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Review

Effects of the conventional HDDR process and the additions of Co and Zr on anisotropy of HDDR Pr–Fe–B-type magnetic materials

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ABSTRACT

Effects of the conventional hydrogenation disproportionation desorption recombination (HDDR) process and the additions of Co and Zr on anisotropy of HDDR PrFeB-type magnetic materials are investigated. The results show that the degree of anisotropy in conventional HDDR $Pr_{13}Fe_{80}B_7$ materials decreases monotonically with the prolonged disproportionation time, and short disproportionation time is helpful for preparing highly anisotropic $Pr_{13}Fe_{80}B_7$ material. However, it is notable that the degree of anisotropy in conventional HDDR $Pr_{13}Fe_{80}B_7$ materials is significantly smaller than that in solid-HDDR $Pr_{13}Fe_{80}B_7$ materials with the same disproportionation time. At the same time, it is found that the addition of Co and Zr may make HDDR Pr–Fe–B materials that have higher anisotropy compared with HDDR pure ternary $Pr_{13}Fe_{80}B_7$ materials under the same HDDR process, but their degree of anisotropy will also decrease monotonically with the prolonged disproportionation time, and will be close to zero when the disproportionation time is greater than 20 h. Based on this, the origin of anisotropy is discussed by X-ray diffraction (XRD) investigations for the disproportionated products of the above alloys. The results show that the origin of anisotropy in HDDR Pr–Fe–B materials with the addition of Co or Zr may differ from that in HDDR pure $Pr_{13}Fe_{80}B_7$ materials, and the former maybe from the residual "$Pr_2(Fe,Co,Zr)_{14}B$" nucleus while the latter is not. Finally, it is also found that HDDR Pr–Fe–B materials with Co or Zr can obtain high-magnetic properties even if the high-desorption temperature is used, and this shows the addition of Co and Zr may make HDDR Pr–Fe–B materials that have a larger process temperature range.

1. Introduction

The hydrogenation disproportionation desorption recombination (HDDR) process is well known as an effective way for producing anisotropic $Nd_2Fe_{14}B$-type magnetic powders [1]. $Pr_2Fe_{14}B$-type alloys are comparable in terms of their intrinsic magnetic properties and phase relations with the advantages of a much lower spin-reorientation temperature [2], so the HDDR process is tried in the preparation of anisotropic $Pr_2Fe_{14}B$-type magnetic powders. It has been shown that both anisotropic ternary Pr–Fe–B and Pr–Fe–B-type powders with alloying additions can be prepared by the appropriate solid-HDDR process [3–9]. However, the origin of anisotropy is unclear till now. Gutfleisch et al. found that there exist intermediate phase Fe_3B and $Pr(Fe,Co)_{12}B_6$ in the solid disproportionated products of $Pr_{13.7}Fe_{80.3}B_6$ and $Pr_{13.7}Fe_{63.5}Co_{16.7}Zr_{0.1}B_6$ alloys, respectively, and the amount of intermediate phase is related to the degree of anisotropy (DOA) in the final products [4,10]. However, he did not find the above two intermediate phases in the corresponding conventional disproportionated products. Cannesan et al. [11] observed the intermediate phase $Pr(Fe,Co)_{12}B_6$ in the $Pr_{13.7}Fe_{63.5}Co_{16.7}Zr_{0.1}B_6$ conventional disproportionated products processed at 860 °C and above, and advanced that the intermediate phase may play a role in inducing texturing on further treatment of the materials. The present authors also investigated the preparation of anisotropic ternary $Pr_{13}Fe_{80}B_7$ powders using the solid-HDDR process and mechanism on the formation of anisotropy [9]. It was found that the degree of anisotropy in final HDDR $Pr_{13}Fe_{80}B_7$ is related to the disproportionation time, and the short disproportionation time is helpful for high anisotropy while long disproportion time will lead to isotropic powders. At the same time, according to investigations for the disproportionated products of $Pr_{13}Fe_{80}B_7$ alloys, no other phases except PrH_2, Fe and Fe_2B, and the origin of anisotropy is found to be related to the early rod-like disproportionation microstructure.

