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Anisotropic HDDR Nd–Fe–B magnetic powders prepared directly from strip casting alloy flakes

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ABSTRACT

The effects of strip casting (SC)–hydrogenation, disproportionation, desorption, and recombination (HDDR) process parameters on the microstructures of Nd–Fe–B alloy flakes and the magnetic properties of HDDR powders are investigated. The results indicate that the alloy flakes prepared by SC speed of 3 m/s display the optimized microstructure. From this as-cast alloy flakes, anisotropic magnetic powders can be prepared by a slow recombination treatment during the HDDR. The hydrogen pressure of slow recombination treatment (HPSR) has an important influence on the microstructures and magnetic properties of powders. The remanence B_r, coercivity H_{cj} and magnetic energy product $(BH)_{max}$ of the magnetic powders all increase firstly, and then decrease with increasing HPSR. While the HPSR is 0.3 bar, the magnetic properties of the powders reach the maximum values of B_r = 1.3 T, H_{cj} = 954.3 kA/m, $(BH)_{max}$ = 259 kJ/m^3, respectively. Our results confirm that highly anisotropic HDDR magnetic powders prepared directly from the as-cast SC alloy flakes without any heat treatment can be obtained.

1. Introduction

The hydrogenation, disproportionation, desorption, and recombination (HDDR) process is an effective technique for producing anisotropic Nd–Fe–B magnetic powders [1,2]. By this process, the original large $Nd_2Fe_{14}B$ crystalline grains are transformed into fine crystalline grains with diameter of around 0.3 μm, which is close to single domain size of $Nd_2Fe_{14}B$ phase [3,4]. In the early stages, the HDDR magnetic powders were commonly prepared from segregated master ingots and the magnetic properties were low due to the existence of soft magnetic α-Fe in the master ingots [5–7]. Afterward, Morimoto et al. [8,9] prepared SC (strip casting) alloy flakes consisting of columnar $Nd_2Fe_{14}B$ grains with width of 10–30 μm and very fine lamellae of the Nd-rich phase, and especially containing no α-Fe, which was very suitable for preparing HDDR magnetic powders. Initially, the HDDR magnetic powders prepared directly from the as-cast SC alloy flakes without any heat treatment were isotropic [8]. Subsequently, anisotropic magnetic powers were obtained by homogenizing SC alloy flakes before the HDDR process. The magnetic properties of such powders were close to the optimum magnetic properties of sintered magnet [9]. However, the homogenizing heat treatment not only engrosses long time, but also consumes huge amounts of energy. Up to date, the preparation of anisotropic magnetic powers directly from the as-cast SC alloy flakes without any heat treatment has still not been reported. In order to save time and energy, and to reduce the cost, this paper will examine the possibility of preparing anisotropic magnetic powders directly from as-cast SC alloy flakes without any heat treatment. In particular, the effects of the wheel speed and the hydrogen pressure of slow recombination treatment (HPSR) on the microstructures of SC alloy flakes and magnetic properties of the powders will be reported.

2. Experimental procedure

The composition of the studied alloys is $Nd_{12.8}Fe_{72}Co_{7.8}B_7Zr_{0.1}Ga_{0.3}$. The molten alloys are ejected onto a copper wheel surface rotating at different speeds from 1 to 4 m/s to form the SC alloy flakes, which are crushed into small pieces less than 5 mm, and then subjected to a modified HDDR process treatment to prepare the magnetic powders. The HDDR process conditions are shown in Fig. 1. First, the SC alloy flakes are heated from room temperature to 800 °C at a heating rate of 15 °C/min under a hydrogen pressure of 1 bar, and then kept at this temperature and pressure for 40 min. Second, the disproportionated mixture is followed by an s-DR (s-DR: a slow desorption–recombination reaction in low hydrogen pressure) treatment at 850 °C for 0.5 h under a partial pressure of 0.1–0.7 bar, and then followed by a c-DR treatment (c-DR: a conventional desorption–recombination reaction, i.e., a fast desorption–recombination reaction in high vacuum) at 850 °C for 1 h. Last, the alloys are quenched by argon gas to room temperature. The microstructures of the Nd–Fe–B alloy flakes and the magnetic powders are observed using a scanning electron microscopy (SEM). After the magnetic powders are aligned in a magnetic field of 1.2 MA m^{-1}, their properties are measured using the vibrating sample magnetometer (VSM) with a maximum field of 2 MA m^{-1} at room temperature. The degree of anisotropy (DOA) of the magnetic powders is evaluated using the ratio of remanence to saturation magnetization (B_r/B_s, the value of B_s is the actually measured value of the magnetic powders).

