A Thermodynamic Study of the HDDR Conditions in the Sm$_2$Fe$_{17}$N$_x$ Compound

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This paper describes the relationship between hydrogen pressure and temperature ($P$-$T$ curve) in the HDDR treatment of the Sm$_2$Fe$_{17}$ compound. The $P$-$T$ curve suggested that the HDDR condition of the Sm$_2$Fe$_{17}$ compound is more sensitive to temperature than that of the Nd$_2$Fe$_{14}$B compound. It was also found that the HDDR treatment of the Sm$_2$Fe$_{17}$ compound has to be controlled in the hydrogen pressure range of one order lower than that of the Nd$_2$Fe$_{14}$B compound, because of its lower optimum HDDR temperature. Using the $P$-$T$ curve, new HDDR treatments named v-HD and s-DR, were carried out in order to induce anisotropic feature. However, the normalized remanence of the new HDDR treated powders was around 0.52, which suggested that the powders were almost magnetically isotropic.

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1. Introduction

The hydrogenation, disproportionation, desorption, and recombination (HDDR) phenomena in Nd–Fe–B alloys have got a lot of attention for the production of anisotropic bonded magnet powders. Many researchers have reported that the additional elements are needed for the production of anisotropic powders. However, Nakamura et al. reported that anisotropic powders in the ternary alloys can be produced by controlling the temperature of recombination reaction in HDDR treatments. They also clarified the temperature dependence of the recombination pressure ($P$-$T$ curve) of the Nd$_2$Fe$_{14}$B compound, and established necessary HDDR treatment conditions for the production of high performance anisotropic ternary alloy powders.

Since the conventional HDDR treatment was composed of heat treatment in hydrogen (c-HD) and in vacuum (c-DR), the newly proposed HDDR pressure was combination of v-HD or l-HD (heating in vacuum or in a low hydrogen pressure during the Hydrogenation Disproportionation stage), and s-DR (heating in Ar or in hydrogen with a certain pressure at the start of the Recombination treatments). However, the HDDR treated Nd–Fe–B powders show large thermal coefficient of coercivity, because of low Curie temperature compound and large grain size.

The Sm$_2$Fe$_{17}$N$_x$ compound exhibits higher Curie temperatures and anisotropy field than the Nd$_2$Fe$_{14}$B compound. Therefore, the compound is a good candidate for bonded magnet powders. The HDDR treatments of the Sm$_2$Fe$_{17}$N$_x$ compound have been reported and high coercivity was obtained. First, the HDDR treatment is performed to the Sm$_2$Fe$_{17}$N$_x$ compound, which causes the reaction described as

$$\text{Sm}_2\text{Fe}_{17} + 2\text{H}_2 = 2\text{SmH}_2 + 17\text{Fe}. \quad (1)$$

Subsequently, the HDDR treated Sm$_2$Fe$_{17}$ powders are subjected into nitrogen gas to form the Sm$_2$Fe$_{17}$N$_x$ compound. However, as those obtained Sm$_2$Fe$_{17}$N$_x$ powders are magnetically isotropic, the production of anisotropic powders is strongly demanded for the production of high performance bonded magnets.

The conventional HDDR treatment reported in the Sm$_2$Fe$_{17}$N$_x$ compound is only composed of c-HD and c-DR treatments, and there is no report using the combination of v-HD (or l-HD) and s-DR treatments. In addition, the relationship between hydrogen pressure and temperature during the HDDR treatment in the Sm$_2$Fe$_{17}$ compound, which leads to the $P$-$T$ curve, has not been investigated yet. Therefore, in this paper, the $P$-$T$ curve of the Sm$_2$Fe$_{17}$ compound was produced, and magnetic properties of the Sm$_2$Fe$_{17}$N$_x$ powders produced by using v-HD and s-DR treatments have been investigated.

2. Experimental Procedure

The composition of the studied alloy was Sm$_2$Fe$_{17}$. The alloys were induction melted under argon atmosphere, and the ingots were homogenized at 1000°C for 50h. Then the ingots were crushed under 63 µm and compacted applying the pressure of 150 MPa.

The hydrogen pressure and temperature of the recombination reaction were measured using the $\Delta Q$ method, in which the hydrogen absorption and desorption characteristics of the alloys can be investigated by monitoring the quantitative change in hydrogen gas flow entering ($Q_{in}$) and exiting the furnace ($Q_{out}$). Details of the $\Delta Q$ method were described elsewhere.

The compacted Sm$_2$Fe$_{17}$ samples were disproportionated by heating up to ~800°C at a rate of 400°C h$^{-1}$ under hydrogen atmosphere with hydrogen pressure of 0.1 MPa. Subsequently, the $\Delta Q$ measurements were performed up to ~1150°C at a rate of 100 and 400°C h$^{-1}$ under a mixture of argon and hydrogen, and with a partial pressure of hydrogen ($P_H2$) that was varied between 0.01 and 0.1 MPa. The total gas flow rate used was 5 × 10$^{-4}$ m$^3$m$^{-1}$. The HDDR treatment carried out in this investigation is shown schematically in Fig. 1. The treatment temperature was 750°C and the heat treatments in disproportionation reaction were performed for 1h using c-HD or v-HD treatment.
Subsequently, the heat treatments in recombination reaction were performed for 10 min using c-DR or s-DR treatment. The magnetic properties were measured using a vibrating sample magnetometer (VSM) with a maximum applied field of 1.2 MA m\(^{-1}\).

