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Effect of Ga, Nb Addition on Disproportionation Kinetics of Nd-Fe-B Alloy

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The effect of Ga and, Nb addition on the kinetics and mechanism of the disproportionation of a Nd-Fe-B alloy were investigated by isothermal thermopiezic analysis (TPA) using $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ (x=0 and 0.3, y=0 and 0.2) alloys. The addition of Ga and Nb retarded the disproportionation kinetics of the Nd-Fe-B alloy significantly, and increased the activation energy of the disproportionation reaction. The disproportionation kinetics of the $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys measured under an initial hydrogen pressure of 0.02 MPa were fitted to a parabolic rate law. This suggested that during the disproportionation of $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys with an initial hydrogen pressure of 0.02 MPa, a continuous disproportionation product is formed and the overall reaction rate is limited by the diffusion of hydrogen atoms (or ions).

Keywords : permanent magnets, HDDR, disproportionation kinetics, activation energy, TPA

1. Introduction

The HDDR (hydrogenation, disproportionation, desorption and recombination) process is a useful means of producing a highly coercive Nd-Fe-B powder with a fine grain structure directly from an ingot alloy [1, 2]. Depending on the control of the HDDR process variables, particularly in the disproportionation step, the final product can be either an isotropic powder or an anisotropic powder. In an isotropic powder, the recombined fine grains are oriented randomly. On the other hand, in an anisotropic powder, the recombined grains are oriented orderly (texture) in such a manner that the magnetisation easy axis (c-axis) of the neighbouring recombined $Nd_2Fe_{14}B$ grains is parallel to each other maintaining the crystallographic orientation of their mother grain [3-11]. For the production of highly anisotropic Nd-Fe-B alloy HDDR powder with good texture, the alloy is usually modified by adding Ga and, Nb, and the disproportionation kinetics should be controlled carefully using a lower hydrogen pressure. Ga- and, Nb- addition increases the coercivity and remanence of the HDDR-treated Nd-Fe-B material, respectively [5, 12]. Nb also helps stabilize the iron boride phase of the disproportionated phases, which acts as a memory site for the texture, and Ga is beneficial for suppressing the excessive growth of the recombined grains [9, 13]. It is believed that the addition of Ga and/or Nb may influence the disproportionation kinetics of the Nd-Fe-B alloy, of which careful control is of utmost importance for improving the texture of the recombined $Nd_2Fe_{14}B$ grains. This study examined the effect of Ga and, Nb addition on the kinetics and mechanism of the disproportionation of a Nd-Fe-B alloy.

2. Experiment

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 used in the present study were prepared by arc-melting of the high purity constituent metals. The prepared alloy buttons were homogenised at 1413 K for 40 hr in argon gas and then pulverised into powder with a particle size of 50~150 μm. The disproportionation kinetics of the powder material was examined by isothermal thermopiezic analysis (TPA). A powder (350 mg) was placed into the TPA reaction chamber with an approximate volume of 160 cm^3. The chamber was evacuated and filled with hydrogen (p=0.1 MPa). The sample was then heated to the desired disproportionation temperature (T_D) at rate of 7 K/min. During heating, the sample was fully hydrogenated up to 673 K, at which temperature the hydrogen pressure in the reaction chamber was reduced to 0.01 MPa by evacuating the reaction chamber. The fully hydrogenated sample was then heated continuously to the

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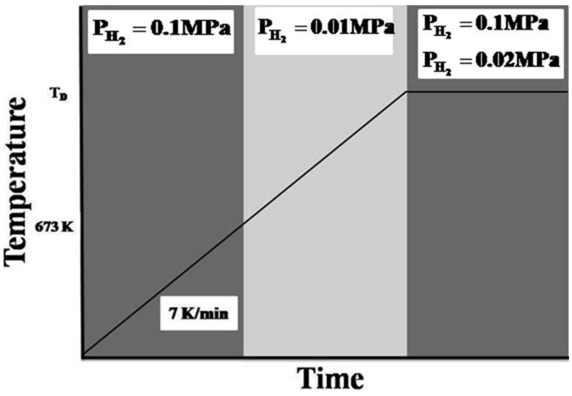

Fig. 1. Experimental scheme for isothermal disproportionation.

desired disproportionation temperature. Heating under low hydrogen pressure (0.01 MPa) prevented the fully hydrogenated alloy from any unwanted disproportionation until the desired isothermal disproportionation temperature had been reached. As soon as the sample reached 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 in hydrogen pressure due to hydrogen absorption during the disproportionation was measured. Fig. 1 shows a schematic diagram of the experimental scheme for isothermal disproportionation.