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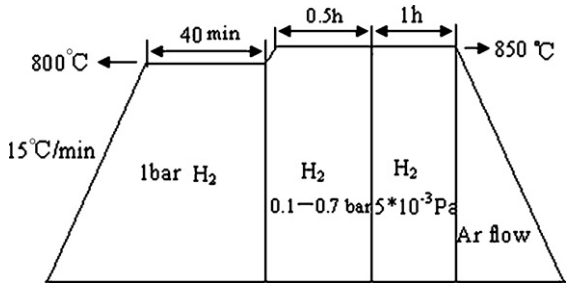
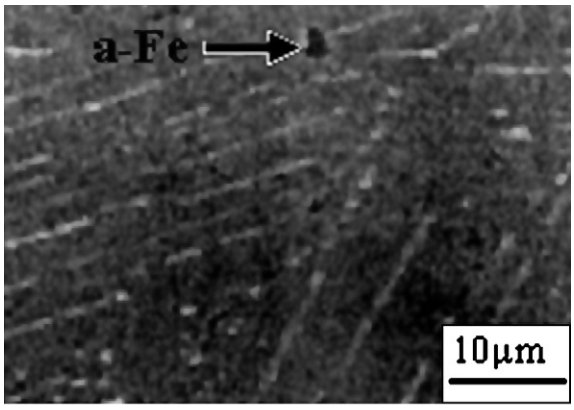


Fig. 1. Sketch of process conditions.

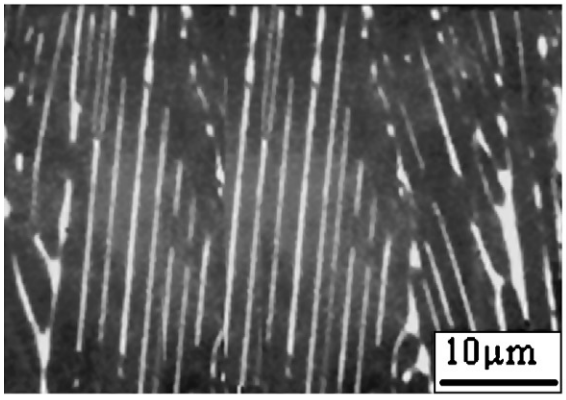
3. Results and discussion

Fig. 2 shows back-scattered electron images of Nd–Fe–B alloy flakes parallel to cooling direction, the corresponding SC speeds are: (a) 2 m/s, (b) 3 m/s, and (c) 4 m/s, respectively. The observation plane is parallel to the direction of solidification. The grey portion is the main phase $Nd_2Fe_{14}B$ and the white portion is the Nd-rich phase in these alloy flakes. And the *c*-axis of individual Nd–Fe–B grain is perpendicular to the strip plane. The microstructures of the SC alloy flakes are closely related to the cooling speed. For the alloy flakes prepared with $v = 2$ m/s, their free surface displays α-Fe dendrites due to the slow cooling speed, the Nd-rich phase segregates and is distributed unevenly. For the alloy flakes prepared with $v = 3$ m/s, the uniformly distributed Nd-rich phase with a width about 0.05–0.1 μm divides the main phase $Nd_2Fe_{14}B$ into lamellae crystals with a width ranging from 0.5 to 2 μm. The main phase lamella crystals show parallel orientation. The Nd-rich phase is distributed uniformly and α-Fe is not present. This is basically consistent with some reports [10,11]. For the alloy flakes prepared with $v = 4$ m/s, there is a pool region of Nd-rich phases near the free surface, which leads to the segregation of the Nd-rich phase. The lamella crystals of the main phase also become narrow. From the above analysis, the alloy flakes prepared with $v = 3$ m/s display the optimized microstructure. Subsequently, the HDDR magnetic powders are prepared from this as-cast SC alloy flakes without any heat treatment.