### 3. Results and Discussion

#### 3.1 The hydrogen pressure-temperature diagram

The recombination pressure and temperature diagram of the disproportionated Sm\(_2\)Fe\(_{17}\) compound was investigated. Figure 2 shows the hydrogen desorption characteristics of disproportionated Sm\(_2\)Fe\(_{17}\) alloys heated at a rate of 400°C h\(^{-1}\) under different partial pressure of hydrogen (\(P_{H_2} = 0.01, 0.05, 0.1\) MPa). The peaks in the figure are associated with the recombination reaction, in which the Sm\(_2\)Fe\(_{17}\) compound is formed from the disproportionated mixture of SmH\(_2\) and Fe. All the peaks shifted to lower temperature with decreasing \(P_{H_2}\) due to the lower stability of the disproportionated mixture at lower \(P_{H_2}\). The same \(\Delta Q\) measurement was carried out by changing heating rate and the starting temperatures of desorption peaks (\(T_s\)) were plotted against the heating rate as shown in Fig. 3. In order to eliminate the influence of the heating rate, the values obtained by extrapolating to 0°C h\(^{-1}\) were used as starting desorption temperature (\(T_s\)).

Figure 4 shows the temperature dependence of normalized hydrogen pressure (\(P_{H_2}/P_0\)), where \(P_0\) is the atmospheric pressure (101.325 kPa). This figure reveals a linear relationship between \(\ln(P_{H_2}/P_0)\) and \(T^{-1}\), which results that the normalized hydrogen pressure are described as

\[
\ln(P_{H_2}/P_0) = -29.489/T(K) + 23.434.
\]

Therefore, the critical hydrogen pressure for recombination reaction (\(P_{\text{recomb}}\)) at temperature (\(T\)) can be expressed as

\[
P_{\text{recomb}} = P_0 \exp(-29.489/T(K) + 23.434).
\]

From this relationship, the \(P-T\) curve of the Sm\(_2\)Fe\(_{17}\) compound is obtained as shown in Fig. 5, indicating the equilibrium hydrogen pressure and temperature of the reaction expressed by the eq. (1). The curve divides the diagram into two regions (I and II) as shown in Fig. 5: (I) the Sm\(_2\)Fe\(_{17}\) compound is stable, (II) the disproportionated mixture is stable.

The \(P-T\) curve of the Nd\(_2\)Fe\(_{14}\)B compound, reported by Nakamura et al., is also shown in Fig. 5. The \(P-T\) curve of the Sm\(_2\)Fe\(_{17}\) compound was flatter than that of the Nd\(_2\)Fe\(_{14}\)B compound, which suggests that the recombination reaction of the Sm\(_2\)Fe\(_{17}\) compound is more sensitive to temperature than that of the Nd\(_2\)Fe\(_{14}\)B. The optimum HDDR treatment temperatures reported in the Sm\(_2\)Fe\(_{17}\) compound\(^8, 9\) are about 100°C lower than those in the Nd\(_2\)Fe\(_{14}\)B compound\(^3, 4\). Therefore, the hydrogen pressure for the HDDR treatment of the Sm\(_2\)Fe\(_{17}\) compound has to be controlled in the hydrogen pressure range one order lower than that of the Nd\(_2\)Fe\(_{14}\)B compound. This indicates that it is difficult to control the hy-
the Sm$_2$Fe$_{17}$ compound.

3.2 The HDDR treatments and magnetic properties

In the case of Nd–Fe–B alloys, the highly anisotropic powders have been obtained by utilizing the v-HD and s-DR treatments under the hydrogen pressure close to the critical $P$–$T$ curve. Therefore, it may also be possible to obtain anisotropic Sm$_2$Fe$_{17}N_x$ powders by utilizing the same treatments as Nd–Fe–B alloys. From the conception, we investigated the magnetic properties of HDDR treated Sm$_2$Fe$_{17}N_x$ powders after v-HD and s-DR treatments. Based on the $P$–$T$ curve obtained in the investigation, the starting hydrogenation pressure ($P_{H_2-HD}$) of HDDR treatment was determined 0.4 kPa, which suggested that the powders were almost magnetically isotropic. Even though the HDDR treatment related to the $P$–$T$ curve was carried out in this investigation, the inducement of anisotropy was not observed in the Sm$_2$Fe$_{17}N_x$ compound. Considering differences from the Nd$_2$Fe$_{14}B$ compound, this result suggests that the presence of the phase such as the iron-boride one in the disproportionated mixture, crystal structure of magnetic phases, and crystal orientation relationships between parent phase and disproportionated mixture, could be important factors in the promotion of anisotropy in the HDDR phenomena.

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