM_{13+x}Fe_{84-x}B_{6.5}$ ribbons in 22 m/s at room temperature. The inset shows the coercivity with the variation of x from 0.5 to 2.5.