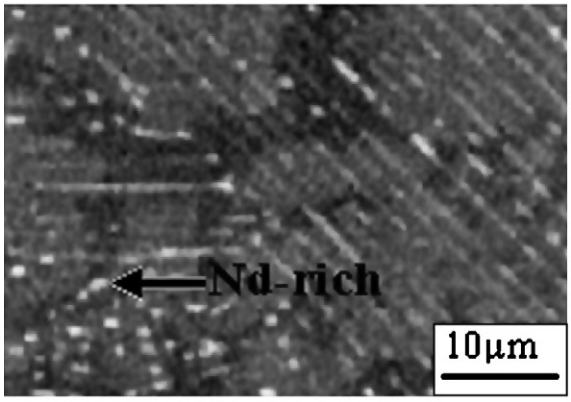
Fig. 3 shows the microstructures of HDDR powder particles corresponding to the HPSR of 0.1, 0.3 and 0.5 bar, respectively. The microstructure observations indicate that the original large $Nd_2Fe_{14}B$ crystalline grains in these alloys are converted into fine recombined grains of sub-micrometre size, the adjacent grains contact directly with each other, and do not involve any boundary phases. However, Ref. [12] pointed out that in fully processed HDDR material, the $Nd_2Fe_{14}B$ crystallites are separated by a crystalline phase. This contradiction between this paper and Ref. [12] may be attributed to different alloy's composition and technical process. For a HPSR of 0.3 bar, the powder particle consists of $Nd_2Fe_{14}B$ grains with a uniform size distribution from 200 to 300 nm, which is close to the single domain size of $Nd_2Fe_{14}B$ phase. For a HPSR of 0.1 and 0.5 bar, respectively, the powder particles all contain $Nd_2Fe_{14}B$ grains with a wider size distribution from 150 to 500 nm, and the granularity of most grains is about 300 nm. These magnetic powders are all anisotropic, and do not contain the soft magnetic phase α-Fe. Ref. [8] reported that the magnetic powders prepared from the as-cast SC alloy flakes did not involve α-Fe either, however, the magnetic powders were isotropic. This is ascribed to their different processing procedures during the recombination stage. In the recombination stage, the disproportionated products are firstly carried out a s-DR treatment before they are carried out c-DR treatment to prepare the magnetic powders in this paper, however, the disproportionated products are directly subjected to a c-DR treatment to produce the magnetic powders in Ref. [8]. From the above



(a) $v = 2$ m/s



(b) $v = 3$ m/s



(c) $v = 4$ m/s

Fig. 2. Back-scattered electron micrographs of Nd–Fe–B alloy flakes parallel to cooling direction, the SC speeds are: (a) 2 m/s, (b) 3 m/s, and (c) 4 m/s, respectively.

analysis, it is concluded that the s-DR treatment carrying out on the disproportionated products is favorable to the inducement of anisotropy. Sugimoto et al. [7] also reported similar results that the s-DR treatment is an effective method for producing highly anisotropic HDDR Nd–Fe–B magnetic powders. This is attributed to the fact that the system free energy changes (ΔG) are closely associated with the hydrogen pressure of the recombination reaction (P), the higher P is, the smaller ΔG is, thus, the driving force (ΔW) of the recombination reaction is also smaller. The nucleation of recombined $Nd_2Fe_{14}B$ grains with the same orientation as the original grains requires only a small ΔG [7]. When the disproportionated mixture is subjected to an s-DR treatment, P is higher, ΔG and ΔW are smaller, thus, the grains orient along the same direction as the original grains. In contrast, while the disproportionated