3. Results and Discussion

The overall disproportionation behaviour of the hydrogenated alloys was examined by heating the alloys continuously in hydrogen gas. Fig. 2 shows the TPA results showing the disproportionation of the fully hydrogenated $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloy during the course of heating. The fully hydrogenated alloys were heated from approximately 673 K in the reaction chamber with an initial hydrogen pressure of 0.02 and, 0.1 MPa, and the pressure change was monitored during the course of heating. The hydrogen pressure appeared to increase up to approximately 950 K due to thermal expansion and then decrease abruptly due to disproportionation. The disproportionation start temperature (T_s) was not influenced significantly by the hydrogen pressure, whereas the disproportionation completion temperature (T_f) was. The T_f is increased significantly under a lower hydrogen pressure. This suggests that the disproportionation kinetics is influenced significantly by the hydrogen pressure [14]. It should be noted that a pressure drop (Δp) occurred in the interval from T_s to T_f, which is equivalent to the amount of hydrogen absorption due to disproportionation, differs depending on the alloys. This is more profound in the results performed under a lower hydrogen pressure. The alloy with the combined addition of Ga and Nb appears to absorb much less hydrogen than that without Ga and Nb. This suggests that the addition of Ga and/or Nb strongly affects the disproportionation kinetics of the Nd-Fe-B alloy. The effect of Ga and, Nb addition on the disproportionation kinetics of the Nd-Fe-B alloy can be seen more clearly in the isothermal TPA results. The fully hydrogenated $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys were subjected to isothermal disproportionation at 933 K with an initial hydrogen pressure 0.02 MPa, as shown in Fig. 3. The addition of Ga and, Nb retards the disproportionation kinetics of the Nd-Fe-B alloy significantly, and more

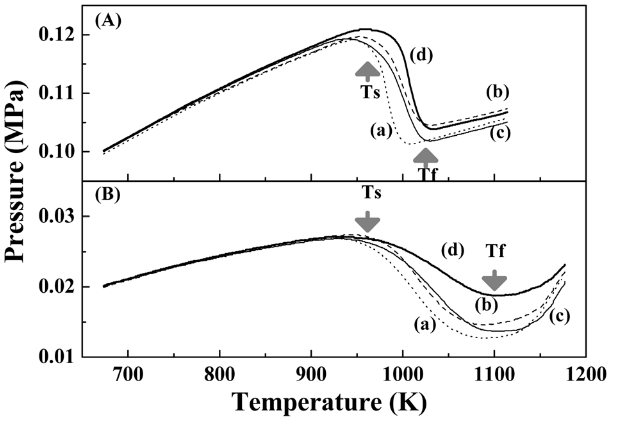

Fig. 2. TPA results during continuous heating under an initial hydrogen pressure of (A) 0.1 and (B) 0.02 MPa for the disproportionation of the $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys. (a) $Nd_{12.5}Fe_{81.1}B_{6.4}$ (b) $Nd_{12.5}Fe_{80.8}B_{6.4}Ga_{0.3}$ (c) $Nd_{12.5}Fe_{80.9}B_{6.4}Nb_{0.2}$ (d) $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$.

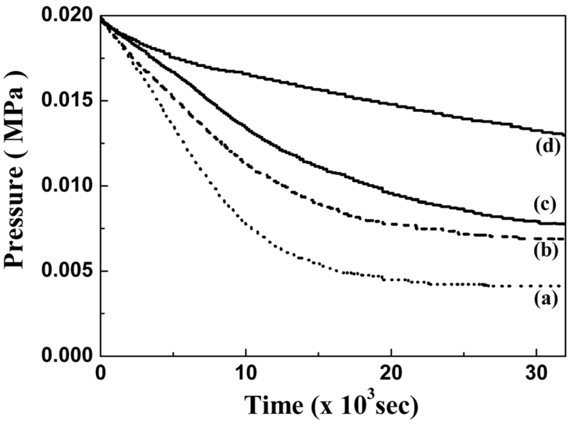

Fig. 3. Isothermal TPA results for the disproportionation of $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys carried out at 933 K under an initial hydrogen pressure of 0.02 MPa. (a) $Nd_{12.5}Fe_{81.1}B_{6.4}$ (b) $Nd_{12.5}Fe_{80.8}B_{6.4}Ga_{0.3}$ (c) $Nd_{12.5}Fe_{80.9}B_{6.4}Nb_{0.2}$ (d) $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$.