To further understand the preparation process of anisotropic Pr–Fe–B powders and how the anisotropy is formed, the effects of the conventional HDDR process and the alloying additions on the anisotropic Pr–Fe–B magnetic powders are firstly investigated in the paper, and then the origin of anisotropy is analyzed on the

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basis of the above results. Finally, effects of alloying additions on the preparation process of HDDR Pr–Fe–B materials are discussed.

2. Experimental procedure

The alloys with a nominal composition of $Pr_{13}Fe_{80}B_7$, $Pr_{13}Fe_{69}Co_{11}B_7$ and $Pr_{13}Fe_{79.8}Zr_{0.2}B_7$ are melted under an argon atmosphere in a vacuum induction furnace. The alloy ingots are homogenized at 1050 °C for 24 h and crushed into powders with a particle diameter size of ~0.2 mm. The above as-cast powders are conventional disproportionated or solid disproportionated at temperature of 800 °C for 5 min–20 h with partial pressure of 0.1 MPa, followed by a slow desorption rate under 2.0×10^{-4} m^3/min at 800–920 °C for 45 min and a 15 min desorption in high vacuum. The HDDR-treated Pr–Fe–B magnetic powders are mixed with epoxy resin, and then molded into bonded magnet in a magnetic alignment field of 1.5 T. Magnetic measurements are carried out on a *B–H* tracer. The degree of anisotropy is calculated by the following equation: $DOA = (Br_{\parallel} - Br_{\perp})/Br_{\parallel}$, where $Br_{\parallel}$ and $Br_{\perp}$ are the remanence of the sample parallel and perpendicular to the alignment field. Microstructure changes are investigated by X-ray diffraction (XRD).

3. Results and discussions

3.1. Effects of the conventional HDDR process on the anisotropy of HDDR $Pr_{13}Fe_{80}B_7$ magnetic materials

Since the degree of anisotropy in the HDDR products is found to be related to the disproportionation time of the solid-HDDR process [9], the effects of the disproportionation time in the conventional HDDR process on the degree of anisotropy is mainly investigated. At the same time, the similar effects in the solid-HDDR process are also listed in the figure for a comparison. The results are shown in Fig. 1.

It is seen that DOA of HDDR $Pr_{13}Fe_{80}B_7$ magnetic materials significantly depend on the disproportionation time of the conventional HDDR process. When the disproportionation time is 0.5 h, the DOA of HDDR $Pr_{13}Fe_{80}B_7$ magnetic material is 0.2. With the prolonged disproportionation time, the DOA of the above materials decreases gradually. When the disproportionation time reaches 4.5 h, the DOA is close to zero, i.e. the final material is isotropic. The above results show that short disproportionation time is also helpful for preparing anisotropic magnetic materials even if the conventional HDDR process is used. This is very similar to the effects of the disproportionation time on the anisotropy in the solid-HDDR process. However, it is notable that the DOA of the conventional HDDR magnetic materials are significantly smaller than that of the solid HDDR magnetic material when the disproportionation time of the above two HDDR process is the same, as is easily seen in the figure.

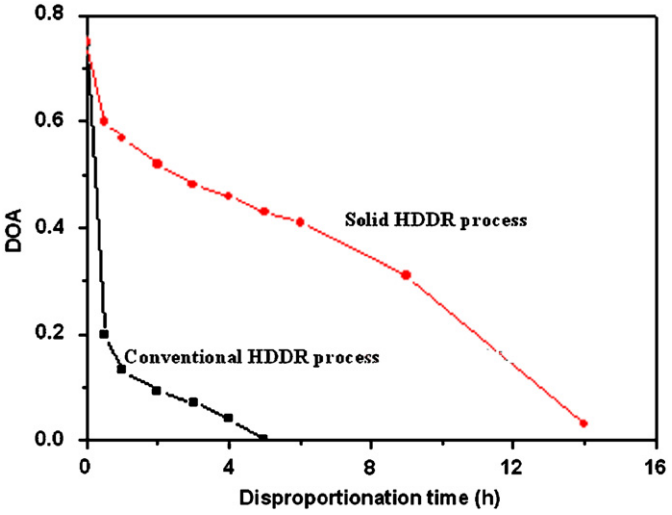

Fig. 1. Effects of disproportionation time on DOA of conventional and solid HDDR $Pr_{13}Fe_{80}B_7$-bonded magnet.