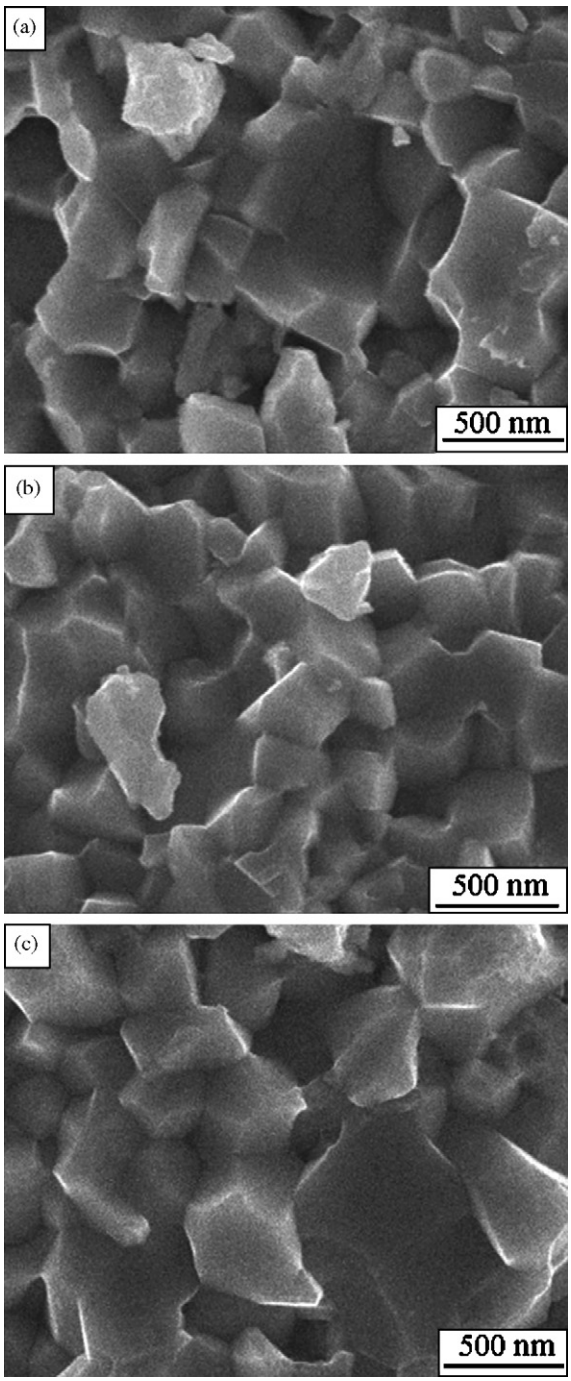


Fig. 3. SEM micrographs of fracture surfaces of $Nd_{12.8}Fe_{72}Co_{7.8}B_7Zr_{0.1}Ga_{0.3}$ powder particles prepared from the optimized as-cast alloy flakes without any homogenizing heat treatment, the particle morphology presents a faceted shape, and its size distributes between 50 μm and 100 μm. The HPSR are: (a) 0.1 bar, (b) 0.3 bar, and (c) 0.5 bar, respectively.

mixture is directly subjected to a c-DR treatment, P is lower, ΔG and ΔW are higher, therefore, a greater number of misoriented nuclei form [7].

Fig. 4 shows the dependence of magnetic properties of the powders on the HPSR. It can be seen that the remanence B_r, coercivity H_{cj}, magnetic energy product $(BH)_{max}$ and degree of anisotropy DOA all increase firstly, and then decrease with increasing HPSR. While the HPSR is 0.3 bar, the magnetic properties achieve the maximum values of B_r = 1.3 T, H_{cj} = 954.3 kA/m, $(BH)_{max}$ = 259 kJ/m^3 and DOA = 0.87, respectively. The ratio of remanence to saturation

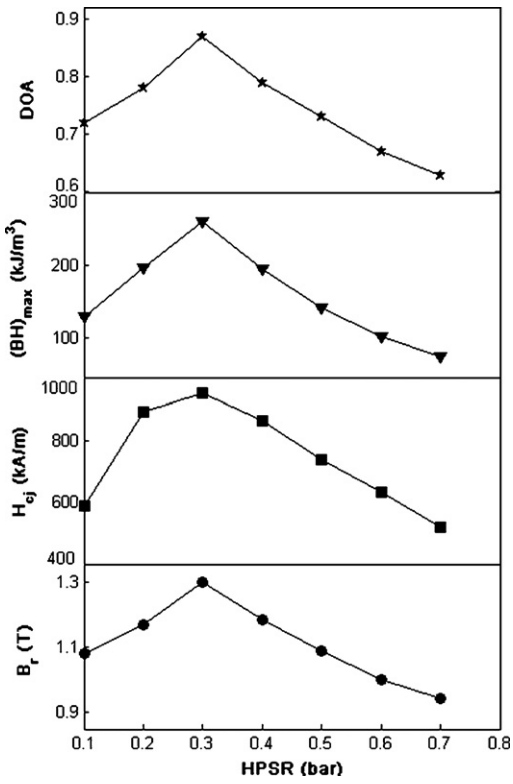


Fig. 4. Dependence of magnetic properties of HDDR Nd–Fe–B powders on the HPSR.