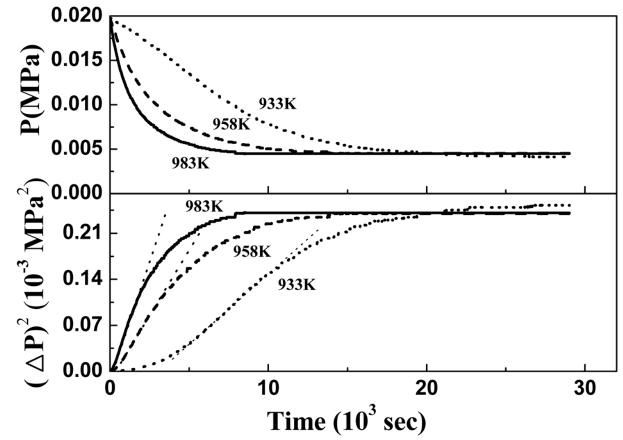

Fig. 4. Isothermal TPA result for the disproportionation of $Nd_{12.5}Fe_{81.1}B_{6.4}$ alloy carried out at various temperatures under an initial hydrogen pressure of 0.02 MPa.

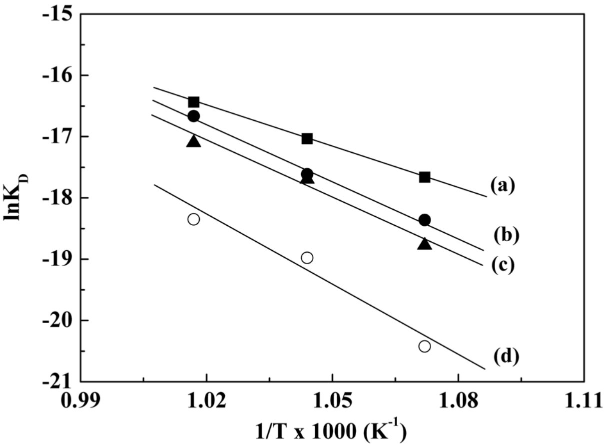

Fig. 5. Plot of ln κ_D against 1/T for the disproportionation of $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys under a hydrogen pressure of 0.02 MPa. (a) $Nd_{12.5}Fe_{81.1}B_{6.4}$ (b) $Nd_{12.5}Fe_{80.8}B_{6.4}Ga_{0.3}$ (c) $Nd_{12.5}Fe_{80.9}B_{6.4}Nb_{0.2}$ (d) $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$.

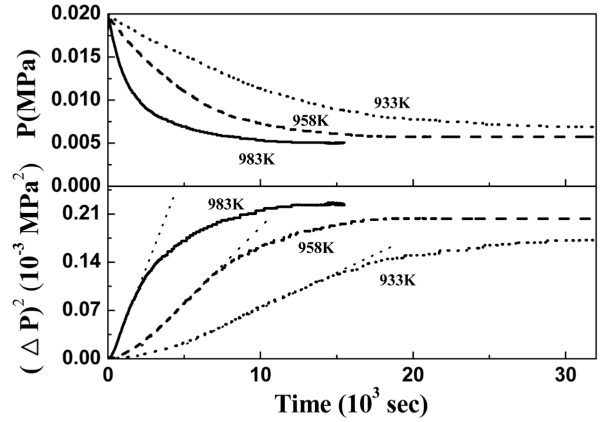

Fig. 6. Isothermal TPA result for the disproportionation of $Nd_{12.5}Fe_{80.8}B_{6.4}Ga_{0.3}$ alloy carried out at various temperatures under an initial hydrogen pressure of 0.02 MPa.

profound retardation of the disproportionation kinetics was observed in the alloy containing both Ga and Nb.

The effect of Ga and, Nb addition on the disproportionation kinetics of the Nd-Fe-B alloy was examined in more detail by isothermal TPA at various temperatures using the fully hydrogenated $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys. Isothermal TPA was carried out with an initial hydrogen pressure of 0.02 MPa, which is the hydrogen pressure commonly used in the disproportionation step for controlling the kinetics and achieving a high texture. An overall reaction rate equation of the disproportionation reaction was modelled and the activation energy was calculated using the isothermal TPA results at various temperatures. Fig. 4(a) shows the isothermal TPA results representing the disproportionation of hydrogenated ternary $Nd_{12.5}Fe_{81.1}B_{6.4}$ alloy at various temperatures with an initial hydrogen pressure of 0.02 MPa. The decrease in hydrogen pressure due to disproportionation occurred more rapidly as the temperature was increased. The overall reaction rate of the disproportionation of the hydrogenated $Nd_{12.5}Fe_{81.1}B_{6.4}$ alloy can be modelled using a parabolic rate equation,

