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Effect of Hydrogen Pressure and Alloying Additives on Disproportionation Kinetics of Nd-Fe-B Alloy

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1. Introduction

The HDDR (hydrogenation, disproportionation, desorption and recombination) process has been established as a useful means of producing highly coercive Nd-Fe-B powder with fine grain structure directly from an ingot alloy. Most attractive feature of the HDDR process is that an anisotropic powder with good $Nd_2Fe_{14}B$ grain texture can be preparedby applying the process to Nd-Fe-B ingot alloy. The anisotropic powder particles can be aligned in a magnetic field and can be used to produce a high performance anisotropic bonded magnet. In the anisotropic HDDR treatment,the critical step playing a key role in determining the texture in the final product is the disproportionation. The hydrogen pressure during the disproportionation controls the kinetics of the disproportionation reaction, and this strongly influencesthe texture in the final HDDR-treated material. Therefore a precise understanding of the kinetics of disproportionation is essential for controlling the texture. In addition, for the production of highly anisotropic Nd-Fe-B alloy HDDR powder with good texture, the alloy is usually modified by addition of Ga, Nb, and the disproportionation kinetics should be controlled carefully by using lower hydrogen pressure. It is known that the Ga-, Nb- addition increases the coercivity and remanence of the HDDR-treated Nd-Fe-B material, respectively. It is also reported that Nb helps stabilizing the iron boride phase of the disproportionated phases, which acts as a memory site for a texture, and Ga is beneficial for suppressing the excessive growth of recombined grains. The authors believe that the addition of Ga and/or Nb may influence the disproportionation kinetics of the Nd-Fe-B alloy, of which careful control is utmost important for improving the texture of recombined $Nd_2Fe_{14}B$ grains. In the present study, the effect of hydrogen pressure and Ga, Nb addition on disproportionation kinetics of Nd-Fe-B alloy and the disproportionation mechanism were investigated.

2. Experiment

The $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$alloy used in the present study was prepared by arc-melting of the high purity constituent metals. The prepared alloy buttons were homogenised at 1413 K for 40 hr under argon gas. The homogenised alloys were pulverised into powder with a particle size of 50 – 150 μm. Kinetics of the disproportionation of the powder material was examined by isothermal thermopiezic analysis (TPA). Powder (350 mg)was placed into a TPA reaction chamber with approximate volume of 160 cm^3, and the chamber was evacuated and then filled with hydrogen (p = 0.1 Mpa). The sample was heated towards a desired disproportionation temperature (T_D) with rate of 7 K/min. In the course of heating, the sample had been fully hydrogenated by heating up to 673 K, at which the hydrogen pressure in the reaction chamber was reduced by evacuating the reaction chamber down to 0.01 Mpa. The fully hydrogenated sample was then continuously heated up towards the desired disproportionation temperature under the low pressure hydrogen (p = 0.01 Mpa). It was confirmed that the hydrogenated material had not been disproportionated under the low hydrogen pressure till reaching the desired disproportionation temperature. As

soon as the sample arrived at the desired disproportionation temperature, the hydrogen pressure in the reaction chamber was increased to the desired pressure (p = 0.02 – 0.1 Mpa) by introducing additional hydrogen gas. From this moment, the sample was kept at a constant temperature, and the decrease of hydrogen pressure, due to hydrogen absorption during the disproportionation, was measured.

3. Results and discussion

In the anisotropic HDDR treatment of the Nd-Fe-B alloy, the critical step determining the texture in the final product is the disproportionation. In the present study, the effect of hydrogen pressure on the disproportionation kinetics of the $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$alloy was examined by isothermal thermopiezic analysis (TPA). It was found that the overall reaction rate of disproportionation of the hydrogenated $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$alloy was influenced strongly by the hydrogen pressure. With the hydrogen pressure of 0.1 and 0.06 Mpa, the overall reaction rate of disproportionation was controlled by simple linear relationship. However, the overall reaction rate of disproportionation with the low hydrogen pressure of 0.02 Mpa was expressed by parabolic rate equation. The activation energy for the disproportionation of $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy with hydrogen pressure of 0.02 Mpa was significantly higherthan those with hydrogen pressure of 0.1, 0.06 Mpa. The activation energy for the disproportionation with hydrogen pressure of 0.1, 0.06 and 0.02 Mpa was calculated to be approximately 272, 262, and 321 kJ/mole, respectively. It was suggested that the disproportionation of the alloy with initial hydrogen pressure of 0.02 Mpa may take place via different mechanism from that with initial hydrogen pressure of 0.1 and 0.06 Mpa.

The effect of Ga, Nb addition on the disproportionation kinetics of Nd-Fe-B alloy and the disproportionation mechanism were investigated by an isothermal thermopiezic analysis (TPA) using the $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ (x = 0 and 0.3, y = 0 and 0.2) alloys. The addition of Ga, Nb retarded significantly the disproportionation kinetics of the Nd-Fe-B alloy, and the combined addition of Ga and Nb showed the most profound effect on the disproportionation kinetics. The activation energy of the disproportionation of the $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys was increased by the addition of Ga, Nb. The alloy with combined addition of Ga and Nb had much higher activation energy with respect to other alloys. The disproportionation kinetic data of the $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys performed with initial hydrogen pressure of 0.02 Mpa fitted to the parabolic rate law. It was suggested that during the disproportionation of the $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys with initial hydrogen pressure of 0.02 Mpa a continuous disproportionation product was formed and the overall reaction rate was limited by the hydrogen atom (or ion) diffusion through it.

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