magnetization is much larger than 0.5, which indicates that the magnetic powders are highly anisotropic. It is assumed that the rate of recombination (RR) in the slow recombination stage only depends on the HPSR. For the HPSR of 0.3 bar, the RR is low, which is beneficial to the preferred orientations of anisotropy nucleus, and is also helpful to the improvement of material properties in thermodynamic terms. Too low values of HPSR quicken the RR. The faster RR is not only harmful for the inducement of anisotropy, but also reduces the magnetic properties of the powders. This is attributed to the assumption that the faster RR can result in random orientations of recombined grains [13], and also cause a complete recombination reaction in a short time. However, the setup of long time for the slow recombination stage results in abnormal growth of the newly recombined $Nd_2Fe_{14}B$ grains. Too high values of HPSR lower the RR. The lower RR also causes the excessive growth of the newly recombined $Nd_2Fe_{14}B$ grain, and even some large grains with irregular boundaries appear, thus, also reduce the magnetic properties. Fig. 3 shows that a too small as well as a too large HPSR (corresponding to a too large and a too small rate of recombination, respectively) all leads to excessive growth of some newly recombined $Nd_2Fe_{14}B$ grains, which is in agreement with the above assumptions.

4. Conclusions

In summary, above analysis indicates that the microstructure of Nd–Fe–B alloy flakes and the magnetic properties of powders sensitively depend on the parameters of SC–HDDR process. As-cast alloy flakes with optimized microstructure can be processed to anisotropic powders by an s-DR treatment during the HDDR process. The s-DR treatment is an effective way of obtaining highly anisotropic HDDR Nd–Fe–B magnetic powders. The magnetic properties of the powders obtained in this paper are lower than that prepared from the SC alloy flakes subjected to a homogenizing heat treatment in Ref. [9], but are much higher than that prepared from

the same as-cast SC alloy flakes in Ref. [8]. Our work shows that long time and huge amounts of energy are saved due to the absence of a homogenizing heat before the HDDR process, and the costs are reduced. So this process has a very important economic implication, beside the possibility to prepare anisotropic powders with high properties.

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References

[1] T. Takeshita, R. Nakayama, Proceedings of the 12th International Workshop on Rare-Earth Magnets and Their Applications, Canberra, 1992, p. 670.
[2] I.R. Harris, Proceedings of the 12th International Workshop on Rare-Earth Magnets and Their Applications, Canberra, 1992, p. 347.
[3] R. Nakayama, T. Takeshita, J. Appl. Phys. 74 (1993) 2719–2724.
[4] T. Takeshita, K. Morimoto, J. Appl. Phys. 79 (8) (1996) 5040–5044.
[5] R. Nakayama, T. Takeshita, M. Itakura, N. Kuwano, K. Oki, J. Appl. Phys. 76 (1) (1994) 412–417.
[6] H. Nakamura, R. Suefuji, S. Sugimoto, M. Okada, M. Homma, J. Appl. Phys. 76 (10) (1994) 6828–6830.
[7] S. Sugimoto, H. Nakamura, K. Kato, D. Book, T. Kagotani, M. Okada, M. Homma, J. Alloys Compd. 293–295 (1999) 862–867.
[8] K. Morimoto, E. Niizuma, R. Nakayama, K. Igarashi, J. Magn. Magn. Mater. 263 (2003) 201–207.
[9] K. Morimoto, K. Kato, K. Igarashi, R. Nakayama, J. Alloys Compd. 366 (2004) 274–278.
[10] J. Bernardi, J. Fidler, M. Sagawa, Y. Hirose, J. Appl. Phys. 83 (1998) 6396–6398.
[11] F. Vial, F. Joly, E. Nevalainen, M. Sagawa, K. Hiraga, K.T. Park, J. Magn. Magn. Mater. 242–245 (2002) 1329–1334.
[12] W.F. Li, T. Ohkubo, K. Hono, Proceedings of the 20th International Workshop on Rare Earth Permanent Magnets, Crete, 2008, p. 114.
[13] J.R. Gao, X.P. Song, X.T. Wang, J. Alloys Compd. 267 (1998) 270–273.