$$(\Delta p)^2 = \kappa_D\, t + C \qquad (1)$$

where Δp is the pressure drop, t is time, κ_D is the parabolic rate constant, and C is a constant. A reaction demonstrating the parabolic rate yields a straight line when the data is plotted as $(\Delta p)^2$ versus time. Fig. 4(b) shows the fit of kinetic data to this model. The overall disproportionation kinetic data could be fitted more or less to a parabolic rate law, even though there was some deviation. This form of parabolic equation is typical of non-steady-state diffusion-controlled reactions. The dependence of κ_D on the temperature, T, is given by the Arrhenius equation:

$$\kappa_D = A\ \exp(-E/\mathrm{RT}) \qquad (2)$$

where A is a constant known as the frequency factor, E is the activation energy for the reaction, and R is the gas constant. The Arrhenius law can be tested by plotting ln κ_D as a function of the reciprocal absolute temperature. According to Eq. (2), the activation energy for the disproportionation of the $Nd_{12.5}Fe_{81.1}B_{6.4}$ alloy was estimated to be approximately 189 kJ/mol from the slope of the straight line [$-E$/RT] (Fig. 5).

Fig. 6(a)~8(a) show the isothermal TPA results showing the disproportionation of the Nd-Fe-B alloys containing Ga and/or Nb carried out at various temperatures. Fig. 6(b)~8(b) gives the fits of the disproportionation kinetic data to the parabolic rate model. It appears that the disproportionation kinetic data of the Ga- and, Nb-

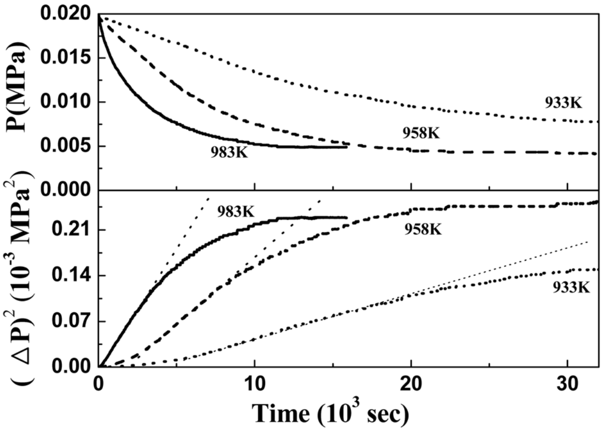

Fig. 7. Isothermal TPA result for the disproportionation of $Nd_{12.5}Fe_{80.9}B_{6.4}Nb_{0.2}$ alloy carried out at various temperatures under an initial hydrogen pressure of 0.02 MPa.

containing $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys also fitted the parabolic rate law. The disproportionation of the Nd-Fe-B alloy follows either a linear relationship or parabolic rate law depending on the disproportionation conditions, particularly the hydrogen pressure during the disproportionation [14]. Under a higher hydrogen pressure, the disproportionation reaction usually follows a linear relationship with a time-independent reaction rate. In this case, the transport of hydrogen atoms (or ions) might be more rapid than the chemical reaction involved in the disproportionation, and the reaction itself will be rate-limiting. The linear relationship suggests that the reaction product is not continuous; i.e., severe cracks may form in the reaction product (Fig. 9(a)) and allow hydrogen gas to remain in contact with the hydrogenated material and maintain a constant reaction rate. Under a low hydrogen pressure, the disproportionation reaction usually follows the parabolic rate law. The parabolic rate law suggests that the reaction product is continuous (Fig. 9(b)), and the diffusion of hydrogen atoms (or ions) through the reaction product may be more sluggish than the chemical reaction involved in the disproportionation process. In this case, the diffusion of hydrogen atoms (or ion) through the reaction product may be the rate-limiting process. Therefore, during the disproportionation of $Nd_{12.5}Fe_{(81.1-(x+y))}$-$B_{6.4}Ga_xNb_y$ alloys with an initial hydrogen pressure of 0.02 MPa, a continuous disproportionation product forms, i.e. a mixture of NdH_x, α-Fe and Fe_2B, and the overall reaction rate is limited by the diffusion of hydrogen atoms (or ions).