3.2. Effects of Co and Zr addition on the anisotropy of HDDR Pr–Fe–B magnetic materials

It has been shown that Co and Zr addition is helpful for preparing anisotropic Pr–Fe–B magnetic materials [4–8], but the study on the detailed relationship between the additions and the DOA of HDDR $Pr_{13}Fe_{80}B_7$ magnetic materials is very limited.

Fig. 2 shows effects of Co and Zr addition on the DOA of solid HDDR Pr–Fe–B magnetic materials. It is seen that Co and Zr is helpful for preparing highly anisotropic materials, and the HDDR $Pr_{13}Fe_{69}Co_{11}B_7$ and $Pr_{13}Fe_{79.8}Zr_{0.2}B_7$ can have higher anisotropy than the HDDR pure ternary $Pr_{13}Fe_{80}B_7$ materials when the disproportionation time is the same. However, it is notable that the DOA of HDDR $Pr_{13}Fe_{69}Co_{11}B_7$ and $Pr_{13}Fe_{79.8}Zr_{0.2}B_7$ magnetic materials also decrease monotonically with the prolonged time, but their decreasing rate is slower than that of the DOA in the HDDR pure ternary $Pr_{13}Fe_{80}B_7$ magnetic materials. Moreover, the decreasing rate of DOA in the HDDR $Pr_{13}Fe_{69}Co_{11}B_7$ materials is slower than that of HDDR $Pr_{13}Fe_{79.8}Zr_{0.2}B_7$ materials when the disproportionation time is longer than 9 h. This results show that the Co and Zr additions can make the final HDDR PrFeB-type materials have higher anisotropy compared with the HDDR pure ternary $Pr_{13}Fe_{80}B_7$ materials under the same HDDR process.

3.3. XRD investigations for the disproportionated products of $Pr_{13}Fe_{80}B_7$ $Pr_{13}Fe_{69}Co_{11}B_7$ and $Pr_{13}Fe_{79.8}Zr_{0.2}B_7$

To understand the origin of anisotropy in the above HDDR Pr–Fe–B materials, XRD are used to investigate their disproportionated products. The results are shown in Fig. 3. It is seen that when the disproportion time is 15 min, there exist some undecomposed $Pr_2(Fe,Co)_{14}B$ and $Pr_2(Fe,Zr)_{14}B$ phase in the disproportionated products of $Pr_{13}Fe_{69}Co_{11}B_7$ and $Pr_{13}Fe_{79.8}Zr_{0.2}B_7$, but no residual $Pr_2Fe_{14}B$ are found in the $Pr_{13}Fe_{80}B_7$ disproportionated products. Further experimental results show that the quantity of undecomposed $Pr_2(Fe,Co)_{14}B$ and $Pr_2(Fe,Zr)_{14}B$ will decrease gradually with

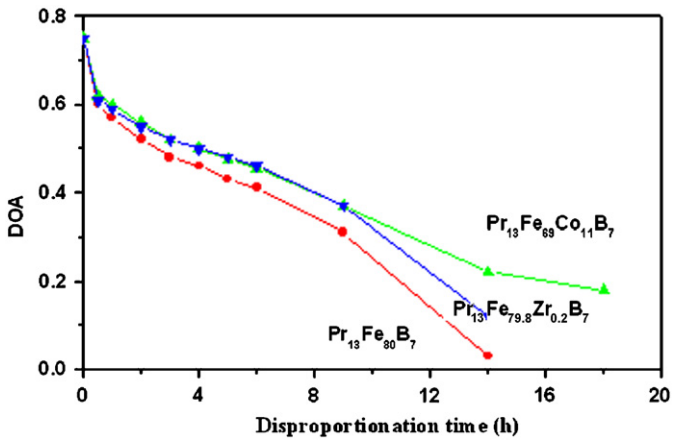

Fig. 2. Effects of disproportionation time on DOA of solid HDDR $Pr_{13}Fe_{80}B_7$, $Pr_{13}Fe_{69}Co_{11}B_7$ and $Pr_{13}Fe_{79.8}Zr_{0.2}B_7$ bonded magnet.