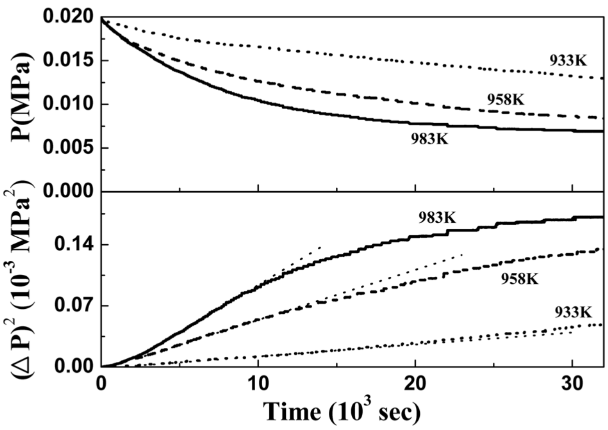

Fig. 8. Isothermal TPA result for the disproportionation of $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy carried out at various temperatures under an initial hydrogen pressure of 0.02 MPa.

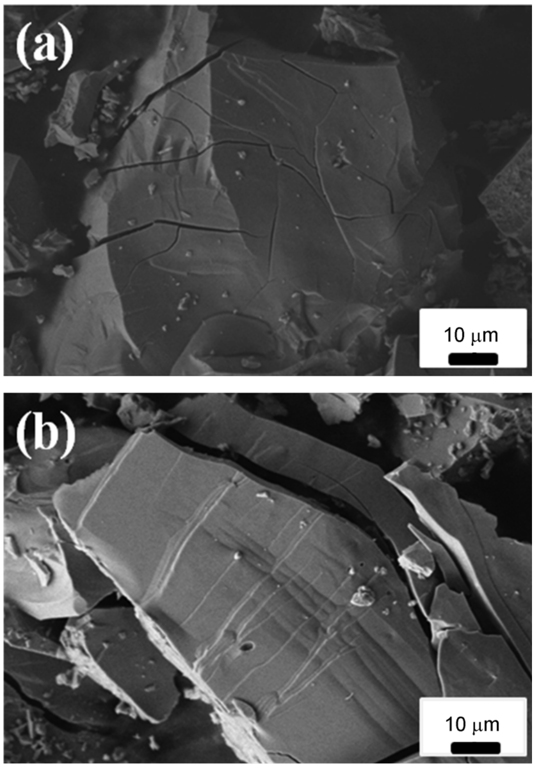

Fig. 9. SEM images showing the particle morphology of the $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy disproportionated (a) at 928 K for 5.5 hrs with an initial hydrogen pressure of 0.1 MPa, (b) at 983 K for 8.5 hrs with an initial hydrogen pressure of 0.02 MPa.

Fig. 5 shows the Arrhenius plots of the disproportionation of the Nd-Fe-B alloys containing Ga and/or Nb. The slope of the Arrhenius plot was higher for the alloys containing Ga and/or Nb. The alloy with the combined addition of Ga and Nb has the steepest slope. The activation energies of the disproportionation reaction of the $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys were calculated, and are summarized in Table 1. The combined addition of Ga and Nb appears to increase the activation energy significantly. The addition of Ga stabilizes the iron boride phase

Table 1. Activation energy of the disproportionation reaction of the $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys.

alloy			
Ga = 0	0.3	0	0.3
Nb = 0	0	0.2	0.2
activation energy (kJ/mole H)			
189	251	256	321

in the Nd-Fe-B alloy and the addition of Nb suppresses the excessive growth of the recombined grains. These findings suggest that in addition to these known effects, the addition of Ga and/or Nb significantly retards the disproportionation reaction of the Nd-Fe-B alloy. Highly anisotropic HDDR powder with good texture is normally produced by modifying the Nd-Fe-B alloy by the addition of Ga and Nb and adopting a lower hydrogen pressure for the disproportionation reaction. Both the lower hydrogen pressure during disproportionation and alloy modification with Ga and Nb retard the disproportionation kinetics remarkably, which is believed to help improve the texture of HDDR-treated Nd-Fe-B alloys.

5. Conclusion

The addition of Ga and, Nb retarded the disproportionation kinetics of the Nd-Fe-B alloy significantly with the combined addition of Ga and Nb having the most profound effect. The activation energy for the disproportionation of $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys was increased by adding Ga and, Nb. The alloy containing both Ga and Nb had a much higher activation energy with respect to the 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 an initial hydrogen pressure of 0.02 MPa was fitted to a parabolic rate law. This suggests that during the disproportionation of the $Nd_{12.5}Fe_{(81.1-(x+y))}B_{6.4}Ga_xNb_y$ alloys with an initial hydrogen pressure of 0.02 MPa, a continuous disproportionation product was formed and the overall reaction rate was limited by the diffusion of hydrogen atoms (or ions).

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